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Evaluation of $PM_{2.5}$ Chemical Speciation Samplers for Use in the EPA National $PM_{2.5}$ Chemical Speciation Network

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Volume I – Introduction, Results, and Conclusions

Final Report

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DISCLAIMER

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EXECUTIVE SUMMARY

To develop improved source-receptor relationships and for better understanding the causes of high $PM_{2.5}$ concentrations in the atmosphere, it is necessary to not only determine concentrations of $PM_{2.5}$ mass, the NAAQS indicator, but also the chemical components of $PM_{2.5}$. A sampling program of this type, which will consist of up to 300 sites nationwide has been initiated by EPA (Speciation Guidance Document, 1999 at http://www.epa.gov/ttn/amtic/pmspec.html). Since the $PM_{2.5}$ Federal Reference Method (FRM) using only Teflon filters is not suitable for determining the chemical composition of the collected aerosol, since carbon can not be directly measured (Speciation Guidance Document, 1999), EPA solicited innovative designs for speciation samplers, based on performance specifications. This led to the development of three slightly different candidate samplers manufactured by Andersen Instrument Inc., MetOne, Inc., and University Research Glassware (URG). These samplers are designed to allow for a nearly complete mass balance of the collected aerosol, while minimizing sampling artifacts for nitrate and allowing flexibility for minimizing organic carbon artifacts in the future. Due to the need to have consistency across this national network, the Speciation Expert Panel (Recommendations of the 1998 Expert Panel, 1998 at http://www.epa.gov/ttn/amtic/ pmspec. html) recommended a methods comparison field study among the new speciation samplers, historically used samplers, and the $PM_{2.5}$ FRM. The program plan for EPA's Chemical Speciation Sampler Evaluation Study (1999, http://www.epa. gov/ttn/amtic/casacinf.html) details the approach and implementation of the study. This report presents the approach and results from the 4-City intercomparison study; Phase 1, of the full evaluation of these samplers. Other Phases are described in Field Program Plan (1999) and include evaluation of denuders and reactive post filters for sampling organic aerosols with minimal artifacts (Phase II, Seattle, WA, J. Lewtas, PI), an evaluation of the chemical speciation samplers under summertime conditions (Phase II, Atlanta, GA in conjunction with the Atlanta Supersites Program, P. Solomon, PI), and an evaluation of the samplers under a variety of environmental conditions to test operational performance and logistics with the National Chemical Speciation Laboratory (Phase IV, 15 Cities throughout the US (Mini-trends network, J. Homolya, PI).

Methods. Because of potential sampling artifacts when using filters and potential differences in inlet cutpoints and sample fractionators, the chemical speciation samplers must be able to properly determine the chemical components of $PM_{2.5}$ under a variety of atmospheric and environmental conditions. Four locations, with different atmospheric chemical and meteorological conditions were chosen and included: Rubidoux, CA (high nitrate and carbon and low sulfate), Phoenix, AZ (high crustal material and moderate carbon and nitrate), Philadelphia, PA (high sulfate, moderate carbon, and low nitrate), and Research Triangle Park (RTP), NC (low $PM_{2.5}$ concentrations). The latter site also allowed for a more thorough evaluation of the samplers' in-field operational performance as it was located near EPA offices in RTP. In addition to the three candidate samplers, a Versatile Air Pollution Sampler (VAPS), an IMPROVE sampler, and an FRM were collocated at each site. Replicate samplers were located at Rubidoux. Samples were collected for up to 20 days during January and February, 1999 using state personnel (Rubidoux and Phoenix) or EPA contractors (Philadelphia and RTP). All sampling periods were 24-hrs in duration. Mass and trace elements were determined on

Teflon filters; sulfate, nitrate, and ammonium were determined on either Teflon, pre-fired quartz-fiber, or nylon filters depending on the sampler; and OC/EC were determined on pre-fired quartz-fiber filters. To minimize variability, all filter preparation, filter changing, and chemical analyses for a particular species were performed by one contractor. Quality assurance/quality control followed EPA guidelines (QAPP for the Four-City $PM_{2.5}$ Chemical Speciation Sampler Evaluation Study, January, 1999 Research Triangle Institute, Project Number 07263-030).

Results. All samplers encountered operational problems that increased variability in the results; however, the Andersen and MetOne samplers collected over 90% of the attempted samples on a site-by-site basis successfully, while the URG and Versatile Air Pollution Sampler (VAPS) collected greater then 75% of the samples attempted on a site-by-site basis. Most manufacturers have resolved operational issues. Other minor engineering changes were made to two of the samplers after the study, to allow for easier operation in the field. A fundamental problem was noted early on with the MetOne spiral inlet, which was allowing particles greater then 2.5 Fm to penetrate the inlet. The spiral inlet has been replaced with a sharp cut cyclone.

Chemical composition of the aerosols at each site were within expectations with the exception of high nitrate and OC in Philadelphia, where nitrate and sulfate both were about 20% of the total $PM_{2.5}$ mass and OC was about 50%. Results from most studies in the eastern US indicate that sulfate is the highest species (~50% of the mass), followed by OC at about 30% of the mass, with nitrate accounting for less than 5% or so of the mass. However, most previous studies have occurred during the summertime, when temperatures are high and ammonium nitrate would be mostly in the gas phase. Finally, coarse particle concentrations were highest in Phoenix and Rubidoux (about equal to the fine particle mass) and only about 20% or less relative to the fine particle mass at Philadelphia and RTP, as expected. Therefore, this study met its objective of testing the chemical speciation samplers under a fairly wide range of chemical conditions.

Means, time series, and regression analyses were performed for all species measured, allowing comparison among the samplers for a given variable at a given site. On the average, the major species agreed within 10-15% among the FRM, Andersen, and Improve samplers. Sulfate had even better agreement, which was observed across all samplers. The MetOne and VAPS samplers tended to be high for species that normally have a coarse particle component (i.e., mass, Si, Fe, Ca, etc.). In general, individual species from all samplers tracked each other, with the majority of correlation coefficients (r) being greater then 0.85. A few exceptions were noted. More variability was observed for trace elements (Si, K, Ca, Fe, Cu, Zn, Pb, and As).

Differences, on the order of up to 1 $\mu g/m^3$ on the average were observed among the samplers for particle nitrate due to a possible positive artifact associated with determining nitrate on pre-fired quartz-fiber filters, which usually is not observed with quartz-fiber filters that have not been pre-treated (Chow, 1995 JAWMA *45,* 320). The quartz-fiber filter was used due to concerns regarding loss of nitrate during vacuum XRF analysis (i.e., XRF has to be performed before the filter is extracted for ions analysis). Tests comparing nitrate concentrations measured on Teflon filters, collected in parallel, with and without having vacuum XRF analysis indicated loss of up to 40% of the nitrate, assumed to be ammonium nitrate. An additional bias for collecting particulate nitrate was observed due to the method of collecting particulate nitrate, where nitrate concentrations determined by the direct method (nitrate measured directly on a filter behind a denuder) were up to 1.5 µg/m^3 lower than nitrate concentrations measured by the indirect method (nitrate measured on a quartz-fiber filter behind a denuder and Teflon filter plus nitrate measured on a quartz-fiber filter in parallel).

Differences also were observed among the samplers for organic carbon and appear to be due to filter face velocity variations among the samplers. Lower flow rates appear to result in higher OC concentrations; although EC is consistent among the samplers. A positive artifact was also noted for OC and ranged from about 3.5 µg/m^3 at Rubidoux to essentially zero at RTP. Based on the design of the study, no information can be implied about OC negative artifacts, but the assumption has been made in the above discussion that negative artifacts for OC are similar between Teflon and quartz-fiber filters operating at the same face velocity.

Differences were observed between EC values reported the IMPROVE OC/EC protocol versus the NIOSH protocol. The IMPROVE protocol reported EC values approximately 2 times higher then the NIOSH method. These differences are currently under investigation.

Ammonium ion as measured by the IMPROVE sampler was on average lower than on the other samplers, even though a similar bias was not observed for nitrate or sulfate. It is postulated that ammonium is being lost due to volatilization of the ammonium nitrate that is collected on the nylon filter in the IMPROVE sampler. While nitric acid volatilized from the collected ammonium nitrate would be collected by the basic (pH) nylon filter, ammonia would not be collected. It also is possible that the basic filter is enhancing ammonium volatilization. More careful experiments need to be conducted to establish if this potential bias is significant or not.

Conclusions. In general, the performance of the candidate samplers is reasonable for their first use in the field. All samplers had operational problems that increased their variability, most of which have been addressed by the manufactures. Tradeoffs exist among the samplers for ease of use, flexibility for sampling, and cost. Performance of the samplers was excellent for sulfate and reasonable for other stable species. However, real differences among the samplers exist for nitrate and organic carbon and possibly ammonium as collected in the IMPROVE sampler. These differences are significant and can possibly affect design of compliance strategies for controlling PM$_{2.5}$ mass concentrations in air, as total differences as high as 3-5 µg/m^3 are observed among the samplers for these two species. Results from this study yield the following recommendations for the collection of nitrate and organic carbon:

- The Teflon filter used for mass and XRF analysis should not be used for ions analysis, particularly nitrate and ammonium ions, as these species are lost during XRF analysis.

- To minimize artifacts for the collection of aerosol nitrate, it should be measured using a denuder (coated with MgO or Na2CO3) followed by a single filter (Nylasorb or Na_2CO_3). Measuring nitrate on a quartz-fiber filter prepared for carbon analysis can results in a significant (1-3 µg/m3) positive artifact for aerosol nitrate, after accounting for volatilized nitrate measured on a nylon filter behind a denuder and Teflon filter.

- Organic carbon should be measured at the same face velocity as the Federal Reference Method. This will result in similar negative biases between OC measured on a quartz-fiber filter and that of a Teflon filter. Positive biases were observed on the quartz-fiber filter collecting aerosol directly behind a $PM_{2.5}$ inlet relative OC measured behind the same inlet that is followed by an XAD-4 coated annular denuder. It is recommended that the speciation network eventually consider use of an XAD-4 denuder or similar denuder for removing potential gas phase artifacts followed by a quartz-fiber filter and a reactive backup filter to obtain OC with minimal bias.

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Part I

Introduction and Experimental Design

INTRODUCTION

On July 18, 1997, the U.S. EPA promulgated a new NAAQS for particulate matter (PM) in 40 CFR Parts 50, 53, and 58, Federal Register (EPA 1997a; EPA 1997b). In addition to slightly revising the previous PM_{10} standard, EPA added a new standard for fine particles less than 2.5 µm in aerodynamic diameter, known as $PM_{2.5}$. To develop meaningful relationships between $PM_{2.5}$ levels at receptors and source emissions and for better understanding the causes of high $PM_{2.5}$ concentrations, in particular secondary components formed in the atmosphere through chemical reactions and condensation, it is necessary not only to sample for $PM_{2.5}$ mass, the NAAQS indicator, but also for the chemical components of $PM_{2.5}$. A sampling program of this type has been initiated by EPA (EPA 1999 ***Guidance Document***) that will consist of up to 300 sites at which the major chemical components of $PM_{2.5}$ will be measured in the collected aerosol. Since information from this network will be used for the identification of sources contributing to high $PM_{2.5}$ mass concentrations, development and evaluation of control strategies, measurement of trends, and support of health studies, it is important that there be national consistency in the species concentrations measured by the $PM_{2.5}$ speciation network. In particular, 54 of these $PM_{2.5}$ chemical speciation sites will become part of the National Air Sampling Stations (NAMS) network and will provide nationally consistent data for assessment of trends (EPA 1997b).

Development of chemical speciation samplers for the National $PM_{2.5}$ Sampler Procurement Contract (National Sampler Contract) was based on performance, rather than design criteria. This has allowed innovation in the development of these samplers and has resulted in the development of three slightly different samplers for meeting the specified performance criteria. Also as a result of this approach, a guidance document on chemical speciation of particulate matter has been prepared by EPA (EPA, 1999) and reviewed by an external peer-review panel (Speciation Expert Panel; Koutrakis, 1998). In their first review, the expert panel recommended an intercomparison among the chemical speciation samplers. The intercomparison also should include other historically accepted samplers (e.g., the improved IMPROVE sampler, the Harvard Sampler, or some other sampler) and the $PM_{2.5}$ Federal Reference Method (FRM). The chemical species to be determined should include those recommended by the expert panel (Koutrakis, 1998) and as specified in the guidance document for chemical speciation (EPA, 1999). The program plan for EPA's Chemical Speciation Sampler Evaluation Study (Solomon et al. 1998) outlines the approach and details the implementation of the intercomparison study to perform an initial evaluation of the chemical speciation samplers developed in response to the National Sampler Contract and several other samplers developed earlier and independently of the EPA national program.

About this Report

This draft final report provides results from EPA's Chemical Speciation Sampler Evaluation Study (4 City Study). The data presented in this report have been validated through Level 2b, that is, the data have undergone multi-variate statistical analyzes for consistency and known physical relationships and interpretive data analysis (NARSTO 1999). Part I of this report outlines the study, provides a summary of the samplers and the chemical analysis methods, and outlines the major questions and hypotheses to be addressed by this evaluation. Part II presents the results. First, quality assurance results are summarized, including operations and maintenance and systems and performance audit results followed by a summary of the chemical characteristics observed at each location. Next, results are presented from the statistical evaluations of the data, including time series analysis, regression analysis, difference analysis, T-test, and Analysis of Variance. In the Discussion Section, each hypothesis noted in the program plan, and Part I of this document is addressed to the extent possible and within the limitations of the study design. Lastly, an overall summary is provided.

Study Objectives

The objective of this sampler intercomparison study is to determine if there are differences among the three $PM_{2.5}$ chemical speciation samplers developed in response to the National Sampler Contract and how these samplers compare relative to other historical samplers, and to the FRM. While the FRM is the “gold” standard for mass, there are no such standards for the chemical components of $PM_{2.5}$. Thus, this intercomparison only establishes the relative equivalence of the samplers to each other on a species by species basis. For semi-volatile species (those in dynamic equilibrium between the gas and particle phases; e.g., for ammonium nitrate), the FRM using Teflon filters provides only a lower limit on the expected mass loading, since there is potential for loss of nitrate and semi-volatile organic species (SVOC) from the inert Teflon filters. For stable species, the FRM should provide an accurate estimate of the mass loading for those species. Chemical speciation samplers used historically [e.g., the Versatile Air Pollution Sampler (VAPS) developed under an EPA contract, the Caltech gray box sampler (Solomon et al., 1989), or the South Coast Air Quality Management District’s PM_{10} Technical Enhancement Program (PTEP) sampler (SCAQMD, 1996) should provide a less biased value for semi-volatile species (i.e., ammonium nitrate) and provide an additional set of samples for comparison; however, they still can only be compared on equivalent bases.

Overview of the Intercomparison

Collecting atmospheric particulate matter using the FRM with Teflon filters can result in negative sampling artifacts associated with the collected sample. Potential artifacts include the loss of volatile species, such as ammonium nitrate (Solomon et al., 1988, Hering et al., 1988; Hering and Cass 1999) and semi-volatile organic compounds (Cui et al., 1997; Eatough et al. 1995). Use of other filter media also may result in negative or positive sampling artifacts. The magnitude of these potential artifacts depends upon the atmospheric concentration of the species being affected, the temperature, relative humidity, and other variables (e.g., for nitrate, Russell and Cass, 1986; Hering and Cass, 1999). The chemical speciation samplers developed for National Sampler Contract have been designed to minimize these potential biases or artifacts by the use of diffusion denuders to remove gas phase species and reactive substrates to collect species that may volatilize during or after sampling from the inert filter (e.g., Teflon membrane) where the aerosol is collected. Therefore, to evaluate the performance of these chemical speciation samplers they must be able to properly determine the chemical components of $PM_{2.5}$ under a variety of atmospheric conditions, each of which will place different stresses on the performance of the sampler designs. For this study, this was accomplished by sampling at different locations throughout the country, since the composition of the atmospheric aerosol is not uniform across the country (Pace, 1998). For example, some areas have high nitrate and low sulfate levels (Los Angeles, CA: Solomon et al., 1989), while others (e.g., the eastern part of the United States) have relatively high sulfate and low nitrate levels (Hidy 1994, Pace, 1998). Still, other areas are dominated by aerosol rich in organic compounds derived from automobile exhaust (Los Angeles, CA: Schauer, 1996) , by organic aerosol derived from wood smoke combustion (Fresno, CA: Schauer, 1998), or from by organic aerosol derived from natural biogenic emissions (e.g., Southeast US). Some areas of the country are highly influenced by crustal material (e.g., Southwest US: Pace 1998; Eldred et al. 1998a). In actuality, several of these conditions exist simultaneously, with one or two components being higher then the others (Pace 1998; Eldred, 1998a, Solomon et al. 1989).

A variety of atmospheric chemical conditions also may be observed at one location during different seasons (Pace, 1998). For example, sulfate is likely highest in the east during the summer when photochemistry is high, while nitrate is highest in the west in the winter when cool temperatures drive the ammonium nitrate equilibrium with nitric acid and ammonia to the aerosol phase. However, due to the need to have results by mid-1999, the study was conducted over about an eight week period at four different locations to obtain as wide a difference in chemical atmospheres as possible. These constraints, however, resulted in limitations, and follow-on studies will have to occur to fully test the equivalency of these samplers under a wider variety of conditions. For example, by sampling in the winter in the east, we missed the highest sulfate concentrations which occur in the summer (Hidy, 1994), we did not sampling at a site with high wood smoke emissions, we sampled in Phoenix for crustal material in the winter when the highest crustal concentrations are likely to be observed in the hot dry summers, and the samplers did not experience extreme cold temperatures as might be expected in the northern mid-west or hot humid summers as experienced during the summer in the east.

Due to time and resource limitations, sampler evaluation is being conducted in four phases. Phase I is centered on sampling in areas with the following atmospheric conditions: high sulfate and low nitrate (east coast US), high nitrate and low sulfate (California), and high crustal material (Phoenix, AZ). The fourth site is located near ORD headquarters in Research Triangle Park to allow for a more thorough evaluation of the samplers and their in-field operational performance. Phase II is taking place in Seattle, WA from March-July, 1999 and is evaluating the efficiency and capacity of organic diffusion denuders and reactive back-up sorbents, including ones not currently planned for the chemical speciation samplers. Phase III is an extensive comparison of the same speciation samplers used in the 4 City Study, as well as several others that have been developed at universities. Comparisons in Phase III also will be made to a number of species specific continuous methods for the major components of $PM_{2.5}$. Phase IV is a ten city study where the sites will have at least 2 speciation samplers and be operated by the States.

The time schedule for Phase I of the study dictated that we sample more frequently than every 6th day, as the results are needed by OAQPS by mid-June, 1999 for input into the decision process for choosing chemical speciation samplers for the National Air Monitoring Stations (NAMS) TRENDS network. Therefore, samples were collected every-other-day. The statistical design required a minimum of 10-15 samples. To ensure that a sufficient number of samples were collected to meet that objective, 20 sampling periods were attempted. Samples were analyzed for the major chemical components using standard analytical techniques as described below and recommended by the expert panel that reviewed the guidance document (Koutrakis, 1998). Data analysis provided a robust test of the equivalency of the samplers studied and, within the limitations of the study, reasons for differences among the methods tested.

Phase II involves sampling in Seattle, WA with a focus on understanding the collection of organic material (aerosol OC and semi-volatile organic compounds) under wood smoke conditions in a manner that will minimize negative and positive sampling artifacts for organic species. These systems include a denuder to remove semi-volatile organic compounds that are in the gas phase and may be collected by the downstream quartz fiber filter, followed by a reactive sorbents (denuder, PUF, or impregnated filter). The evaluation includes determining capacity, efficiency, and comparability of two denuder systems and an evaluation of the sorbents located behind the quartz fiber filter. The first system uses XAD-4 coated onto annular denuders as was proposed for use in two of the chemical speciation samplers procured through the National Sampler Contract (University Research Glassware and Andersen Instruments). The second system uses a multi-channel parallel plate denuder composed of carbon impregnated filters (CIF) (Eatough et al., 1993). Both denuders are followed by quartz fiber filters which are then followed either by second XAD-4 coated denuder, an CIF filter, an XAD-4 impregnated Whatman filter, PUF cartridge, or an XAD-4-sorbent bed. XAD-4, PUF cartridges, and quartz fiber filters can be extracted and individual species can be determined to obtain a mass balance between the SVOC, aerosol organic species collected on the quartz fiber filter, and the SVOC volatilized from the quartz fiber filter and collected on the reactive back-up medium, on a species-by-species basis. The CIF filter can be analyzed for organic carbon using thermal desorption.

Phase III will involve sampling in Atlanta, GA where biogenic VOC emissions are known to be high in the summer (Chameides et al. 1988). The Atlanta intercomparison is an integral part of the EPA Supersites Program (EPA 1998). The same set of chemical speciation monitors will be operated in Atlanta as were operated in the 4 City Study. In addition, several other speciation samplers are included in the intercomparison along with the potential for comparisons to a number of species specific continuous methods for sulfate, nitrate, ammonium, trace elements (Na - Pb), organic carbon, and elemental carbon. Details of the Atlanta study are described in Hering (1999).

Phase IV, the Ten City Study is still in planning. It is anticipated, that each site will have at least two different chemical speciation samplers, operate on a 1 in 3 day schedule from about October 1999 through March 2000, and have chemical analysis performed in the national laboratories established to support the chemical speciation sampling network. The goal of this study is to evaluate the samplers under more severe extremes of temperature, as well as higher crustal material and wood smoke loadings.

Study Design

The design of this program is constrained by limitations in the time frame allowed for the experiment and in resources available to complete the program (e.g., number of samplers, personnel, and funding). However, the statistical design was prepared understanding these limitations and the design chosen provides a robust evaluation of the samplers relative to each other, to several samplers used historically to obtain similar data, and to the FRM. The overall design is detailed below.

Statistical Design

The primary objective of this study is to determine if there are differences in the measured concentrations of the chemical components of $PM_{2.5}$ mass as determined by the three $PM_{2.5}$ chemical speciation samplers available on the National Sampler Contract . Comparisons also will be made to two historical samplers and to the FRM using these samplers as a relative reference. A secondary objective of this study is to evaluate the operational performance or practicality of the samplers in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements.

There are three major scientific hypotheses to be addressed by this intercomparison study.

- One is associated with reconstructing the FRM mass.
- The second is associated with comparing the measured chemical concentrations among the various speciation samplers, which consists of two parts:
    - The first part is associated with examining differences among the samplers, without regard to why there are differences, if they exist.
    - The second part examines why there are differences, if they exist. Some are expected due to the slightly different methods employed.
- A third set of hypotheses is given dealing with the potential affect of different analytical methods on measured concentrations of the chemical components of $PM_{2.5}$. These include the effect of vacuum X-ray fluorescence (XRF) or atmospheric pressure XRF on nitrate concentrations measured on Teflon filters and the effect of thermal optical reflectance (TOR) vs. thermal optical transmittance (TOT) on the determination of organic and elemental carbon (OC/EC) concentrations from pre-baked quartz fiber filters.

The first two hypotheses are predicated on the assumption that the cutpoints (50% collection efficiency) for the samplers used in this study have essentially the slope and 50% cutpoint. This is a required assumption to address these hypotheses. Also, it is important to establish the precision of the instruments, which was obtained by collocating samples at one site (Rubidoux, CA). While this provides only a limited assessment of the precision, it provides a first cut estimate of the precision for the statistical analyses performed to understand the data. If for example, the precision is estimated at 50%, then determining differences among samplers is not as informative as if the precision were 10-15%. As a benchmark, the coefficient of variation for the differences in concentrations from collocated FRM instruments is required to be less than 10%, according to 40 CFR Part 58, Appendix A. Depending on the species, we anticipate a range of precision from less than 10% to about 30%.

A detailed list of hypotheses is given in the Statistical Analysis section.

EXPERIMENTAL

Sampler Types and Rationale

Chemical speciation samplers have been developed and built by three different manufacturers under the National Sampler Contract procurement. The need for $PM_{2.5}$ chemical speciation monitoring is described under 40 CFR, Parts 53 and 58 (EPA 1997). The three samplers are the Reference Ambient Air Sampler (RAAS) developed by Andersen Instruments Incorporated (Andersen), Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassware Corporation (URG), and Spiral Ambient Speciation Sampler (SASS) developed by Met One Instruments (MetOne). The external peer-review committee (Koutrakis, 1998) recommended comparison of these samplers under field conditions in different areas of the country and different seasons. They also recommended comparison to samplers used previously that have been accepted historically as providing data of known uncertainty, and to the FRM.

Historical methods included in this study were the National Park Services' IMPROVE (Interagency Monitoring of Protected Visual Environments) sampler modified to include 47 mm filters as suggested by the expert review panel (Koutrakis, 1998), the Versatile Air Pollution Sampler (VAPS)(URG Corporation; four available), and the PTEP sampler (SCAQMD, 1996) operated by the South Coast Air Quality Management District (SCAQMD) at their Rubidoux, CA site. These samplers are well characterized for collecting relatively unbiased samples suitable for chemical analysis of major PM composition.

Two FRM samplers were operated at each site to allow for chemical characterization of the collected sample similar to that being obtained by the chemical speciation samplers. One FRM collects aerosol samples on Teflon filters for mass and trace elements (Na - Pb), while the other FRM used quartz-fiber filters for determination of ions ($SO_4^=$, NO_3^-, and NH_4^+), OC, and EC.

The FRM should provide a suitable reference for stable species, such as many of the trace metals and sulfate. The historical samplers should provide a reference for labile compounds (nitrate ion and semi-volatile organic compounds [SVOC]) as they used diffusion denuders and reactive backup filters, similar to the chemical speciation samplers, thus minimizing the potential gain or loss of these species when using only Teflon or quartz fiber filters. The IMPROVE sampler should provide nearly artifact free data for nitrate, while the VAPS should provide nearly artifact free data for nitrate and organic carbon. During Phase I, only the VAPS used a denuder for removing gas-phase semi-volatile organic compounds (referred to here after as an organic denuder), as there is currently considerable uncertainty in using organic denuders as well as the desire to leave research oriented approaches to more careful examination. Collection of organic carbon using denuders and reactive collection media is addressed in Phase II activities.

Both the VAPS and the IMPROVE samplers have been used and evaluated in numerous studies over the last decade, and thus, provide a reference to many other databases (Shaibal et al. 1997;

Sommerville et al. 1994; Stevens et al., 1993; Pinto et al. 1998; Mathai et al. 1990; Cahill, 1993). The PTEP sampler, only operated at Rubidoux, also falls into this category as it has been used for nearly a decade by the South Coast Air Quality Management District (SCAQMD) in southern California (Teffera et al., 1996; SCAQMD, 1996). The PTEP sampler also uses methods similar to the chemical speciation samplers.

Sample analysis, which is described in more detail later, included mass by gravimetric analysis, ions (sulfate, nitrate, and ammonium) by ion chromatography (IC), OC/EC by thermal-optical reflectance (TOR), and elemental analysis by energy dispersive X-ray fluorescence (XRF). Mass was always determined on Teflon filters following FRM protocol for filter equilibration and weighing. Concentrations of trace elements (Na - Pb), were measured on the same filter used for mass determinations. Ions are determined from aqueous extracts of either Teflon (wet with 50 µl ethanol before extraction), quartz-fiber, or nylon filters. Nylon filters analyzed for only for nitrate were extracted in IC eluent and those analyzed for nitrate, sulfate, and ammonium ions were extracted in water. OC and EC were measured on quartz-fiber filters that have been baked at 600°C for 2 hours to lower background carbon levels below 0.2 $\mu g/cm^2$ total carbon. Quartz-fiber filters analyzed for ions were split to allow for carbon and ions analysis. All other filters were kept whole for analysis.

Sampler Descriptions - The Chemical Speciation Samplers

Design of the three chemical speciation samplers for the National $PM_{2.5}$ Network can be found in the EPA chemical speciation guidance document (EPA, 1999). The draft guidance document outlines the general design of these samplers as envisioned for the $PM_{2.5}$ network; although they are not likely the final designs to be implemented, as this and future field evaluations of the samplers may result in modifications to the samplers. Specific designs of the samplers for this intercomparison are given below. In general, each sampler draws air at a specified flow rate through a size selective inlet that removes particles greater than a specified size with a 50% collection efficiency or cutpoint. For the samplers employed in this study the cutpoint is 2.5 µm. As recommended by the expert peer-review panel (Koutrakis, 1998), the efficiency of collection (slope and cutpoint) for each sampler should closely resemble that of the FRM, and that was under the control of the manufacturers. Described below are the three samplers provided to EPA for the National Sampler Contract procurement by URG, MetOne, and Andersen.

Reference Ambient Air Sampler (RAAS) developed by Andersen Instruments

A schematic flow diagram of the Andersen RAAS is shown in Figure 1a, with a picture of the sampler given in Figure 1b. It consists of a size selective inlet followed by two $PM_{2.5}$ cyclones in parallel, the outlets of which are connected to separate sampling manifolds. These cyclones are used to remove particles greater than 2.5 micrometers with a 50% collection efficiency, when operated at 24 Lpm. The flow is then split in each manifold into 2 channels (maximum of 3) for at total of up to 6 channels. Of the four channels used in this study, the first channel (labeled 1 in Figure 1a) is used to estimate atmospheric concentrations of particulate organic and elemental carbon (OC/EC). The flow rate in this channel is

7.3 Lpm. In the second channel (labeled 2 in Figure 1a), particulate matter is collected on a Teflon filter for analysis of mass and trace elements (Na - Pb) by energy dispersive X-ray fluorescence (XRF). The flow rate through this channel 2 is 16.7 Lpm. In the third channel (labeled 3 in Figure 1a) particulate matter also is collected on a Teflon filter, which is extracted in water and analyzed for sulfate, nitrate, and ammonium ion concentrations by ion chromatography (IC). The last channel (labeled 4 in Figure 1a) is used to obtain a nearly unbiased estimate of fine particle nitrate by removing acidic gases (e.g., HNO_3) from the air stream using a diffusion denuder coated with MgO and collecting aerosol nitrate on a reactive Nylasorb (nylon) backup filter. This assumes the denuder is efficient for HNO_3 and other acidic gases that might be collected on the nylon filter and analyzed as nitrate and that the nylon filter does not collect NO_2. The filter is extracted in IC eluent and analyzed by IC for nitrate. In all channels, critical orifices control the flow and the flow rates are monitored using electronic mass flow sensors. All internal components before the filter holders or denuders are Teflon® coated and no grease or oil is used in the sampler's design. The system also monitors continuously relative humidity (RH), barometric pressure (BP), orifice pressure (OP), ambient temperature (T), manifold temperature (MT), meter temperature (MeT) and cabinet temperature (CT). Data can be downloaded through a RS-232C serial port, which also allows for two way remote communication (Andersen, 1999).

Spiral Ambient Speciation Sampler (SASS) developed by MetOne

A schematic flow diagram for the MetOne SASS sampler is presented in Figure 2a, with a picture of the sampler shown in Figure 2b. The SASS has 5 separate channels, operated through a common controller and pump. For the current Four City Study, each channel contained a spiral impactor designed to give a 2.5 µm cut-point (50% collection efficiency) with a slope and cutpoint similar to the FRM when operated at 6.7 Lpm (MetOne, 1999). {Note, results from this study indicted that under high coarse particle loading conditions, the Spiral impactor allowed large particles to penetrate to the filter. The Spiral is being replaced by a sharp cutpoint cyclone (SCC) developed by BGI, Incorporated. The rest of the design for the SASS sampler is staying essentially the same.} The first channel (labeled 1 in Figure 2a) collects particulate matter on a Teflon filter that is analyzed for atmospheric concentrations of $PM_{2.5}$ mass and trace elements (Na - Pb). The second channel (labeled 2 in Figure 2a) also collects particulate matter on a Teflon filter that is analyzed for sulfate, nitrate, and ammonium ion concentrations. A MgO coated aluminum honeycomb diffusion denuder is located behind the spiral impactor in the third channel (labeled 3 in Figure 2a). This denuder is used to remove acidic gases (e.g., HNO_3) from the sampled air stream. The MgO denuder is followed by a Nylon filter that is analyzed for nitrate as described above. As in the RAAS sampler, the denuder/reactive filter pair is used to obtain a nearly unbiased estimate of aerosol nitrate. This assumes the denuder is efficient for HNO_3 and other acidic species that might be analyzed as nitrate, and that the nylon filter does not collect NO_2. The fourth channel (labeled 4 in Figure 2a) contains two baked quartz-fiber filters located behind the spiral impactor. The first quartz-fiber filter is analyzed for OC/EC by thermal-optical reflectance, while the second quartz-fiber filter is archived. The fifth channel (labeled 5 in Figure 2a) also contains 2 baked quartz-fiber filters as a replicate set to channel 4. This set of quartz fiber filters are archived for future use. In Phase III (Atlanta), it is anticipated that a elemental carbon honeycomb diffusion denuder will be available for use in channel 5. This denuder is used to remove semi-volatile organic compounds that may interfere, as a positive artifact, with the OC measurement. The flow rate through each channel is nominally 6.7 Lpm and is controlled by a critical orifice. The flow rate in this instrument is monitored using electronic mass flow sensors.

Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassware (URG)The URG MASS sampler is shown in Figure 3a with a picture of this sampler given in Figure 3b. This sampler consists of two modules (URG MASS 400 and MASS 450), each with an FRM PM_{10}size selective inlet and a WINS impactor for the collection of $PM_{2.5}$ aerosol. The MASS 400 is equipped with a Na_2CO_3 denuder before the WINS impactor but after the PM_{10} size selective inlet. This denuder is used to remove acidic gases much like the MgO denuders discussed above. The particles less than 2.5 µm are collected on the top filter of a dual filter pack, which is an inert Teflon filter that is analyzed for $PM_{2.5}$ mass and trace elements (Na - Pb). The backup nylon filter efficiently collects nitrate that may have vaporized from the front Teflon filter during sampling. Nitrate ion is quantified using IC after extraction from the Teflon and nylon filters as described above for the RAAS sampler. The sum of nitrate measured on the Teflon and nylon filters provides a nearly bias free estimate of fine particle nitrate. This assumes the denuder is efficient for HNO_3 and that the nylon filter does not collect NO_2. The MASS 450 contains a single filter pack containing one pre-baked quartz-fiber filter. This filter is split in half with OC and EC determined from one half and sulfate, nitrate, and ammonium ions determined on the other half. An organic denuder (XAD coated annular denuder) is not used here, but will be used in Phase III of the study following recommendations from Phase II. The flow rate through each module is nominally 16.7 Lpm. Flow is monitored using a dry gas meter with a feed back loop to the controller to adjust for variations in flow rate as particles are collected on the filter.

Sampler Descriptions - Historical Samplers
Historical samplers include the IMPROVE, VAPS, FRM, and PTEP samplers, the latter being operated only at Rubidoux as part of a SCAQMD PM chemical characterization study (SCAQMD, 1996).

IMPROVE Sampler
Detailed descriptions of the IMPROVE sampler can be found in Eldred et al. (1998b). A schematic diagram of the IMPROVE is given in Figure 4a with a picture of the sampler given in Figure 4b. In general, the IMPROVE sampler consists of several modules each of which is dedicated to collecting a series of related chemical components of the atmospheric aerosol. Each module consists of a size selective inlet, a cyclone to provide a $PM_{2.5}$ size cutpoint based on the specified flow rate, filter media for sample collection, a critical orifice that provides the proper flow rate for the desired size cutoff, and a vacuum pump to produce the flow. Flow rate is not monitored continuously, but are verified prior to and after each sampling period. The IMPROVE samplers consist of up to four parallel modules, and a common controller (timer) as described in Eldred et al. (1998). Only three modules are used in this study, as the fourth is typically used to collect PM_{10}. The first module (labeled 1 in Figure 4a) collects $PM_{2.5}$ on a Teflon filter, for determining atmospheric concentrations of $PM_{2.5}$ mass and trace elements (Na - Pb). The second module (labeled 2 in Figure 4a) includes a Na_2CO_3 denuder before the $PM_{2.5}$

cyclone to remove acidic gases (e.g., HNO_3) followed by the cyclone and a nylon filter. This nylon filter is analyzed for sulfate, nitrate, and ammonium ions. The third module (labeled 3 in Figure 4a) collects PM on a pre-baked quartz-fiber filter. This filter is analyzed for OC and EC.

Versatile Air Pollution Sampler

The VAPS sampler is shown in Figure 5a with a picture of the sampler given in Figure 5b. A $PM_{2.5}$ cutpoint is obtained using a size selective impactor followed by a virtual impactor with a $PM_{2.5}$ cutpoint. The coarse particles follow the minor flow (3 Lpm) and are collected on a Teflon filter from which coarse (PM_{10}-$PM_{2.5}$) particles mass is obtained. The fine (< $PM_{2.5}$) particle flow (30 Lpm) is split evenly between two channels. One channel (labeled 1 in Figure 5a) contains a diffusion denuder coated with Na_2CO_3 followed by Teflon/nylon filter pack as described above. The Teflon filter will be analyzed for mass and trace elements (Na - Pb). The Na_2CO_3 denuder is extracted and analyzed for nitrate to give an estimate of ambient nitric acid concentrations. The second channel (labeled 2 in Figure 5a), contains an XAD coated annular denuder, designed specifically for the VAPS (Gundel, personal communication) to remove gas phase semi-volatile organic compounds that might be collected by the quartz-fiber filter that follows the denuder. The quartz-fiber filter is analyzed for OC and EC concentrations.

Sampler Descriptions - Federal Reference Method

The experimental design of the two FRM samplers is schematically illustrated in Figure 6a with a picture of the samplers given in Figure 6b. Two FRM samplers will be used at each site to obtain a chemical characterization of the collected aerosol in a manner similar to the other samplers. One FRM uses a Teflon filter to obtain $PM_{2.5}$ mass and trace elements (Na - Pb). The second FRM uses a pre-baked quartz-fiber filter that is split in half with one half being analyzed for OC and EC and the other half for sulfate, nitrate, and ammonium ions. As mentioned above, the FRM is the reference method for $PM_{2.5}$ mass and should provide a suitable reference for non-volatile species, such as sulfate and many of the trace elements determined by XRF. The semi-volatile species, such as ammonium nitrate and some of the organic species are collected with less bias by the VAPS sampler and in Rubidoux by the PTEP sampler. Thus, the VAPS will provide a reference for semi-volatile species.

SCAQMD PTEMP Sampler

The PTEP sampler, like the Andersen sampler is based on the design of the Caltech Gray Box sampler (Solomon 1989). Air is drawn through an inlet and a $PM_{2.5}$ cyclone to obtain the desired cut-point. Air is split into several sample streams, with a fraction of the air passing through denuders and into filter packs or directly into filter packs. The PTEP sampler is schematically illustrated in Figure I-7 and described below. Additional details of the design and the network this sampler is employed can be found in SCAQMD (1996).

As shown in Figure I-7, the PTEP sampler has four channels and ten sampling lines for measurement of PM_{10} and $PM_{2.5}$ mass, and chemical and gaseous components. : $PM_{2.5}$ is sampled in Channels II (Lines

3, 4 & 5) and III (Lines 6 and 7). A Teflon-coated AIHL Cyclone (John and Reischi, 1980) is used to obtain a nominal $PM_{2.5}$ size fraction in Channel II. Three sampling lines are located below Channel II for the measurement of aerosol nitrate and ammonium and their gas phase counter parts, nitric acid and ammonia. Ammonia and nitric acid losses were minimized by the use of a short Teflon line into the cyclone and coating the cyclone internally with Teflon. Channel II contains two stainless steel denuders used for ammonia and nitric acid. Line 3 feeds into the ammonia denuder columnar box consisting of strips of citric acid impregnated quartz filters that are efficient scavengers of ammonia gas (Stevens et al., 1985). Due to the high ammonia levels sometimes found in the Los Angeles Basin, these ammonia denuders were changed every month. An acid impregnated filter in a Gelman aluminum filter holder is connected to the ammonia denuder. Line 4 feeds into the nitric acid denuder, which consists of a stainless steel columnar box with anodized aluminum plates. A dual filter pack, quartz followed by nylon, is mounted below this denuder. The quartz filter collects the particulate nitrate and the nylon filter is used to quantitatively trap any gaseous nitric acid that has penetrated through the denuder and volatilized from the front quartz filter.

Line 5 consists of an all-Teflon filter pack (Savillex) with three stages. A quartz filter followed by a Nylasorb (Gelman) and then a citric acid impregnated quartz filter are all mounted in series in line 5. This line collects $PM_{2.5}$, nitric acid, and ammonia gas, and is used as the non-denuded leg of the denuder system. This line measures total nitrate and ammonium (gas and particle). The difference between this line and lines 3 and 4 provide an estimate of gas phase nitric acid and ammonia by the denuder difference method (Solomon et al., 1988).

Channel III (Lines 6 & 7): $PM_{2.5}$ mass, organic and elemental carbon, and inorganic trace metals are obtained from Channel III (Lines 6 & 7). $PM_{2.5}$ size fractionation is obtained using a stainless steel Sensydyne model 240 cyclone (Lippmann and Chan, 1970). A stainless steel bowl with stainless steel mesh protects the inlet of the cyclone. Because of the high-volume flow characteristics (110 Lpm) of the cyclone, a stilling or mixing chamber coated with Teflon is used prior to the splitting of the flow into two lines (Fitz et al., 1989). Since the carbon analysis and trace elemental analysis utilizes techniques that are precision-sensitive to the homogeneity of particle deposits on the filter, flow homogenizers were used. The homogenizers are 30 cm long stainless steel tubes with internal diameters of 4.5 cm. Line 6 samples $PM_{2.5}$ carbon while line 7 collects aerosol samples for the determination of mass and inorganic trace element concentrations.

Chemical Speciation and Chemical Analysis

The chemical components of $PM_{2.5}$ measured in this study are the same as those specified for the National $PM_{2.5}$ Chemical Speciation Network (EPA, 1998) and recommended by the expert peer-review panel (Koutrakis, 1998). Chemical characterization includes mass, sulfate, nitrate, and ammonium ions, elements (Na through Pb), organic carbon (OC) and elemental carbon (EC). Appropriate filter media were used to allow for chemical analysis by routine methods as described in EPA (1998), Koutrakis (1998), Chow (1995), and recommended by the vendors. As described above, these media combined with appropriately coated diffusion denuders should minimize sampling artifacts. The field study described here, however, will not involve comparisons to independent certified methods that would allow for an estimate of accuracy. However, comparison to the historical samplers (IMPROVE, VAPS, and FRM) provide for a comparison to samplers that have been operated under a number of conditions. Differences in nitrate losses and possibly losses (negative artifact) or gains (positive artifacts) of SVOCs can be initially evaluated as a result of this intercomparison.

Chemical analysis of aerosol on the collected filters is by routine methods as described in EPA (1998) and Chow (1995). Figures I-1 through I-7 illustrate the experimental design for each sampler and show which analytes were determined on which filters. A tabular summary of the species measured by each sampler is given in Table I-1. Appendix A summarizes the chemical analysis methods. Detailed standard operating procedures (SOPs) have been prepared (RTI, 1999), and are listed in Table I-2, and can be found in Appendix B. These SOPs were followed for all analyses. In general, $PM_{2.5}$ mass is determined gravimetrically on Teflon filters. Elements (Na – Pb) are determined on the same filter as $PM_{2.5}$ mass by energy dispersive X-ray fluorescence (XRF). Anions (sulfate and nitrate), and ammonium ion are determined from aerosol collected on several different filter media (Teflon, quartz-fiber, or nylon). Each filter is extracted in water or a carbonate/bicarbonate buffer solution (IC eluent for anions if only anions are being determined from the filter) and quantified in the extract using ion chromatography. The nylon filter is analyzed only for nitrate, except for the IMPROVE sampler, where nitrate, sulfate, and ammonium ion concentrations are determined from the sampler collected on the nylon filter. Organic and elemental carbon (OC/EC) are determined on the quartz-fiber filters using thermal-optical reflectance (TOR).

The following provides a brief description of the chemical analysis methods used in this study by species.

$PM_{2.5}$ Mass

$PM_{2.5}$ mass, is determined gravimetrically on Teflon filters using a microbalance (see Appendix B) following procedures outlined in the Federal Register for $PM_{2.5}$ FRM mass measurements in ambient air. Prior to sampling filters are equilibrated for 30 days at the specified temperature (T) and relative humidity (RH), followed by a one week equilibration period in the temperature range from 20-25 C and an RH in the range of 20-30%. Filters are weighed, sealed in petri dishes, and stored until they are sent out to the field. During storage and transport, filters are maintained at < 4 C. Prior to weighing sampled filters, they are again equilibrated at the same T and RH as they were for pre-weights. $PM_{2.5}$ mass is determined by the difference between the post- and pre-weighed filters. Atmospheric concentrations are obtained by dividing the mass per filter by the volume of air sampled.

Trace Elements (Na-Pb)

Teflon filters analyzed for mass also are analyzed for trace elements from Na to Pb by atmospheric pressure X-ray fluorescence (see Appendix B). In this method, the filter is open to the atmosphere, but surrounded by a sheath of He gas. Secondary x-rays are used primarily as the excitation source resulting in virtually no heating of the filter or collected sample. Quantification of XRF spectra are obtained by comparing to standards of known concentration as described in the SOP. Atmospheric concentrations are obtained by dividing the loadings per filter, usually in nanograms (ng) by the volume of air sampled.

Sulfate, Nitrate, and Ammonium Ions

Sulfate, nitrate, and ammonium ions are determined in filter extracts from Teflon or quartz-fiber filters by ion chromatography (IC). Filters used for ion analysis are identified Figures I-1 to I-3, I-5, and I-6 (also see SOPs in Appendix B, and). For the IMPROVE sampler, anions (i.e., sulfate and nitrate) and ammonium ion are determined from the nylon filters used in that sampler. Volatilized nitrate is determined directly in the extract from the nylon filters located behind the Teflon filter used for mass and XRF analysis in the URG and VAPS samplers. Anions are determined from a section of the quartz-fiber filter in the URG 450, VAPS, and FRM samplers. These are being compared to anions determined from extracts of Teflon filters used in the MetOne and Andersen samplers. This helps to ensure that nitrate and sulfate collected on the quartz-fiber filter can be used for anion and cation determinations if nitrate and ammonium are lost from the Teflon filter during XRF analysis. Standards are run according to the procedures outlined in the SOP (Appendix B) and used to quantify the concentrations of the anions and cations in the extract. Atmospheric concentrations are obtained by dividing the loadings per filter by the volume of air sampled.

Organic and Elemental Carbon

Organic and elemental carbon collected on pre-baked quartz-fiber filters are determined by the thermal/optical reflectance method (TOR) (see SOP in Appendix B). In this method, a portion of the quartz-fiber filter is heated first in He to remove organic material and then in He with 2% oxygen to remove elemental carbon. The volatilized carbon is converted to CO and then to methane, which is detected by an flame ionization detector. Optical reflectance of the sample is monitored to correct the TOR OC/EC analysis for possible charring during the highest temperature step in 100% He. Concentrations are determined by comparison to standards of known amounts. Atmospheric concentrations are obtained based on the amount of filter used and the volume of air sampled.

Special Studies: XRF and Thermal Analysis for OC/EC

Loss of Nitrate During XRF Analysis

Atmospheric pressure XRF, with secondary ion excitation will likely minimize loss of volatile species e.g., nitrate and condensed SVOCs, during XRF analysis relative to vacuum XRF, thus, these filters might be able to be analyzed for nitrate, sulfate, and ammonium at a later date, or archived for other uses (e.g., QC check on final mass). However, most analytical laboratories use vacuum XRF and both primary and secondary excitation procedures, all of which would likely result in a significant loss of volatile species from the filter and limit it use for other analyses. Therefore, determining the effect of vacuum XRF on volatile species is important for two reasons. First, the URG MASS sampler, as specified from the manufacture uses the same filter to obtain mass, trace elements by XRF, and ions (sulfate and nitrate). If volatile species, i.e., nitrate and ammonium, are lost during vacuum XRF, then subsequent determinations of those species will be biased by the amount lost. Secondly, the FRM sampler, in the compliance network is being used only for mass determination. If vacuum XRF does not bias the nitrate, ammonium, and organic carbon determinations, then these filters can be archived and, if needed re-weighed at a later time, or analyzed for sulfate, nitrate, and ammonium to provide a more detailed chemical composition of the collected aerosol from the FRM sampler. One alternative would be requiring atmospheric pressure XRF analysis of all Teflon filters, assuming it does not drive off semi-volatile species in the analysis process. The other alternative would be not using the filters for further chemical analysis or mass determinations. To examine the potential loss of volatile species from the collected Teflon filter during vacuum XRF (see SOPs and Appendix B), 40 filters are analyzed by vacuum XRF, after atmospheric XRF analysis, and then analyzed for sulfate, nitrate, and ammonium by extraction and IC analysis as described below. These ions are compared to their concentrations collected by the same sampler and by collocated samplers.

As just described, analysis of Teflon filters by atmospheric pressure XRF also may result in the loss of volatile species due to the phase equilibrium shifting to the gas phase as He passes over the sample. Teflon filters previously analyzed by atmospheric pressure XRF are being analyzed for sulfate and nitrate concentrations. These are being compared to nitrate and sulfate concentrations obtained by the same sampler and by collocated samplers.

TOR vs TOT Analysis for OC and EC

Two methods have been widely used for bulk analysis of OC and EC on quartz-fiber filters; thermal optical reflectance (TOR) and thermal optical transmittance (TOT). TOT is the NIOSH 5040 method that is being used by the national laboratories for OC/EC determinations. At the names imply TOR employs reflectance to help adjust the OC/EC analysis for charring during the thermal evolution of OC, while TOT uses transmittance to accomplish the same objective. There are other differences between the methods. For example, the temperature ramps are different and the maximum temperature used for obtaining OC and EC are different. For these reasons, investigators have observed differences between the two methods for OC and EC determinations. Therefore, in this special study, a series of filters will be analyzed by both methods, including standards of known concentrations.

Splitting Filters for Multiple Analyses

As described above, some of the filters are used for more then one analysis or the analytical method itself requires only a section of the filter. For example, Teflon filters for anion and cation analysis are split in half so that each half can be extracted using the appropriate solution. Quartz-fiber filters are sectioned and only a small section (about 1 to 1.5 cm^2) is used for analysis. As well, in the case of the URG chemical speciation sampler, the VAPS, and the FRM the filter is split in half, with one half used for ion analysis and the other for TOR analysis. The SOP for sample sectioning is found in Appendix B.

Filter and Denuder Preparation

Several of the filters require pretreatment to lower blank levels and diffusion denuders need to be coated with a reactive substance to allow for efficient removal of specific gas phase species. For example, Teflon filters are equilibrated at specified T and RH as described earlier, quartz-fiber filters used for OC/EC analysis are baked for several hours (Chow, 1995) at 900 C to lower blank levels to 1 ug C cm^{-2} of filter material, while nylon filters must be cleaned before use to ensure consistently low blank levels if acceptance testing indicates variable blank levels or contamination greater then 1 ug NO_3^- per filter. Nylon filters are cleaned by soaking in a NO_2CO_3 solution followed by a thorough rinse using DI water. Table I-3 lists the filters by sampler type and indicates general filter preparation needs. Denuders must be coated initially, cleaned or refurbished, and recoated as needed. As described in Table I-3, MgO denuders only require the initial coating as they are believed to have sufficient capacity for the 20 day study and are not extracted for chemical analysis. The Na_2CO_3 coated denuder, requires cleaning and re-coating after every use, or at least after every three uses. In the VAPS, this denuder was extracted after each sampling period and analyzed for HNO_3. The XAD denuders, must be refurbished after every sampling period, and re-coated after every tenth sampling period.

Sampling Locations and Rationale

Sampling locations are identified based upon the following criteria. First, the statistical design requires testing each sampler under different chemical atmospheres and varying environmental conditions. Secondly, locations are needed where PM sampling is ongoing with preference given to locations where PM chemical speciation sampling is occurring at the time of the study. Finally, sufficient infrastructure needs to be available with local support to assist with filter changing and sampler operations. Four locations were chosen that meet these criteria: Philadelphia, PA, Phoenix, AZ, Rubidoux, CA, and Research Triangle Park, NC. Philadelphia represents a typical east coast situation where high sulfate and organic material are present in the aerosol, but nitrate is typically low (Pace, 1998). Phoenix represents an area with the potential for high crustal material, which typically is the dominant material above 2.5 Fm, but with a tail in the less than 2.5 Fm size range (Pace, 1998; Solomon et al., 1986). Phoenix also has a strong nitrate and organic material component. Rubidoux represents an area with very high nitrate, moderate organic material, low sulfate, and relatively low crustal material (Solomon et al., 1989; SCAQMD, 1996). The RTP site is to allow for a more thorough evaluation of sampler performance and provide a site where PM levels are near the lower limit of detection for the species measured by the samplers being tested.

Of the four sites, Rubidoux is the prime site because it provides the most stringent test of the samplers for examining collection efficiencies of nitrate and semi-volatile condensed organic compounds, has a full complement of PM, gaseous, and meteorological sampling equipment, including full chemical speciation using the SCAQMD's PTEP sampler, and the characteristics of the air at Rubidoux have been well characterized by several studies over the last decade (e.g., Solomon et al., 1989). Two sets of samplers are collocated at Rubidoux to obtain precision estimates. Table I-4 outlines the existing sampler equipment located at Rubidoux, CA. Table I-5 lists the existing equipment located at Phoenix, AZ. These two sites are well equipped to support this study with both additional PM measurements, meteorological measurements (the most important of which are relative humidity and temperature), and supporting gas phase measurements, such as ozone, nitrogen oxides, and sulfur oxides. PM_{10} sampler meteorological data are collected at the Philadelphia site. At RTP, samplers were installed at the new NERL sampling platform; however, supporting data are not available at this site.

These sites represent Phase I of this program to evaluate the chemical speciation samplers for use in the National Chemical Speciation Network. We recognize however, that the study is limited in scope, not only geographically, but seasonally. Conditions that were not represented are the high sulfate season on the east coast and areas with either high biogenic organic material or high wood smoke emissions. The highest season for crustal material in Phoenix is during the summer, thus, the samplers were not challenged with the highest concentrations of crustal material. The samplers were not evaluated for operations in either very cold or very hot conditions, nor under conditions of severe weather. As discussed earlier, these other conditions will be tested during Phases II and III of this evaluation. Figures I-8 through I-11 show the samplers at each site.

Program Schedule

Overall Program Schedule

Table I-6 summarizes the overall schedule for this study. The schedule was driven by three criteria: 1) a draft report was due to OAQPS by the middle of March, 1998, 2) 20 sample sets would be collected at each site to help ensure that a sufficient number of samples would be collected simultaneously on all samplers to meet the statistical design objectives, and 3) the study could not begin until all five sets of the three chemical speciation samplers and the IMPROVE sampler were delivered to ORD (the original delivery date was August 15, 1998, and only MetOne met that schedule). The latter included delivery of a sufficient number of spare parts, extra filter holders, and denuders to allow for every-other-day sampling. These three criteria uniquely define the schedule for the program and dictated that sampling must be performed simultaneously at the four locations chosen for this study. Sampling was to begin around September 1, 1998. However, all samplers and spare parts were not delivered until nearly the end of November 1998 (Andersen was the last sampler to arrive), which with seasonal holidays delayed the start of sampling until nearly the middle of January, 1999. The due date for submission of the draft final report to OAQPS was then re-scheduled for the end of June 1999.

Sampling Schedule

Sampling was conducted in January and February of 1999. Samplers were operated for 24-hr sampling periods every other day, except at Rubidoux. Sampling at Rubidoux was every third day to sample simultaneously with the PTEP sampler.

To meet the every other day sampling schedule, filters and holders were shipped overnight to the contractor immediately after collection according to the sampling schedule illustrated in Table I-7. Filters, the XAD denuder in the VAPS, and all Na_2CO_3 denuders were shipped by overnight mail. Three full sets of filter holders and denuders were available for this purpose, which required continuous shipping of filters to and from the laboratory. This turned out to be a rigorous schedule to maintain with site operators and laboratory personnel working 7 days per week. Delays only occurred when the overnight service failed to delivery the filters as expected.

Preliminary Evaluation and Training

Once samplers were received at EPA in Research Triangle Park, they were configured for use in this field study and underwent a quick shakedown. One representative from each manufacturer was available to ensure proper assembly of their samplers and to train contractor personnel. The shakedown included, for example, running each sampler for two-12 to 24 hour periods to ensure that samplers were turning on and off as expected, flow rate checks, flow control checks, leak checks, etc. Standard operating procedures in the form of operating manuals were made available from the manufacturers when the samplers were delivered to RTP. The contractor prepared condensed installation and operating SOPs for easy use by field and laboratory operators. A list of SOPs is given in Table I-2 and Appendix B.

Site Installation and Decommissioning

All sites were equipped with one of each of the three chemical speciation samplers, one IMPROVE, one VAPS, and one set of two FRM samplers. Rubidoux had a collocated second set of all samplers except the VAPS sampler. EPA contractor personnel installed the samplers at all sites, trained site operators at Rubidoux and Phoenix, and conducted initial systems and performance audits prior to the start of the study. At the end of the study, EPA contractors performed a final audit and then decommissioned the site and returned the equipment to EPA at Research Triangle Park, NC. A mid-study audit was also conducted.

Power and platforms were provided by the states or local districts. At Rubidoux and Phoenix, local state or local district operators normally working at those sites operated the samplers. At Philadelphia and RTP, the sites were operated by EPA contractors.

Sampler Operation and Filter Shipping and Storage

Samplers were operated according to the SOPs as given for each sampler and referenced Table 1-2 and in Appendix B. Three full sets of filter holders and denuders were required for each sampler to meet the rigorous schedule described above. The three sets of filter holders and denuders also allowed time for these items to be shipped to the contractor for exchange, thus, removing site-to-site variability for filter changing. Filters were shipped in coolers at reduced temperature with a max/min thermometer. Each cooler contained sufficient blue ice, sealed in plastic bags or some other closed system, to keep the filters cool for 24-hours. At the field site, the filters were stored before and after sampling at reduced temperatures in a refrigerator, especially after sample collection. Except for equilibration of filters for mass determination, filters with collected aerosol were stored in sealed petri dishes at reduced temperatures at or below freezing.

Quality Assurance/Quality Control (QA/QC)

A thorough QA/QC effort was implemented for this study to ensure the quality of the data. These efforts included audits of the samplers prior to, during, and after the field program, even though the study was only 2 months in duration. Laboratory quality assurance and control followed already established procedures and included external audits of the analyzers in conjunction with ongoing studies.

Field QA/QC

Quality assurance consisted of system and performance audits at the beginning, middle, and end of the study. These audits were conducted by contractor staff. Initial QA audits of the samplers were performed prior to the first sample if possible, or as quickly after the initiation of the program as possible. A second set of system and performance audits was performed in the middle of the program, between the 8th and 10th sampling periods, depending on the site. A third set of audits was performed after the last sample, but before decommissioning of the samplers by the EPA contractor. Initial system audits checked installation of the samplers, site setting, site operations and operators, and custody management. Performance audits checked flow rates, check for vacuum leaks, and other performance characteristics of the samplers. Quality control consisted of checking flow rates before and after each sample on every filter unless automatically logged by the sampler, maintaining appropriate operations logs, checking filter holders and denuders prior to and after each sampling period, and other items as specified on the data log sheets.

Laboratory QA/QC

Laboratory systems and performance audits were conducted for each species according to schedules already in place in the laboratories. Results will be reported to EPA staff in the contractors final report, which has not been received to date.

STATISTICAL ANALYSIS

Questions or Statistical Hypotheses Being Tested

As described above in the introduction, the primary objective of this study is to determine if there are differences among the three chemical speciation monitors for their estimation of the concentrations of the chemical components of $PM_{2.5}$ mass. Comparisons also are made to two historical samplers (IMPROVE and VAPS) and to the FRM using these samplers as a relative reference. Reference standards do not exist for any of the species, only for mass and that is defined by the FRM; therefore, this study is testing the equivalency of the samplers to each other, rather then comparing the samplers to a known value that provides an estimate of their accuracy.

There are three major questions to be addressed by this intercomparison study.

1. How do the concentrations of the measured chemical components as determined by the FRM compare to those measured by the chemical speciation monitors?

2. Can FRM mass be reconstructed within expected uncertainties from the sum of the chemical components as measured by the chemical speciation monitors?

3. How well do the concentrations of the measured chemical components of $PM_{2.5}$ from the various speciation samplers agree?

4. What are the causes of the differences, if they exist. Some are expected due to the different methods employed by the different samplers? and

5. What is the potential effect of different analytical methods on measured concentration of the chemical components of $PM_{2.5}$. These include the effect of vacuum XRF vs. atmospheric pressure XRF on nitrate concentrations measured on Teflon filters and the effect of thermal optical reflectance vs. thermal optical transmittance on OC/EC concentrations.

The following hypotheses are predicated on the assumption that the collection efficiency (slope of the efficiency curve and cutpoint) for the samplers in this study are essentially the same. Also, it is important to establish the precision of the instruments and this was done by collocating samples at Rubidoux. While this provides only a limited assessment of the precision (one site, one time of the year, one set of atmospheric conditions), it does provide a first cut estimate of the precision needed for the statistical analyses performed here. If for example, the precision is estimated at 50%, then determining differences among samplers is not as informative as if the precision were say 10-15%. As a benchmark, the coefficient of variation for the differences in mass concentrations from collocated FRM instruments is required to be less than 10%, according to 40 CFR Part 58, Appendix A. Depending on the species, based on the authors' prior experiences, we anticipate a range of precision from less than 10% to about 30%.

In the following discussion, the phrase "speciation samplers" includes the Andersen RAAS, the URG MASS, the Met-One SASS, the IMPROVE, and the VAPS.

The following hypotheses are related to the first two questions, how do the samplers compare to the FRM and can FRM mass be reconstructed from the species measured by the speciation samplers. For each of these hypotheses, the concentrations, on a species-by-species basis, from each of the speciation samplers is compared to the respective concentration from the FRM. The concentrations from the speciation samplers are not compared to each other. The specific hypotheses are:

1. $PM_{2.5}$ mass concentrations measured on the FRM by weighing a Teflon filter is compared to $PM_{2.5}$ mass as measured by weighing filters collected by the Teflon filters in the chemical speciation monitors. The hypothesis is that the mass concentration from each of the speciation samplers is not statistically different from the mass on the FRM filter. This is the starting point. The next eight hypotheses delve further into understanding why the mass concentrations do or do not compare favorably.

2. $PM_{2.5}$ trace elements or groups of trace elements determined on samples collected by the Teflon filter in the FRM as determined by XRF are compared to trace elements determined on samples collected on Teflon filters collected by the speciation samplers. The hypothesis is that there is no statistical difference between the concentrations from each of the speciation samplers to that determined from samples collected by the FRM. These concentrations should be comparable since these species are stable.

3. $PM_{2.5}$ sulfate on the FRM quartz filter is compared to sulfate on the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that determined from samples collected by the FRM. These concentrations should be comparable since sulfate is a stable species.

4. $PM_{2.5}$ ammonium determined from samples collected by the quartz-fiber filter on the FRM is compared to ammonium ion determined from samples collected on the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to

that determined from samples collected by the FRM. These concentrations may not be comparable since ammonium is volatile when in the form of ammonium nitrate.

5. $PM_{2.5}$ nitrate determined from samples collected on the quartz-fiber filter in the FRM is compared to nitrate determined from samples collected on the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypotheses is that there is no difference between the concentrations from each of the speciation samplers to that determined from samples collected by the FRM. These concentrations should be comparable since the collection of nitrate on these filters should all be biased by the loss of nitrate due to volatilization, with the exception of the IMPROVE.

6. $PM_{2.5}$ nitrate on the FRM quartz filter is compared to nitrate on the nylon (RAAS, SASS, IMPROVE), or quartz+nylon (MASS, VAPS) filters in the speciation samplers. The hypothesis is that the nitrate from each of the speciation samplers is greater than or equal to the nitrate on the FRM Teflon filter, due to negative artifacts in the FRM. This addresses questions about the amount of nitrate volatilized from the FRM Teflon filter.

7. $PM_{2.5}$ elemental carbon (EC) determined on samples collected on quartz-fiber filters by the FRM is compared to EC determined on quartz-fiber filters collected by the chemical speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since elemental carbon is stable.

8. $PM_{2.5}$ organic carbon (OC) determined on quartz-fiber filters collected by the FRM is compared to OC determined on quartz fiber (MASS, RAAS, SASS, IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that determined from samples collected by the FRM. These concentrations should be comparable since as designed in this study, all the speciation samplers potentially suffer from negative or positive artifacts.

9. $PM_{2.5}$ OC determined on samples collected on the quartz-fiber filter in the FRM is compared to OC determined on samples collected on the quartz-fiber filter from the VAPS. The hypothesis is that OC collected by the FRM is greater then the OC collected by the VAPS denuded channel if there are positive artifacts, or less than the VAPS denuded channel if there are negative artifacts. No difference would be inconclusive.

The following hypotheses compare the concentrations of the chemical components determined on samples collected by the chemical speciation samplers to address why there are differences among measured concentrations, if they exist. For each of these hypotheses, only the concentrations from the speciation samplers are compared.

10. $PM_{2.5}$ mass and chemical composition as determined according to the manufacturer's guidelines are compared among the speciation samplers. The hypothesis is that all species of interest are comparable among the chemical speciation samplers when concentrations are determined according to manufacturer's guidelines.

11. $PM_{2.5}$ mass concentrations determined by gravimetric analysis using Teflon filters are compared among the samplers. The hypothesis is that there is no difference in these masses.

12. $PM_{2.5}$ trace element concentrations (individually or in groups) determined by XRF from samples collected by Teflon filters are compared among the samplers. The hypothesis is that there is no difference in these concentrations as these elements are stable during sampling and analysis.

13. $PM_{2.5}$ nitrate concentrations determined from samples collected using nylon (RAAS, SASS, IMPROVE) or Teflon+nylon (MASS, VAPS) filters are compared among the samplers. The hypothesis is that there is no difference in these concentrations.

14. $PM_{2.5}$ sulfate determined from samples collected using Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that there is no difference in sulfate concentrations as sulfate is stable during sampling and analysis. We also will look at sulfate estimated from XRF sulfur (S times 3 is approximately equal to sulfate) to see how well XRF sulfur estimates sulfur determined by IC from both Teflon or quartz filters.

15. $PM_{2.5}$ organic and elemental carbon determined from samples collected by quartz-fiber filters where no denuder is used is compared among the speciation samplers. Since the VAPS used a denuder, it will not be included in this hypothesis. The hypothesis is that the concentrations of OC and EC are the same provided no denuder is employed.

16. $PM_{2.5}$ organic and elemental carbon determined from samples collected by quartz-fiber filters, including speciation samplers where a denuder is used is compared among the samplers. The hypothesis is that samplers that use denuders (VAPS) will have lower OC concentrations since the potential for positive artifact due to organic vapors has been minimized. Nothing can be said about negative artifacts.

17. $PM_{2.5}$ ammonium determined from samples collected by the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that the concentrations of ammonium are the same for all speciation samplers as all potentially suffer from negative artifacts.

18. Ammonium nitrate equilibrium is a function of temperature and relative humidity and thus, nitrate concentrations measured on reactive filters behind a base coated denuder are compared as a function of temperature and RH to determine if these factors bias sample collection. The hypothesis is that there is no difference in the samplers as a function of temperature or RH.

19. Crustal related elements are typically associated with particles greater than 2.5 um AD, however, differences in the inlet the efficiency (slope and cutpoint) may result in different concentrations of crustal related material being measured by these samplers. The hypotheses is that the crustal related material as determined from summing the oxides of Fe, Ca, and Si (Solomon et al., 1989) are not statistically different among the samplers. If differences are observed they are related to the coarse particle mass as measured by the VAPS or by other collocated PM_{10} monitors. Wind speed also is a variable of interest in this analysis.

The above hypotheses examine the first four major questions stated above. Statistical differences are examined with in sites using primarily the paired t-test at alpha = 0.05. Added variability due to site-to-site variations in the chemical composition limit the paired t-test to individual sites, as missing data are minimized. The data also are examined by looking at means, time series analysis, regression analysis, difference analysis on a species by species basis relative to the FRM.
Several tests are being conducted to examine the affect of different analytical methods on the concentration of the species measured. These include the effect of vacuum XRF or atmospheric XRF on nitrate concentrations measured on the filter after XRF analysis and the use of TOR vs. TOT for OC/EC analysis as stated in the fifth question presented at the beginning of this section.

a. Examine the effect of vacuum vs. atmospheric pressure XRF on nitrate concentrations measured on the Teflon filter after XRF analysis. The hypothesis is two fold. First, there will be a greater loss of nitrate from Teflon filters after vacuum XRF than after atmospheric pressure XRF. Secondly, losses that occur during atmospheric pressure are minimized, such that nitrate measured after atmospheric pressure XRF is not different than nitrate measured on a Teflon filter that has not undergone XRF analysis. It is important to understand the magnitude of the loss of nitrate from Teflon filters after vacuum or atmospheric XRF because the proposed design of the URG sampler has ion analysis occurring after XRF analysis of the only Teflon filter in the system. There is also great potential for the FRM Teflon filter to be used for XRF analysis and ion analysis after mass determination to obtain additional speciation data at FRM sites.

b. Examine difference between OC and EC as measured by TOR and TOT. The hypothesis is that these two methods are statistically not different from each other for determining OC and EC from samples collected on quartz-fiber filters. However, differences have been noted, especially with samples collected in areas with high wood smoke emissions.

Finally, the samplers will be evaluated in terms of their operational performance or practicality of use in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements. Field operators were asked to maintain detailed logs of their operational performance and they completed an extensive survey after the study on these issues. As well cost data are presented for the samplers and spare parts.

Data Reporting Format

The concentrations for each analyte will be compiled as a flat ASCII file organized as follows:

1) Format
ASCII text file with defined columns and rows.

2) Site ID's:
1 = Rubidoux
2 = Phoenix
3 = Philadelphia
4 = Research Triangle Park

3) Sampler ID's:
FRM - Teflon = FRM-T
FRM - Quartz = FRM-Q
VAPS = VAPS
Met One-SASS = MET
URG-MASS = URG
Andersen RAAS = AND
Improve = IMP

4) Analytes (mass/m^3)
C-1 = $PM_{2.5}$
C-2 = SO_4
C-3 = NO_3
C-4 = NH_4
C-5 = OC
C-6 = EC
C-7 = S-XRF
C-8.Cn = Individual metals – XRF

5) Reporting Duplicate Sampler Results (Rubidoux)
Identify as "Repeat 1" and "Repeat 2".

6) Limit of Detection (LOD) or MDL for Total Method (Sampling Plus Analysis)

The LOD for mass is determined based on Federal Reference Method procedure (40 CFR, Part 50, Appendix L). The LOD sulfate, nitrate, and ammonium based on 3 time the noise in the baseline noise in the chromatogram since field blanks were non-detectable, while for OC and EC it is based on three times the standard deviation of the field blanks. XRF limits of detection are based on propagating errors associated with the analytical method and flow rates. In general, LOD values were within the expected ranges.

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Table I-1. Analyte Listing for Speciation Sampler Intercomparison

Analytical Method	**Analyte (Concentration Units)**	**Sampling Systems**						
		Met One	**MASS**	**RAAS**	**IMPROVE**	**FRM-T**	**FRM-Q**	**VAPS**
Gravimetric	$PM_{2.5}$ Mass	x	x	x	x	x	-	x
Ion Chromatography	$SO_4^=$, NO_3^-, NH_4^+,	x	x	x	x	-	x	x
Thermal/Optical Ref. Method	OC/EC	x	x	x	x	-	x	x
Atmospheric Pressure XRF	S, Si, Ca, Mn, Fe, Cu, Zn, Pb, Groupings of metals, etc.,	x	x	x	x	x	-	x

Table I-2. List of Standard Operating Procedures for Field and Laboratory Efforts During the Chemical Speciation Monitor Evaluation Study.

Field Related SOPs

SOP	Prepared By
Spiral Ambient Speciation Sampler	MetOne
Reference Ambient Air Sampler	Andersen
Mass Aerosol Speciation Sampler	URG Corp.
IMPROVE Sampler	UC Davis
Versatile Air Pollution Sample	RTI
PM2.5 Federal Reference Method	RTI
Filter Pack and Cassette Handling in the Field	RTI
Denuder Handling and Shipping in the Field	RTI
Receiving, Laboratory and Field	RTI
Shipping at Reduced Temperatures	RTI

Laboratory Related SOPs

SOP	Prepared By
Filter Pack and Cassette Handling in the Lab	RTI
Denuder Preparation – Na_2CO_3	RTI
Denuder Extraction – Na_2CO_3	RTI
Denuder Preparation – MgO	RTI
Denuder Preparation – XAD	RTI
Denuder Regeneration – XAD	RTI
Denuder Extraction – XAD	RTI
PUF Cartridge Cleaning and Preparation	RTI
Filter Preparation – Nylasorb (nylon)	RTI
Filter Preparation – Teflon	RTI
Filter Preparation – Quartz-Fiber	RTI
Acceptance Testing of Filters	RTI
Filter Sectioning Procedures	RTI
Filter Extraction – Nylasorb	RTI
Filter Extraction -- Teflon	RTI
Filter Extraction – Quartz-Fiber	RTI
Mass by Gravimetric Analysis[1]	RTI
Anions by Ion Chromatography	RTI
Cations by Ion Chromatography	RTI
XRF – Atmospheric Pressure	Mantech/NERL
XRF – Under Vacuum	DRI/Reno
Thermal-Optical Reflectance (TOR)	DRI/Reno
Thermal-Optical Transmittance (TOT)	Sunset Labs
Data Validation	RTI

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[1] Federal Register for FRM.

Table I-3. Experimental Design Including Filter and Denuder Preparation.

Sampler	Filter Type (Channel)	Denuder Type	Analysis	Filter and Denuder Preparation
Andersen RAAS	Teflon (2) Teflon (3)		(2) Mass and elements[1] (3) ions[2]	Filters are equilibrated before weighing Filters are wet with ethanol before extraction
	Nylon (4)	MgO	Fine particle NO_3	Nylon filters are cleaned before use and extracted in IC eluent; MgO denuders are not changed or cleaned during the study
	Quartz (1)		OC/EC	Quartz filters are baked before use
Met-One SASS	Teflon (1) Teflon (2)		(1) Mass and elements (2) ions	Filters are equilibrated before weighing Filters are wet with ethanol before extraction
	Nylon (3)	MgO	Fine particle NO_3^-	Nylon filters are cleaned before use and extracted in IC eluent; MgO denuders are not changed or cleaned during the study
	Quartz (4)		OC/EC	Quartz filters are baked before use
	Quartz (5)		OC/EC	Quartz filters are baked before use; Carbon denuders need to be heat treated every 7 samples
URG MASS	Teflon		Mass and elements	Filters are equilibrated before weighing
	Nylon	Na_2CO_3	Volatilized nitrate	Nylon filters are cleaned before use and are extracted in IC eluent; Na_2CO_3 denuders are cleaned and re-coated daily
	Quartz		OC/EC, ions	Quartz filters are baked before use; Filters are split in half to allow for ion analysis
IMPROVE	Teflon		Mass and elements	Filters are equilibrated before weighing
	Nylon	Na_2CO_3	Volatilized nitrate	Nylon filters are cleaned before use and are extracted in water since NH_4^+ also is analyzed in the extract; Na_2CO_3 denuders are cleaned and re-coated daily
	Quartz		OC/EC	Quartz filters are baked before use
VAPS	Teflon	Na_2CO_3	Mass and elements Denuder for HNO_3	Filters are equilibrated before weighing Na_2CO_3 denuders are extracted and re-coated daily
	Nylon	Na_2CO_3	Volatilized nitrate	Nylon filters are cleaned before use. Nylon is the backup filter in a Teflon/nylon filter pack
	Quartz	XAD-4	Filter for OC/EC, ions Denuder for SVOCs	Quartz filters are baked before use; XAD-4 denuders must be rinsed daily, re-coated every 10 samples
FRM	Teflon		Mass and elements	Filters are equilibrated before weighing
	Quartz		Ions and OC/EC	Quartz filters are baked before use; Filters are split in half to allow for ion analysis

1. Elements refer to those obtained from XRF analysis, potential Na to Pb.
2. Ions include nitrate, sulfate and ammonium.

Table I-4. Measurements Made at Rubidoux, CA in Conjunction with the Chemical Speciation Sampler Evaluation Study.

Species	**Measurement Method**	**Duration/Frequency**[1]
PM2.5 and PM_{10} Mass and Chemistry	Sierra Anderson Dichotomous Samplers, PTEP Sampler	24 hrs/1 in 3 days
PM2.5 Elemental Carbon	Magee Scientific aethalometer with a Harvard Impactor PM2.5 inlet	5 minute average, C
Light scattering	Optec nephelometer	1 hour average, C
PM2.5 EC/OC	Rupprecht & Patashnick Total Carbon Analyzer	1 hour average, C
PM_{10} Mass	Rupprecht & Patashnick PM_{10} Federal Equivalent Method TEOM	1 hour average, C
Methane/NMHC	TEI hydrocarbon analyzer	1 hour average, C
NOx/NOy	TEI NO_x/NO_y analyzers	1 hour average, C
O_3	One Dasibi ozone analyzer	1 hour average, C
CO	TEI CO analyzer	1 hour average, C
NO, NO_2, NOx	TEI NOx analyzer	1 hour average, C
Wind Speed	AGL	1 hour average, C
Wind Direction	AGL	1 hour average, C
Standard Deviation of Wind Direction	AGL	1 hour average, C
Air Temperature	2 meters AGL, nephelometer height	1 hour average, C
Relative Humidity	2 meters AGL, nephelometer height	1 hour average, C
Delta Temperature		C

[1] O6-one in six days; C-continuous; D-Daily; OD-Every other day.

Table I-5. Measurements Made at Phoenix, AZ in Conjunction with the Chemical Speciation Sampler Evaluation Study.

Species	Measurement Method	Duration/Frequency[2]
$PM_{2.5}$, Coarse PM, & PM_{10} Mass and Chemistry	4 - Sierra Anderson Dichotomous Samplers	6 and 24 hours/O6, (2 w/ quartz, 2 w/ Teflon filters)
$PM_{2.5}$, Coarse PM, & PM_{10} Mass and Chemistry	2 - IMPROVE 25mm 4-module samplers	24 hours/OD, (each w/ Teflon, nylon, quartz, & PM_{10} Teflon filters, respectively)
$PM_{2.5}$ Elemental Carbon / Light Absorption	2 - Magee Scientific aethalometers, each with a Harvard Impactor $PM_{2.5}$ inlet	5 minute average/C
Ambient light scattering	Optec nephelometer (NGN-2)	1 hour average/C
$PM_{2.5}$ EC/OC	Rupprecht & Patashnick Total Carbon Analyzer	1 hour average/C
PM_{10} Mass	Rupprecht & Patashnick PM_{10} Federal Equivalent Method TEOM	1 hour average/C
Methane/NMHC	TEI hydrocarbon analyzer	1 hour average/C
NOx/NOy	TEI NOx/NOy Trace level analyzers	1 hour average/C
O_3	Dasibi O_3 analyzer	1 hour average/C
CO	TEI CO analyzer	1 hour average/C
NO, NO_2, NOx	TEI NOx analyzer	1 hour average/C
SO_2	Monitor Labs SO_2 analyzer	1 hour average/C
Wind Speed	10 meters AGL	1 hour average/C
Wind Direction	10 meters AGL	1 hour average/C
Standard Deviation of Wind Direction	10 meters AGL	1 hour average/C

[1] O6-one in six days; C-continuous; D-Daily; OD-Every other day.

Table I-6. Overall Planned Study Schedule[1].

Date	Deliverable
1998	
November 10	Standard operating procedures received from the 3 chemical speciation sampler manufacturers and for the IMPROVE and VAPS samplers
October 1-Nov. 20	Sites prepared for sampler installation. Power and platforms installed as needed to accommodate all samplers (see Tables 1 and 2 for listing of samplers at each site).
Nov 1 - 30	Samplers will undergo an evaluation and RTP field personnel will be trained on installation, operation, and quality control
Nov 12-24	External review by the expert peer-review panel on chemical speciation.
Nov 20-Dec 10	Samplers shipped to sampling sites and local operators trained.
Dec 8-Dec 12	Systems and performance audits performed with help from local agency (Rubidoux and Phoenix)
Dec 14	First day of sampling. (Rubidoux and Phoenix)
1999	
Jan 4-Jan 5	Systems and performance audits performed with help from local agency (Phoenix and Philadelphia)
Jan 6	First day of sampling (Philadelphia and RTP)
Jan.1-4	Systems and performance audits performed with help from local agency.(optional)Chemical analysis of first half of samples should be started.
March 1	Last day of sampling. Systems and performance audits performed with help of local agency.
March 2-5	Decommission sites.
March 20	Chemical analyses complete.
April 15	Level II data delivered to EPA for all chemical analyses.
April 15-May 1	EPA reviews data and begins initial statistical analysis[2]
May 1-May-15	All final statistics prepared, including plots, tables, and figures
May 15-May 30	Prepare report and submit to internal NERL review group for comments
June 15	Address comments from internal review group
June 25	Provide OAQPS with draft report.

[1] Actual schedule for data delivery was delayed. However, OAQPS also delayed implementation of samplers and both schedules then coincided.

[2] Detailed initial results are forwarded to OAQPS at this point or earlier.

Table I-7. Field Operations Sampling Schedule.

Sample Day	**Rubidoux**	**Phoenix**	**Philadelphia**	**RTP**
1	1/6/99	1/6/99	1/17/99	1/15/99
2	1/9/99	1/8/99	1/19/99	1/17/99
3	1/15/99	1/14/99	1/21/99	1/19/99
4	1/18/99	1/16/99	1/23/99	1/21/99
5	1/21/99	1/18/99	1/25/99	1/23/99
6	1/24/99	1/20/99	1/27/99	1/25/99
7	1/27/99	1/22/99	1/29/99	1/27/99
8	1/30/99	1/24/99	1/31/99	1/29/99
9	2/2/99	1/26/99	2/2/99	1/31/99
10	2/5/99	1/28/99	2/4/99	2/2/99
10 (blank)	2/9/99	1/29/99	2/5/99	2/5/99
11	2/11/99	2/3/99	2/8/99	2/6/99
12	2/14/99	2/5/99	2/10/99	2/8/99
13	2/17/99	2/7/99	2/12/99	2/10/99
14	2/20/99	2/9/99	2/14/99	2/12/99
15	2/23/99	2/11/99	2/16/99	2/14/99
16	2/26/99	2/13/99	2/18/99	2/16/99
17	3/1/99	2/15/99	2/20/99	2/18/99
17 (blank)	3/2/99	n/a	n/a	n/a
18	n/a	2/17/99	2/22/99	2/20/99
19	n/a	2/19/99	2/24/99	2/22/99
20	n/a	2/21/99	2/26/99	2/24/99
20 (blank)	n/a	2/24/99	2/27/99	2/25/99

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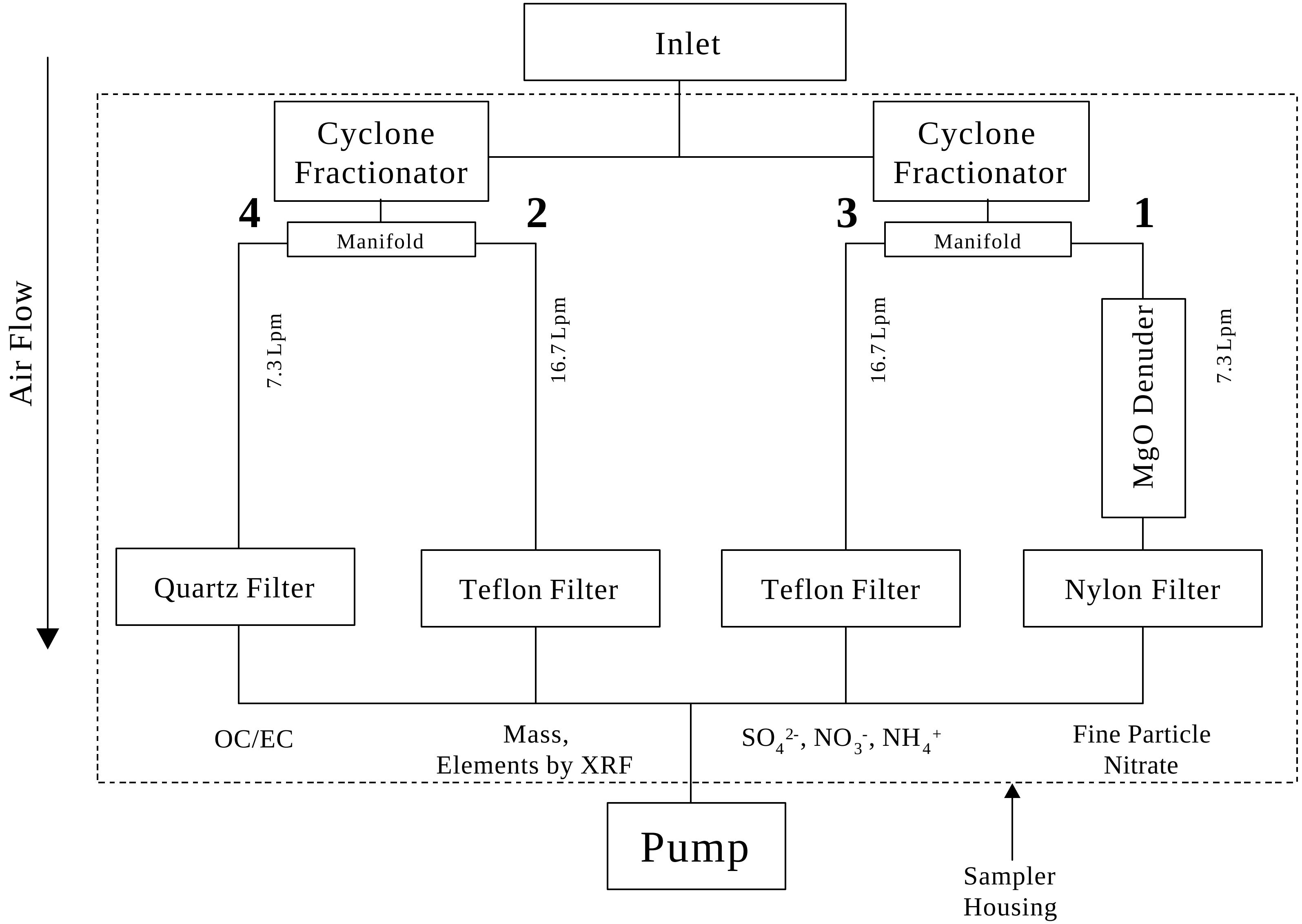


Figure I-1a. Schematic of the Andersen RAAS Sampler.

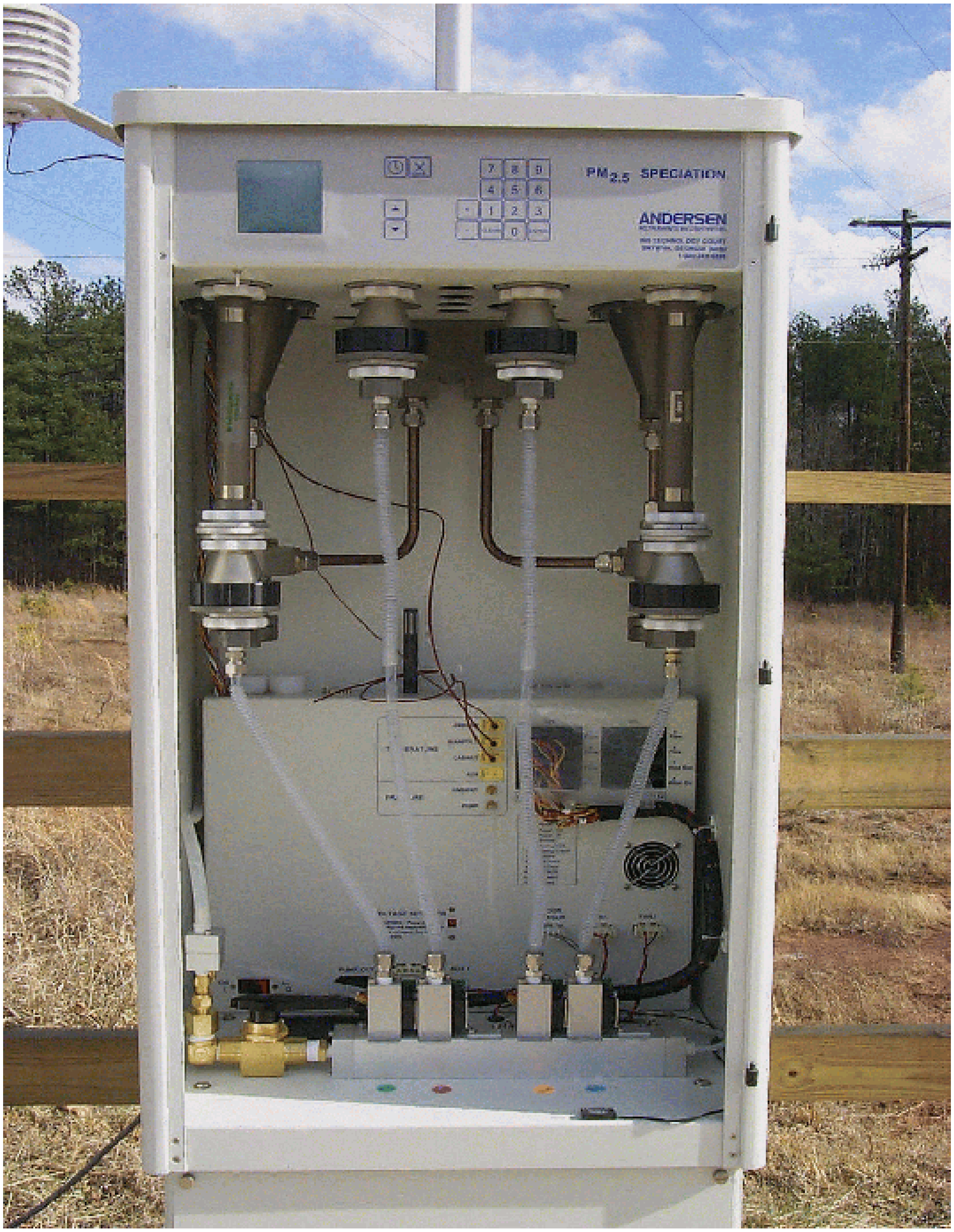


Figure I-1b. Picture of the Andersen RAAS Sampler Deployed in the Field at RTP.

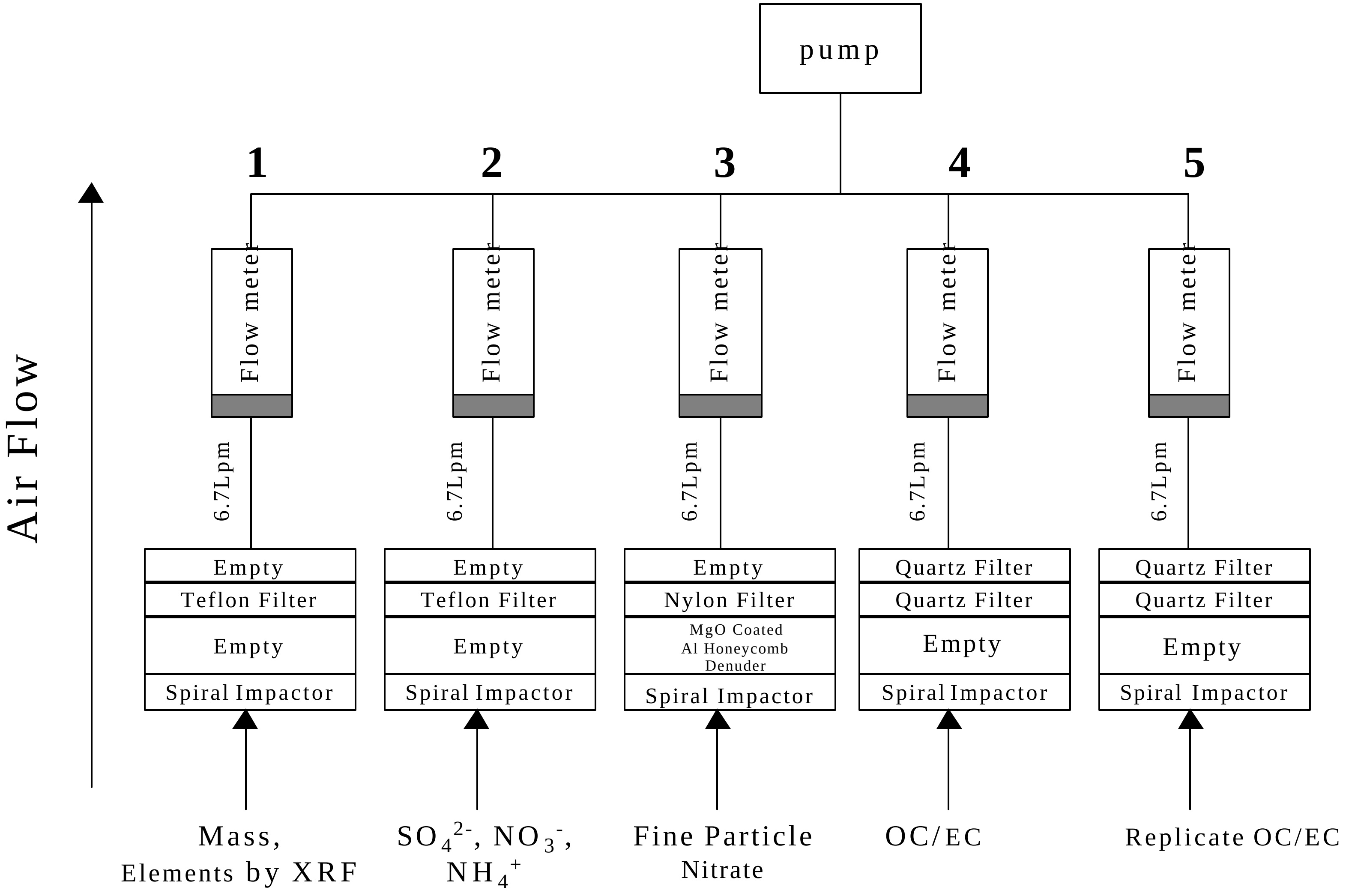


Figure I-2a. Schematic of the MetOne SASS Sampler.

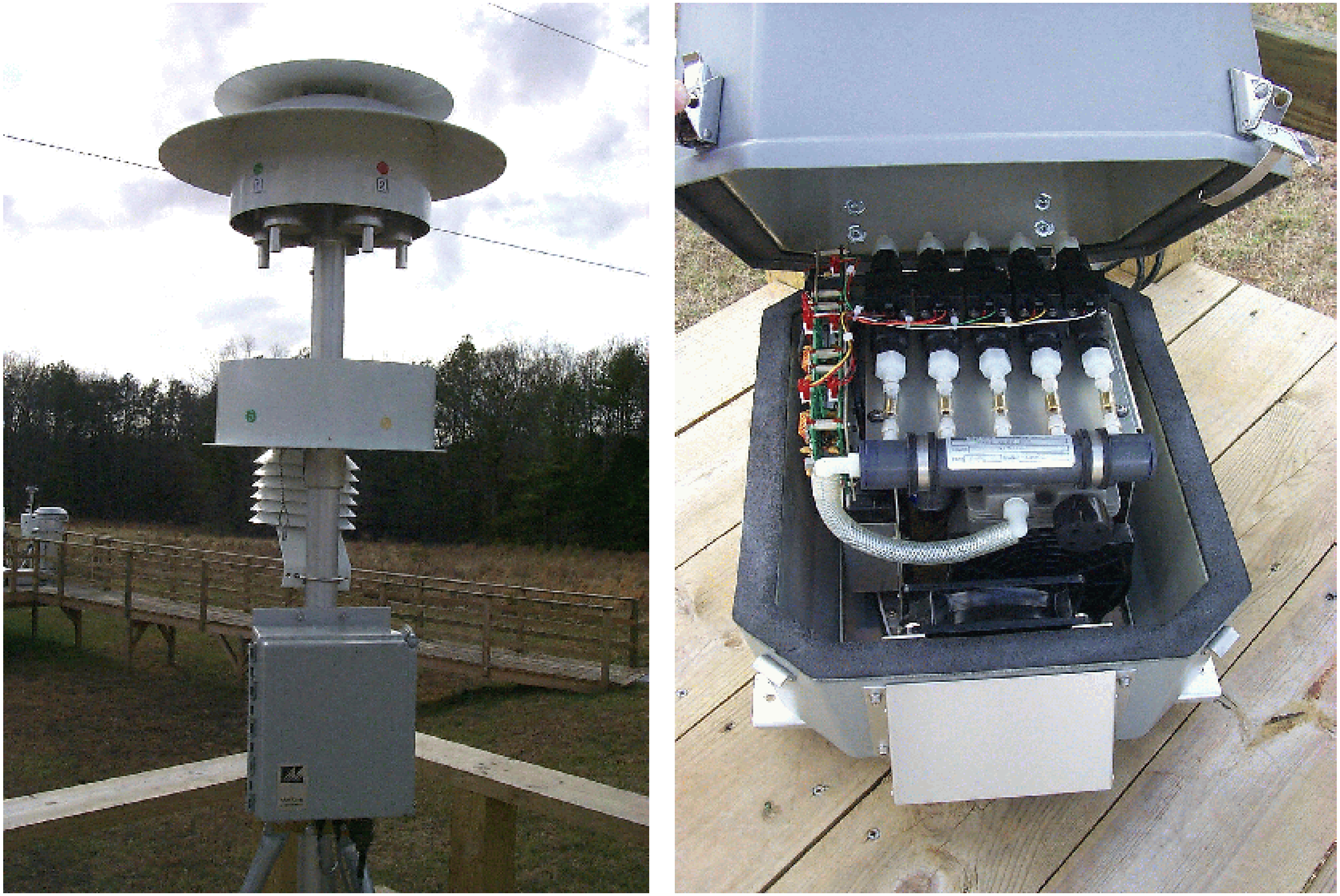


Figure I-2b. Picture of MetOne Sampler Deployed in the Field at RTP. Left – Inlet, Filter Holders, and Meteorological Sensor. Right-Pump box.

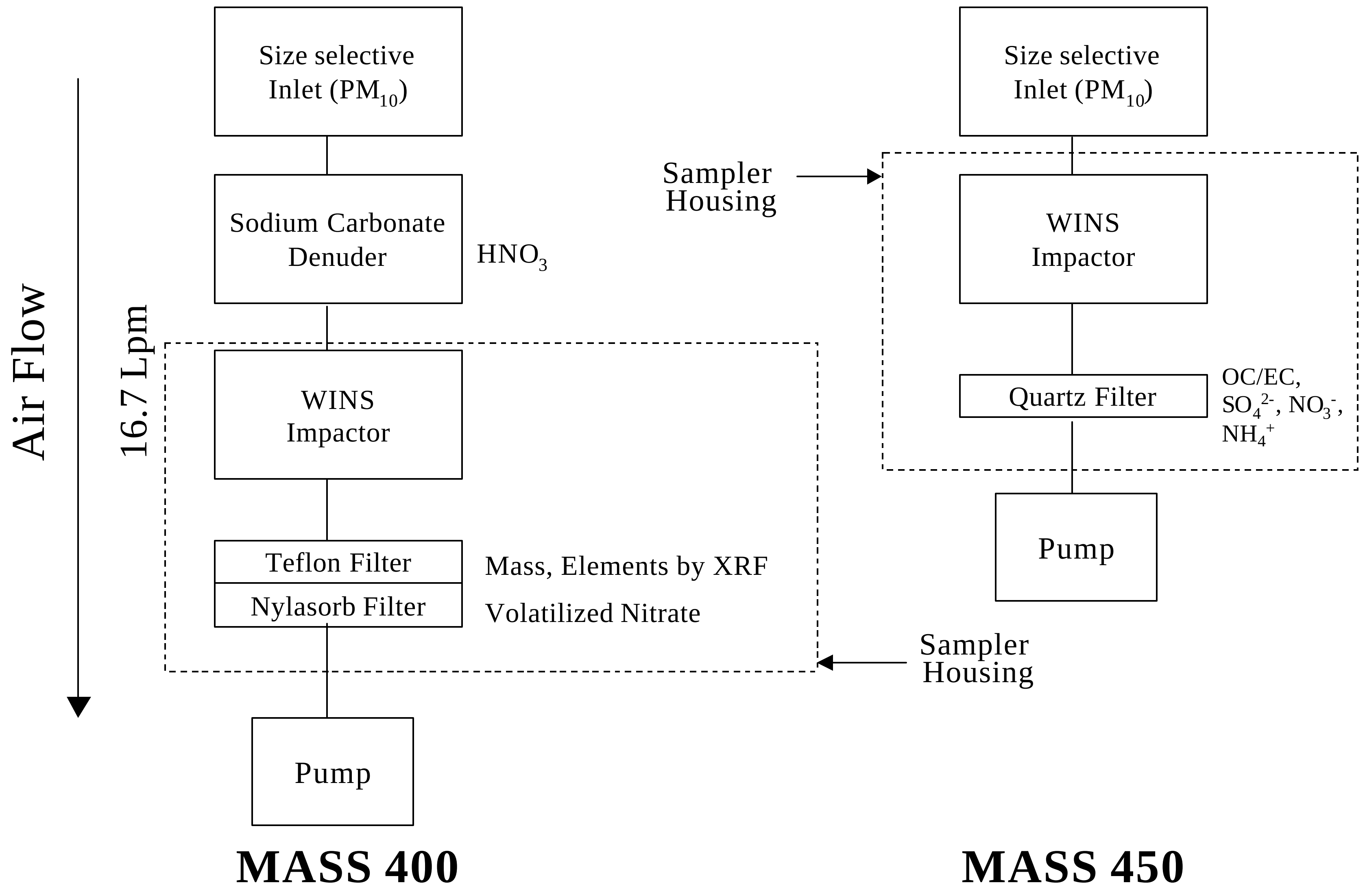


Figure I-3a. Schematic of the URG MASS Sampler.

Figure I-3b. Picture of the URG MASS Sampler Deployed in the Field at RTP.

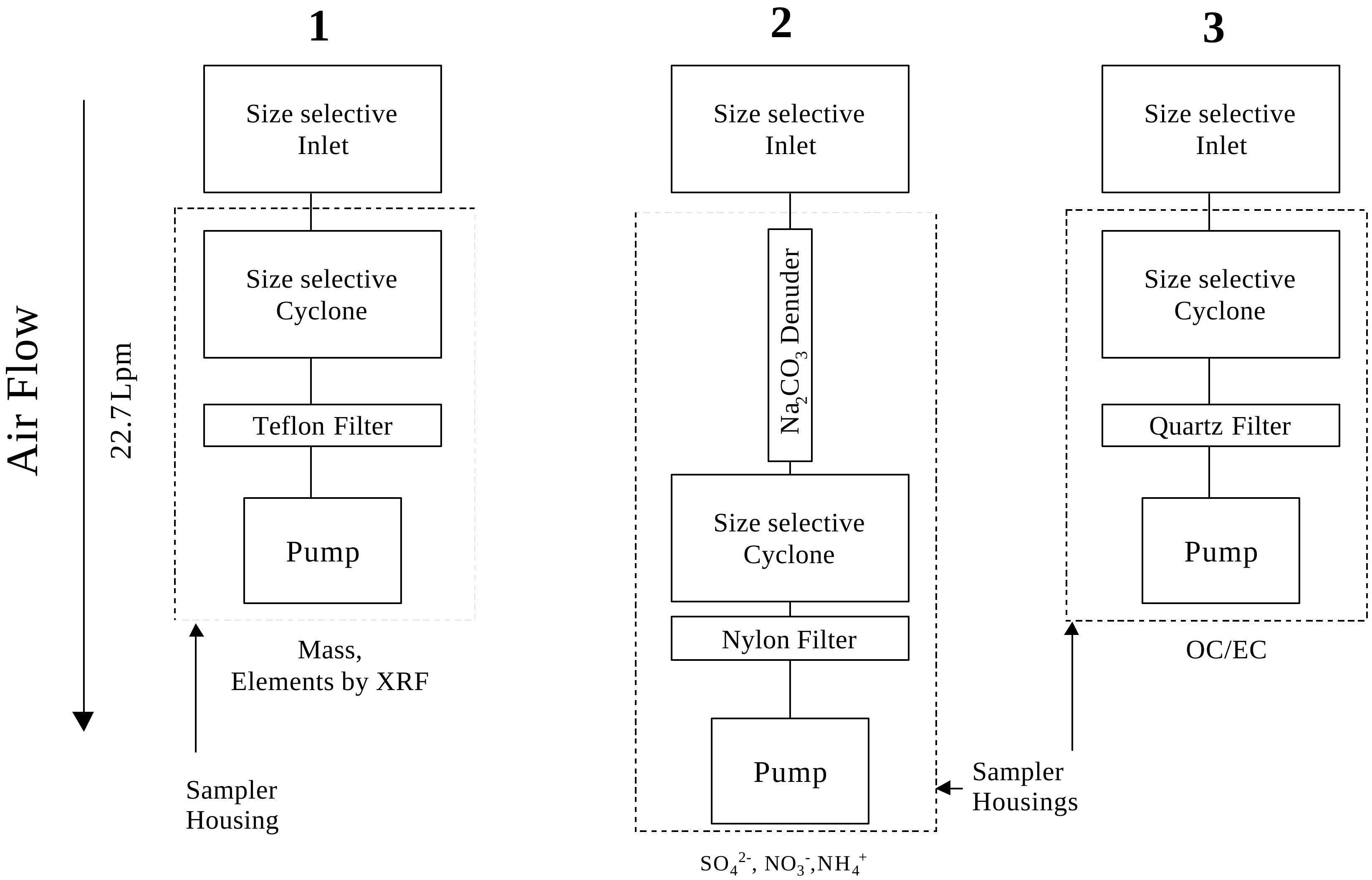


Figure I-4a. Schematic of the IMPROVE Sampler.

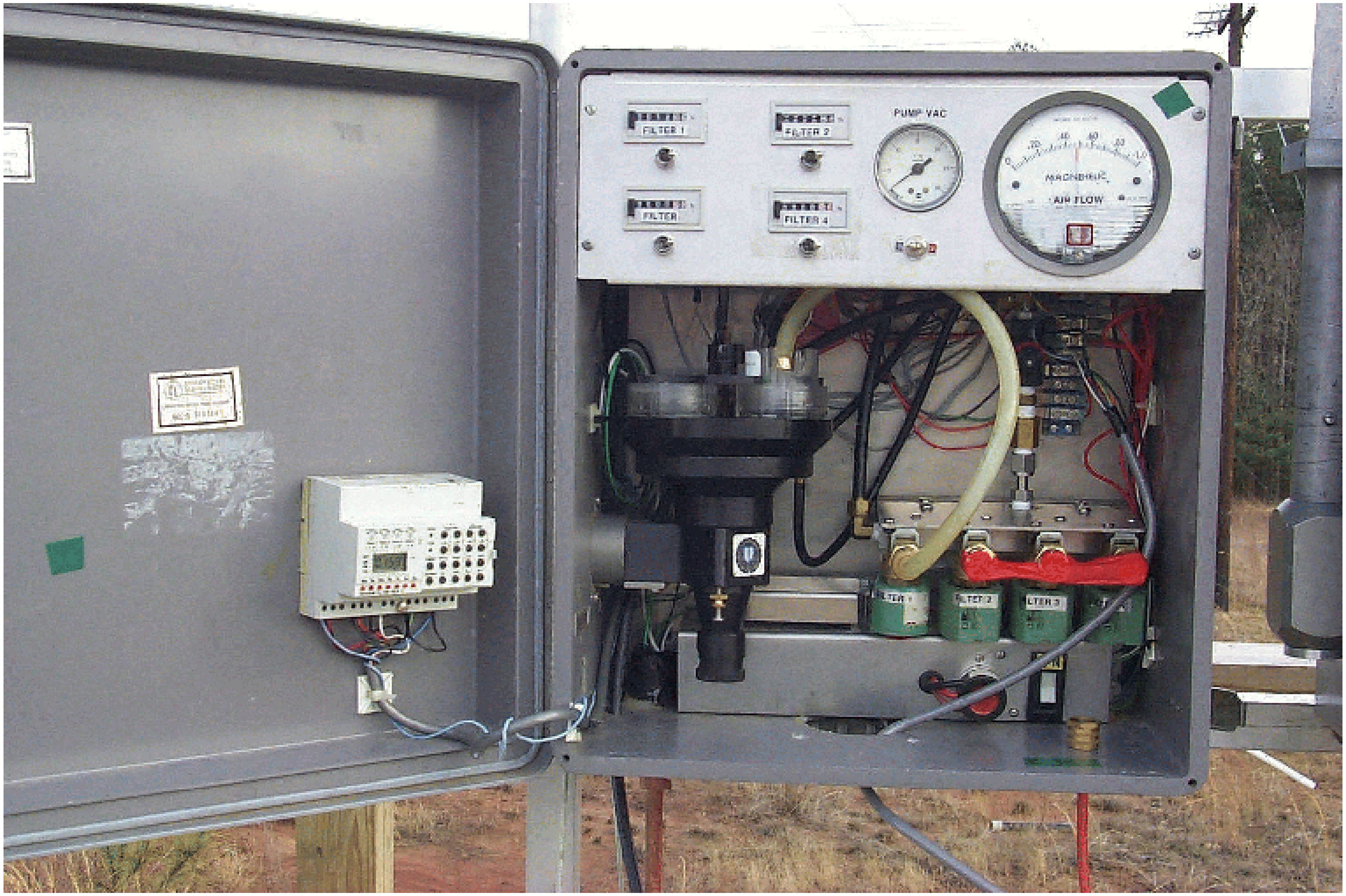


Figure I-4b. Picture of the Filter Position, Control Box, and Timer for One of the Three Modules of the IMPROVE Sampler as Deployed in the Field at RTP.

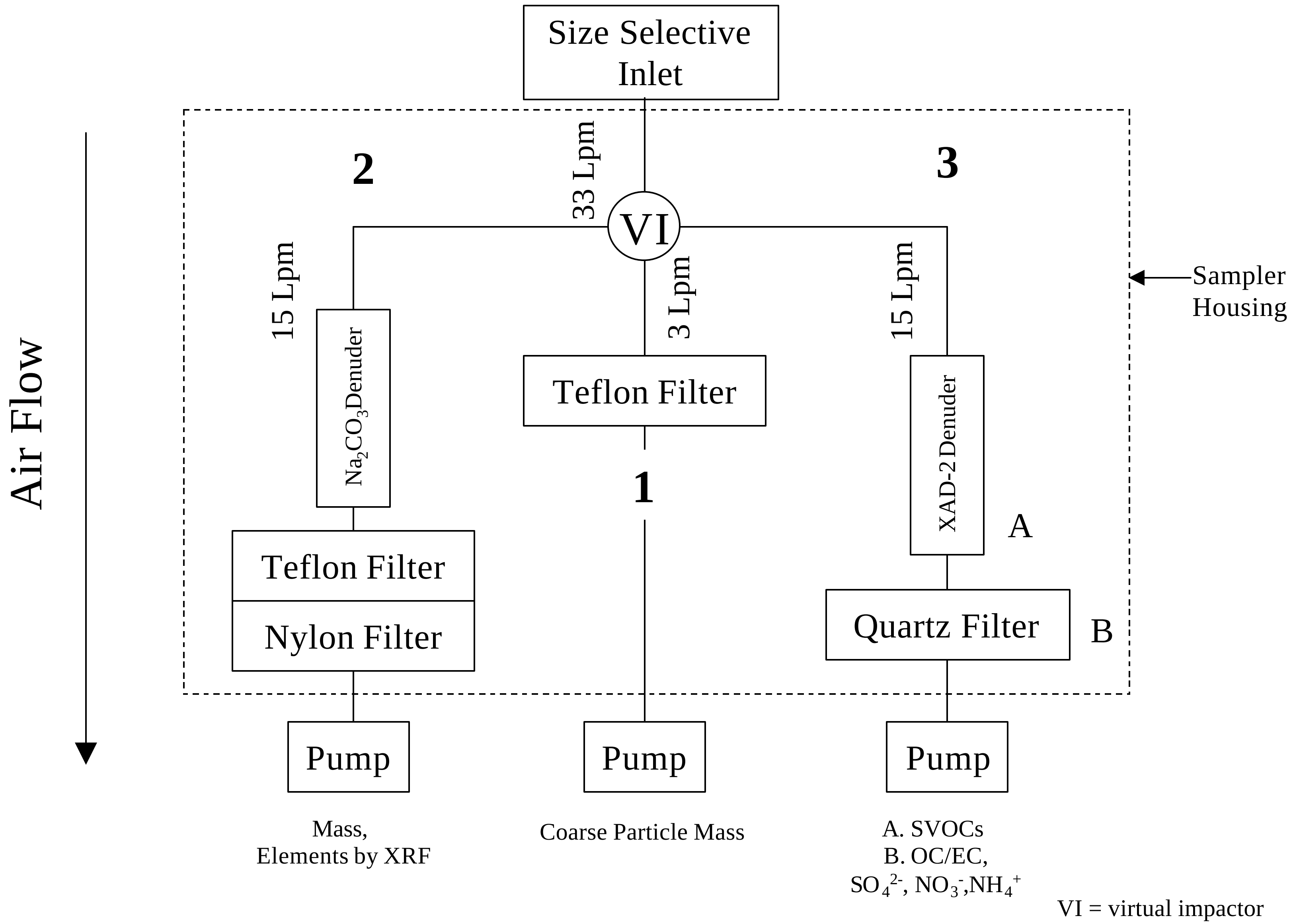


Figure I-5a. Schematic of the VAPS Sampler.

Figure I-5b. Picture of VAPS Sampler Deployed in the Field at RTP. Left – VAPS Filter Box Showing XAD Denuder on Right and Sodium Carbonate Coated Annular Denuder on Left. Right – Pump Box and Dry Gas Meters for Monitoring Flow.

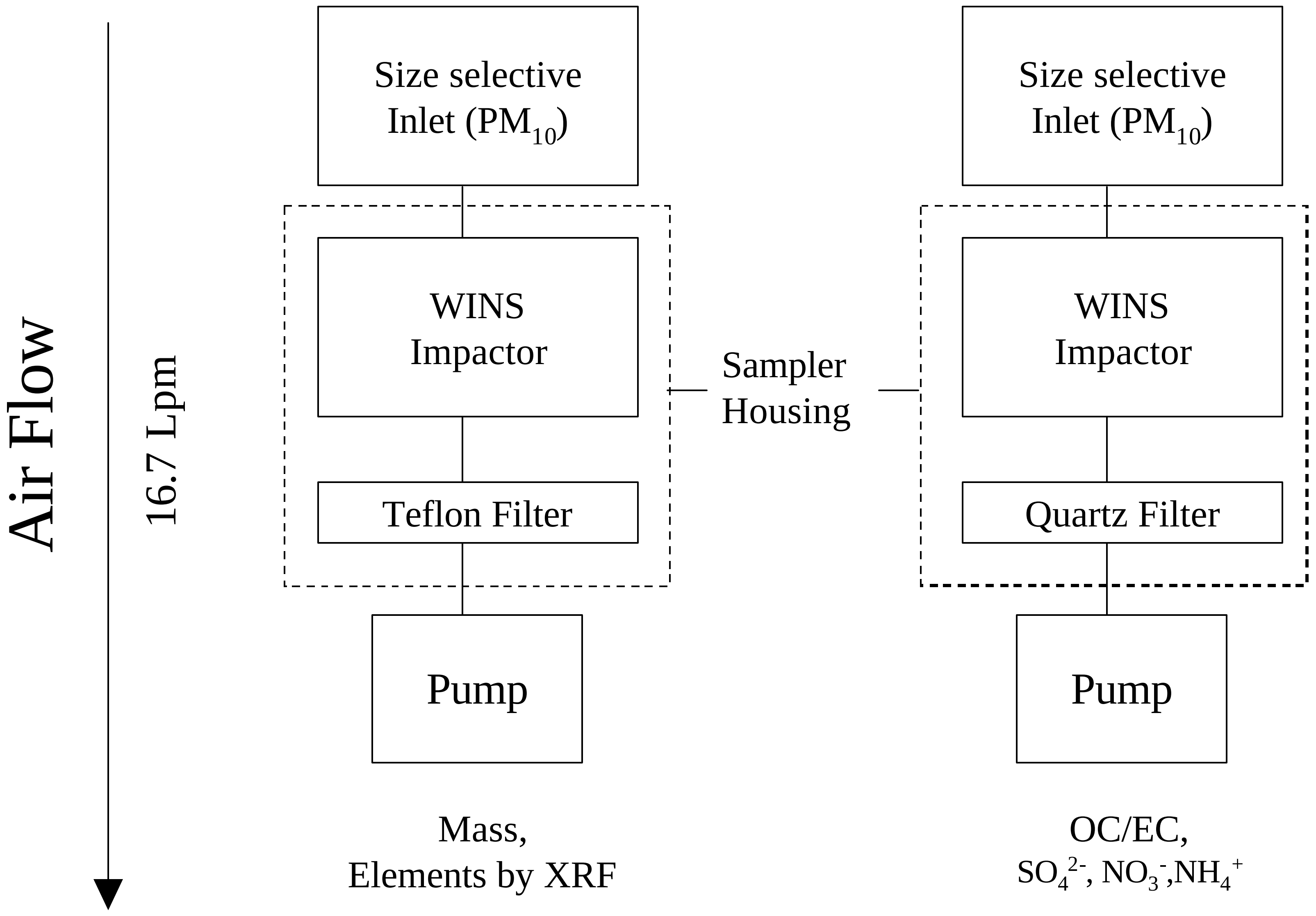
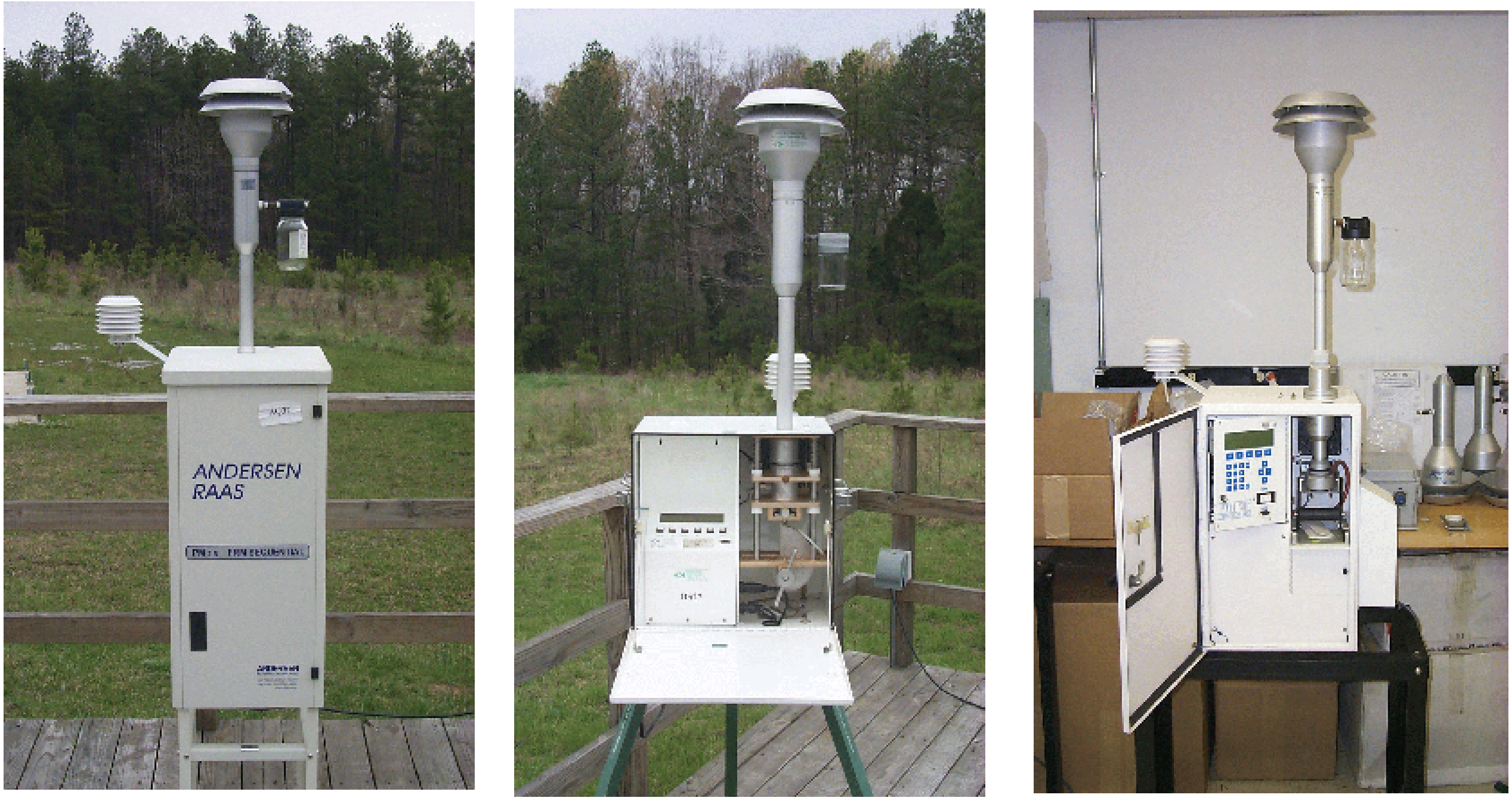


Figure I-6a. Schematic of the Federal Reference Method Samplers



Andersen BGI R&P

Figure I-6b. Picture of FRM Samplers Deployed in the Field at RTP.

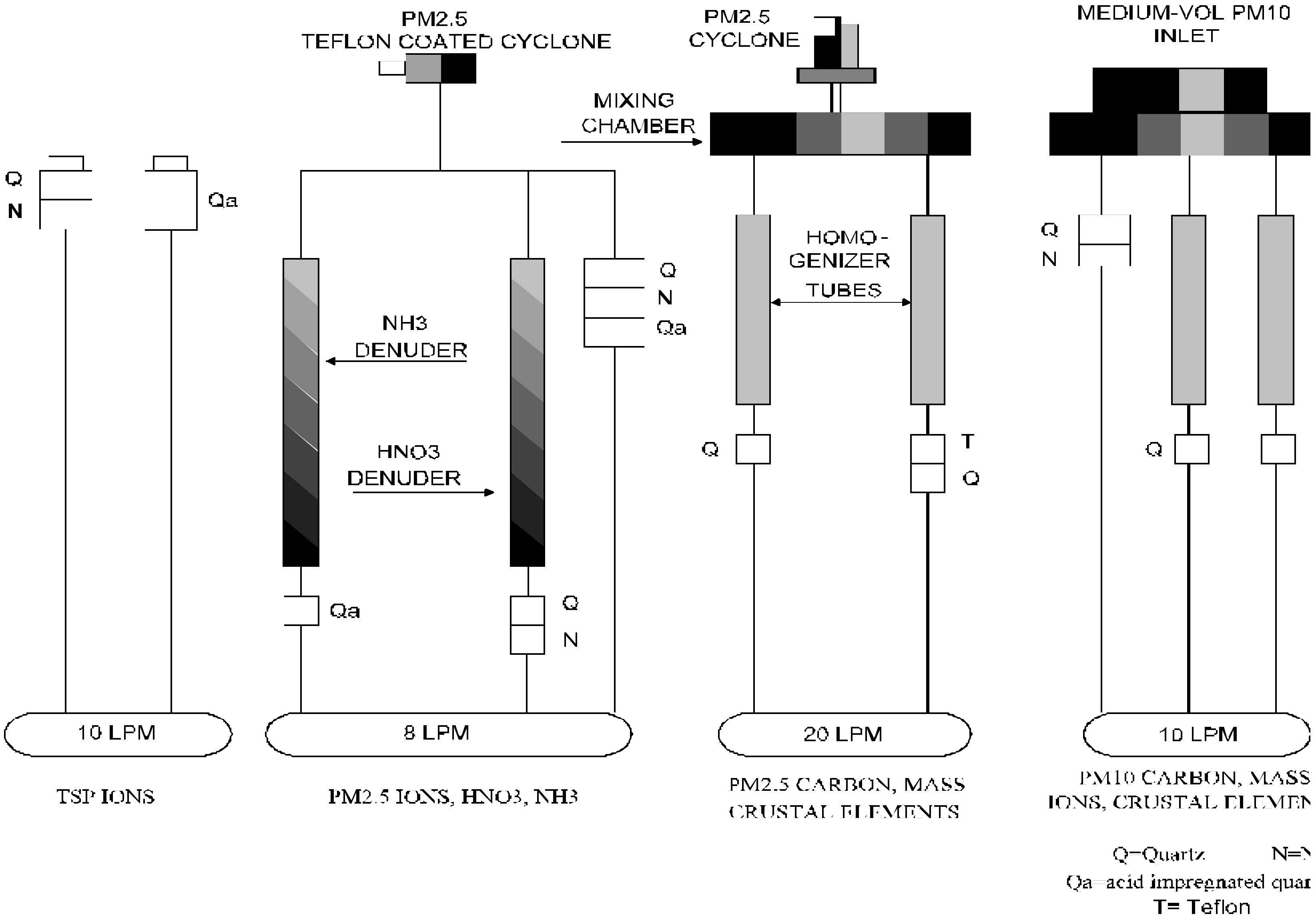


Figure I-7. Schematic of the SCAQMD Multi-Channel Fine Particulate Sampler.

Figure I-8. Top – Samplers on the Platform at Rubidoux, CA. Bottom – View of the Sampling Platform and Surrounding Area at Rubidoux, CA.

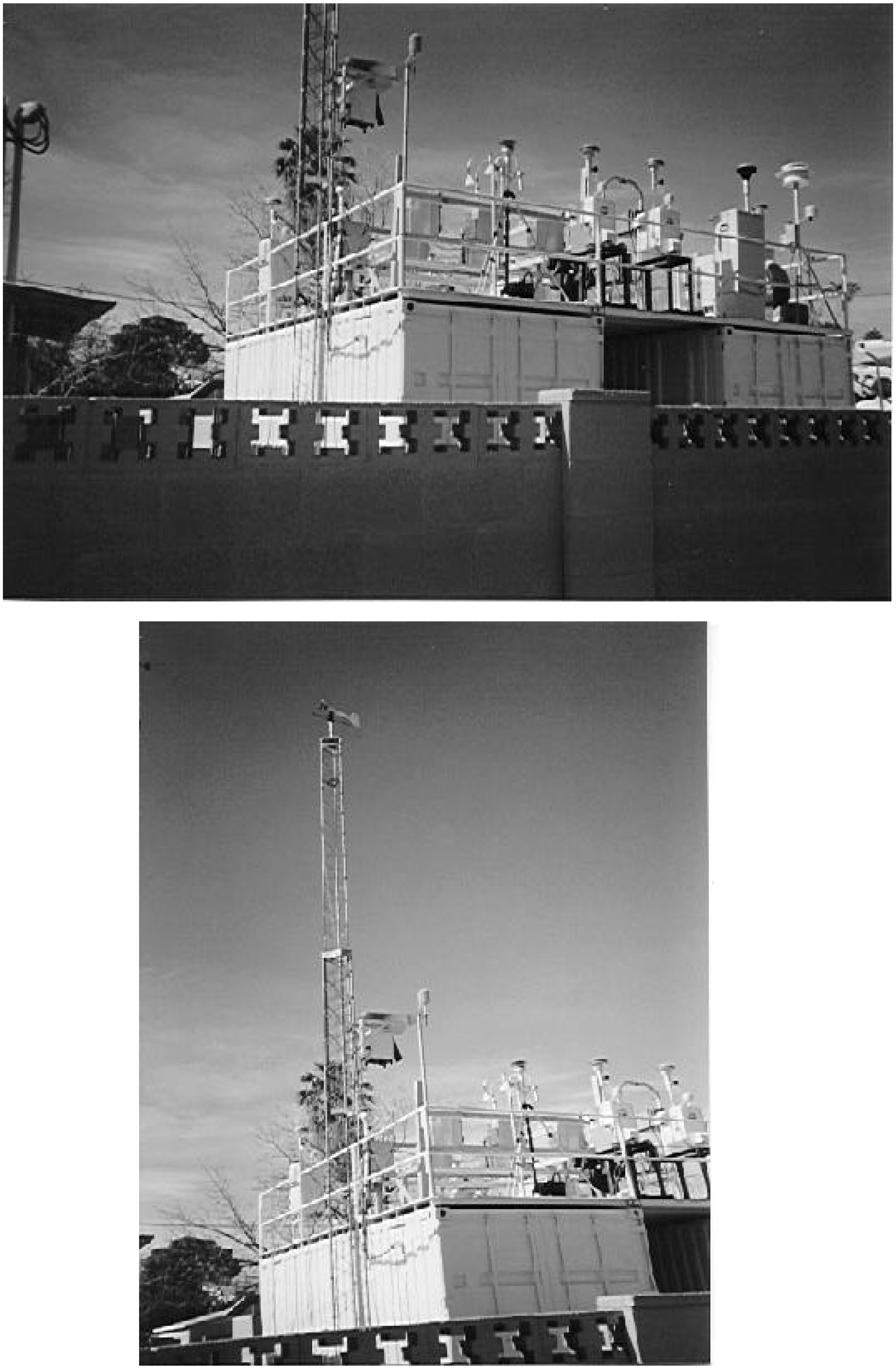


Figure I-9. Sampling Platform at Phoenix, AZ.

Figure I-10. Philadelphia Sampling Site. Top – Roof View. Bottom –View From the Road.

Figure I-11. Research Triangle Park Sampling Site.

Part II

Results, Discussion, Conclusions, and Implications

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RESULTS
Quality Assurance Results

Performance Audit Methods and Verification

As part of the overall field evaluation of the candidate speciation samplers, periodic performance evaluations were conducted at each of the four sampling sites. Following the initial calibration of each sampler and site installation, a pre-sampling evaluation was conducted to ensure that each sampler was operating according to manufacturer's specifications. The pre-sampling evaluation consisted of single-point verification of each sampler's operating flow rate and ambient temperature, and pressure measurements. Subsequent mid- and post-study performance evaluations consisted of similar evaluations. Pre-sampling audits were typically conducted approximately one day prior to the initiation of Run 1, while the mid-study audit was conducted following Run 10. The final site audit was conducted shortly after the last sampling period.

Flow Rate Audit Equipment

The flow rate audit consisted of a single-point measurement conducted at the operational flow rate of each channel for each sampler. Depending upon the sampler and the specific channel being audited, one of two flow audit devices was typically used. A Chinook Engineering Streamline flow transfer standard (FTS #980819) was used for the majority of the channel audits. Prior to its purchase, the Streamline FTS was calibrated by the manufacturer against a set of precision NIST traceable critical flow venturis. Following its purchase, its performance was verified in the laboratory at RTI. The second in field flow audit device used in this study was a Schlumberger dry gas meter. Its traceability was established in the laboratory using EPA Method 40 CFR60, Appendix A, Method 5, Section 7.

Barometric Pressure Audit Equipment

Laboratory calibrations and field audits of speciation sampler pressure sensors were conducted using a PSI Tronix Model PG 2000 digital pressure gauge. Laboratory validation of the Model PG 2000's response was obtained using a certified mercury barometer previously adjusted to local station pressure.

Temperature Audit Equipment

Two instruments were used for laboratory calibration and auditing of speciation sampler ambient temperature response. A Tegum Model 847 thermo-calibrator was used to calibrate and audit Type K thermocouples used in some speciation sampler designs. Other samplers were audited using a Fluke Model 8022A digital multi-meter in conjunction with a Model 80T-150U temperature probe. Traceability of the Fluke probe was established using a traceable Hewlett Packard quartz probe (S/N 725A Model 2833A).

Field Audit Results

Results of the pre-, mid-, and post-study field flow rate audit results are summarized in Table II-1. Values are given for flow audit results that were outside of < 10% and > 10%, all others are within ±10% of the audit device. All flow channels were audited as well as audits of all temperature and pressure measurement devices associated with each sampler. Pressure and temperature audit results for the IMPROVE and VAPS were not obtained, since these devices do not measure these quantities.

As seen in the Table II-1, only 9 flow audit values were outside the range of < 10% and > 10%. This represents less than 3% of the total number of possible flow audits. Of those outside the 10% range, only three were greater then 20%. The two highest values were associated with the Andersen sampler and were apparently due to malfunctioning flow sensors; although the flow rates were likely correct. However, since the actual flow rate was not known, these data were invalidated in the data archive. Nineteen values fell in the range of +5% to 10% and (-5%) to (-10%) of which 8 were associated with the IMPROVE sampler at the Phoenix site that used 25 mm filters, thus, leaving only 11 values in this range overall sampling lines.

Ambient pressure response of the speciation samplers was generally acceptable with the majority of measured values within 5 torr of actual pressure. Occasional relative biases in excess of 7 torr were experienced with the Andersen and URG speciation samplers. Of the approximately 80 individual audits, only one value exceeded 10% of the audit value.

Audits of the ambient temperature monitors associated with the speciation samplers indicated excellent agreement with the audit devices. All temperature audits, throughout the study, agreed to within 1.6 C of the audit device or to within 5%.

Noted biases in sampler flow rates require additional attention since they adversely influence overall sampler measurement accuracy to a greater degree than do biases in ambient temperature and pressure response. Response problems with the Andersen’s flow sensing module resulted in indicated flow rates differing dramatically from audited values. Mean flow bias for all channels in the Andersen samplers over all sites was +2.9% with a standard deviation of approximately 23%. In particular, the two Andersen speciation samplers in Rubidoux experienced higher flow variations than the other three sites. In one extreme instance, a bias in the indicated flow rate of +168% was observed. However, since the Andersen sampler uses critical flow orifices, the actual flow rate was likely within acceptable limits of the channel’s design value. When making post-sampling calculations incorporating the sampler’s indicated flow rate, however, biases in indicated flow rates will result in calculated biases in species concentrations.

Flow rates indicated by the Met One’s five sampling channels generally agreed well with the audit values. Mean flow bias for all channels at all sites was -0.6% with a standard deviation of only 1.2%. A maximum indicated flow bias of -4.3% was observed during the entire study for the Met One speciation sampler.

Flow problems were initially observed with the URG MASS 400 sampler due to limitations of the sampler's pumping system in conjunction with the inherently high pressure drop associated with use of the nylon filter in the Teflon/nylon filter pack. This problem was corrected by the manufacturer by adding a second pump. Following the correction of the system's flow design, mean flow bias for the URG sampler was -0.9% with a standard deviation of 2.0%.

Unlike the previous three samplers, the IMPROVE sampler does not provide a direct reading of sampling flow rate. For purposes of the audit, therefore, biases are expressed in the audited flow rate relative to the design flow rate of 23 lpm. Flow audit results showed that the sampler's actual response agreed well with the design value. Mean flow bias for the IMPROVE sampler was -0.6% with a standard deviation of 2.6%. Maximum flow bias in the IMPROVE sampler during the study was -13.3%.

Similar to the IMPROVE sampler, the VAPS sampler does not provide an instantaneous reading of the flow rate in liters per minute. In the VAPS, dry gas meters are used to indicate integrated sample volumes over a known time period and the mean flow rate is then calculated. At Rubidoux, Phoenix, and RTP measured flows agreed well with the audit flow rates, while at Philadelphia flow bias was more variable, particularly near the end of the sampling program. Mean flow bias for the VAPS sampler at all sites was +2.4% with a standard deviation of 5.7%.

Averaged over all four sites, the $PM_{2.5}$ FRM samplers provided the lowest overall flow bias with a mean value of -0.1% and a standard deviation of 2.7%. Deviations were consistently low at all sites with average measured biases of -0.5%, +0.2%, -0.3%, and -0.1% observed at Rubidoux, Phoenix, Philadelphia, and RTP, respectively.

Limits of Detection

Table II-2a lists the limit of detection (LOD) for each species and the analytical methods used to determine the species concentrations. The LOD for mass is determined based on Federal Reference Method procedure (40 CFR, Part 50, Appendix L). The LOD sulfate, nitrate, and ammonium based on 3 time the noise in the baseline noise in the chromatogram since field blanks were non-detectable, while for OC and EC it is based on three times the standard deviation of the field blanks. XRF limits of detection are based on propagating errors associated with the analytical method and flow rates. In general, LOD values were within the expected ranges.

Field Blanks

Two field blanks were collected at each site for every channel in all samplers. Filter samples used for field blanks were handled in the same manner as filters used on regular sampling days, however, the filters were loaded and unloaded a few minutes later and the sampler was not turned on for field blanks. Table II-2b summarizes average field blank data by sampler averaged across sites, as well as the standard deviation of the 10 blanks taken on each sampler over all sites. On the average, for the major species (those listed in $\mu g/m^3$), field blank values were close to the limit of detection for the analytical method employed and in virtually all cases less than the associated uncertainty of the measurement.

Precision

Precision results, as coefficient of variation reported in percent (CV%), are presented in Table II-2c. Precision estimates were obtained from collocating samplers at the Rubidoux site for all sampling periods. These precision data are limited, that is, they provide a set of data for one time period and under one set of atmospheric conditions. Nonetheless, they provide important information needed to evaluate the samplers performance relative to each other. In general, precision values are in the range expected from past experience. For the major species, the CV% is typically less then 10 percent, except for particle nitrate which is less then 20 percent. Trace elements have reported precision estimates that are typically less then 20 percent, except Si which has reported precision values in the range of 20- 30 percent, which may be due to the higher uncertainty in the field blank data (Table II-1b). The cause for the higher precision values for OC measured on the IMPROVE sampler, relative to the other samplers, has not been determined.

Data Validation

Level 1a Data Validation

The contractor managing the field and laboratory operations was responsible for validating the data through Level 1a. This first validation process occurred during all phases of laboratory and field operations. As part of field operations, site operators were first responsible for ensuring that samples received from the preparation laboratory were complete, properly labeled, and correctly matched the entries on the supplied field data sheets. Following sample collection, the site operator was responsible for ensuring that pertinent run data were entered on the field data sheet with particular attention given to records of atypical sampling events such as unusual weather conditions, sampler malfunctions, or unusual site conditions. The site operator also was responsible for ensuring that all collected field samples were properly labeled, packed, and accompanied by the completed field data sheets and chain of custody records.

Upon receipt of the collected field samples at the laboratory, the sample cooler was carefully unpacked and inventoried to ensure that all samples, field data sheets, and chain of custody records were correctly received. Personnel responsible for sample retrieval also were responsible for recording unusual observations associated with the samples, such as torn filters, improperly loaded filter cassettes, etc., which might adversely affect data quality. All field data sheets were then transferred to the Data Manager who inspected the sheets for completeness. Missing or suspect information on the field data sheets were brought to the attention of the Program Manager who was then responsible for contacting the appropriate site operator to obtain the correct information. Once each data sheet was inspected, the data manager manually entered the field data into the appropriate spreadsheet for subsequent analysis. As in all phases of data entry, the Data Manager was responsible validating data entry and correcting errors due to transcribing information from hard copy to digital format.

The Data Manager also was responsible for collecting and validating analysis results obtained from each of the analytical laboratories responsible. Data received were entered into the appropriate spreadsheet and inspected for possible outliers. If suspect data could not be resolved with accompanying notes from field or laboratory data sheets, the appropriate analytical laboratory was contacted and asked to verify the reported results. If the analysis results could not be resolved through review of the analytical or reporting procedures, the Laboratory Manager would be contacted to determine if re-analysis of the suspect sample would be appropriate.

Potential data outliers that could not be adequately resolved at this point were brought to the attention of the Program Manager. Based on discussions with site personnel, laboratory support technicians, and the Data Manager, the Program Manager was then responsible for determining the validity of the data under review. Once the Level Ia validity of all data was performed, the data set was formally released to EPA for Level 1b and Level 2 data validation and subsequent interpretation.

A complete listing of Level 1a data validation comments is given in Appendix C.

Level 1b Data Validation

EPA scientists were responsible for Level 1b data validation (single variate comparison of the data). First a printout of the data set was scanned visually on a site-by-site, sample-by-sample, analyte-by-analyte, run-by-run basis to identify obviously anomalous values. For each anomalous value identified, the laboratory and field records associated with that sample were examined to see if there was an explanation that would permit the value to be either adjusted (e.g. transcription error, incorrect units, etc.) or invalidated. A computer scan also was conducted on the data set to identify values that were less than 5 times the MDL for that analyte. The values were to be excluded from the statistical analysis because of the greater uncertainty associated with data near the limits of detection. The remaining data were considered valid for this analysis.

Level 2b Data Validation

Data have been validated through Level 2b through continued diagnostic and interpretive data analysis (see Part II results and discussion). This includes multi-variate analyses in space and time where appropriate and cross-comparisons to other samplers, in the case of this study. Physical relationships among variables were also reexamined among samplers.

Data Capture

Table II-3 summarizes the percent valid data capture (at data validation Level 2) for each sampler by groups of species collected on the same filter. The shaded boxes in the table indicate valid data capture less than 90% percent. The Andersen sampler had better then 94 percent valid data capture at all sites for all analytes. The FRM, IMPROVE, and MetOne samplers also all had excellent valid data capture with most over 95 percent, but a few were as low as 85 percent. Only the URG and VAPS samplers had data capture below 80 percent. The low percentages for the URG are likely do to flow problems associated with the flow through the MASS 400 sampler. The pump initially installed with that sampler was unable to pull 16.7 Lpm through the Teflon/nylon filter pack. Flow rates on the order of 9.5 Lpm were noted. This problem was noted during the initial days of Phoenix and Rubidoux, the first two sites installed. As can be seen, the problem was quickly solved by URG and better data capture was achieved at Philadelphia and RTP. The overall poorest data capture was observed on the VAPS sampler. Operational problems are discussed later in this report.

Problems resulting in loss of data are presented in detail in Appendix C. Sampler specific problems are summarized in Table II-4. Problems with sampler operations were brought to the attention of the manufacturer as soon as they were identified so they could be corrected as soon as possible. For example, with the Andersen the indicated flows were not stable and often reported values different from the audit flow; the lack of performance with the URG pump achieving only 60 percent of the desired flow due to the added pressure drop of using a Teflon/nylon filter pack, and the coarse particle penetration observed with the MetOne sampler. In all these cases and others, the manufacturer attempted to solve the problem as expeditiously as possible. Andersen has subsequently upgraded their flow indicator system, URG has installed a larger pump on their new units, and MetOne has developed a new inlet based on the Sharp Cut Cyclone (BGI) (Kenny et al. 1999).

Chemical Characteristics of $PM_{2.5}$

Chemical Components Reported in the 4 City Study Database

Atmospheric particulate matter in the $PM_{2.5}$ size fraction was collected on all samplers as discussed in the introduction. Coarse particle mass also was measured by the VAPS sampler. Mass and major and trace chemical components were determined for each sampling period and sampler. Methods are described in the Introduction. The major components include $PM_{2.5}$ mass, sulfate, nitrate, ammonium, organic carbon, and elemental carbon. We limited the analysis of trace chemical components to a few species to allow for a manageable data base and because many of the species measured by XRF are often below the limits of detection for ambient samples by the XRF method. As well, to perform a meaningful comparison among samplers, species concentrations needed to be at least 3 to 5 times their limit of detection and present on all or at least most samplers simultaneously. XRF data reported by the laboratory, therefore, were limited to S, Si, K, Ca, Mn, Fe, Zn, Cu, As, and Pb, knowing a priori that these elements were the most likely to be observed above the limit of detection most of the time. Subsequently we have limited the data base further by minimizing our use of Mn, Cu, As, and Pb, due to their low levels (i.e., since significant number of values for these species are reported below the methods limit of detection). The complete database, including Mn, Cu, As, and Pb is provided in Appendix D and D1 for replicate data at Rubidoux.

It also is important to note that sulfur measured by XRF times three was in very good agreement with sulfate measured by ion chromatography. This comparison was done using data from the FRM, thus, sulfur by XRF was determined from Teflon filters, while sulfate by IC was determined using quartz-fiber filters. The ratio ($S*3/SO_4^=$ ranged from 1.06 at Rubidoux to 1.01 at RTI. This also indicates that Teflon or quartz-fiber filters are suitable for the measurement of $SO_4^=$ in $PM_{2.5}$ samples under the conditions of this experiment.

$PM_{2.5}$ and Chemical Components Collected by the FRM

One of the requirements of this experiment was to collect chemically speciated $PM_{2.5}$ samples in different regions of the country where we would expect to sample different chemical atmospheres, as described in the Introduction of this report. The purpose of this was to stress the samplers over as wide a range of $PM_{2.5}$ chemical composition as possible in a limited time frame. To examine the success of meeting the above requirement we describe below the general chemical characteristics of the data using the $PM_{2.5}$ FRM data as a reference, noting the possibility that the aerosol nitrate measured on the $PM_{2.5}$ FRM Teflon filter and the organic carbon measured on the $PM_{2.5}$ FRM might be biased low due to volatilization of ammonium nitrate or organic compounds, respectively, during sample collection and storage or the organic carbon might be biased high due to positive sampling artifacts. A more thorough discussion of the chemical characteristics of $PM_{2.5}$ mass and composition observed during this 4-City study are given in Tolocka et al.(2000).

Average concentrations of $PM_{2.5}$ mass and chemical components as measured by the FRM samplers are given in Table II-5. These data do not include the first two days of sampling at each of the sites, as they were considered shakedown periods. Mass and trace elements were determined from the sample collected on the Teflon filter, while ions and OC/EC were determined from the sample collected on the quartz-fiber filter. Average $PM_{2.5}$ mass concentrations ranged from 11 µg/m^3 at RTP to 28.4 µg/m^3 at Rubidoux. Standard deviations about the means ranged from about 5 µg/m^3 at RTP to 20.6 µg/m^3, indicating considerable day-to-day variability at each site. Maximum values at each site were about twice the mean, except at Rubidoux where the maximum value was about three times the mean. Of the possible 20 samples that could be collected at each site, except Rubidoux, which had a maximum number 16, 12 valid samples were collected at Rubidoux, 17 at Phoenix and Philadelphia, and 16 at RTP. Reasons for lost samples were discussed earlier and are summarized in Tables II-4 and presented in detail in Appendix C.

As is typically observed, the most abundant species, of those measured, were NO_3^-, $SO_4^=$, NH_4^+, OC, EC, and Si, Fe, and Ca; although relative abundances varied from site-to-site. For example, OC was the most abundant species at all sites except Rubidoux, where nitrate was the most abundant species at 11.8 µg/m^3 Nitrate was lowest at RTP at 0.7 µg/m^3 as expected, with moderate values at Phoenix and Philadelphia. Also as expected, $SO_4^=$ was highest at the east coast sites around 3-4 µg/m^3 and lowest at the western sites, in the range of 1-2 µg/m^3 At Philadelphia and RTP, $SO_4^=$ was the second most abundant species. In general, the other species, primarily Fe, Ca, and Si accounted for less than a total of 1 µg/m^3, not adjusting for their oxide form.

Frequency distributions are illustrated in Figures II-1 for the major species as measured on the FRM using box and whisker plots. These plots show the average, median, 25%, 75%, 5%, and 95% values observed in the data base. Each plot shows the data for a single species at all four sites to allow for easy comparisons between sites. Note, the scales are different on each plot, so care should be taken in comparing among the different species. These data help to show the variability of the concentrations from site-to-site and by species. Except for sulfate, lowest concentrations of all variables shown in Figures II-1 are observed in RTP. Highest values were observed at Rubidoux for mass, nitrate, ammonium ion, and calcium with the largest variability, as well. Phoenix had the highest OC and Fe concentrations, all with equivalent variability for a given species. Under the conditions observed during this study, nitrate, OC, EC, and crustal related elements appear to be high in the western part of the US then in the east. On the other hand, sulfate clearly dominates the east coast $PM_{2.5}$ aerosol. Ammonium ion is more complex as it is associated with both nitrate and sulfate.

A rough mass balance of the collected aerosol can be obtained by adjusting OC for missing hydrogen and oxygen atoms to obtain organic material and major elements (Fe, Ca, and Si) for missing oxygen atoms. Here, OC is adjusted by multiplying OC by 1.4 and Fe, Ca, and Si are adjusted by multiplying by 1.43 for an estimate of Fe_2O_3, 1.4 for an estimate of CaO, and 2.14 for an estimate of SiO_2 (Solomon et al., 1989, Eldred et al., 1998). The sum of Fe, Ca, and Si oxides provides an estimate for crustal material, although this is a low estimate because Al, Mg, and Ti oxides also are used typically in obtaining an estimate of crustal material (Solomon et al. 1989, Chow and Egami, 1997). Other species are used directly with no adjustment. Table II-6 presents the results of the mass balance calculation, while Figure II-2 illustrates the results graphically. As indicated above, nitrate was the most abundant species at Rubidoux accounting for about 40% of the mass, followed by organic material (27% of the mass), while organic material was the most abundant species at the other three sites, ranging from 4.8 to 10.7 µg/m^3 or 31% to 53%. The highest organic material concentrations were observed at Phoenix 10.7 µg/m^3 or about 53% of the measured mass. Sulfate was highest at the east coast sites accounting for nearly a quarter of the mass on average between the two sites. Sulfate was a factor of two to four lower at the western sites, accounting for only about 5% of the measured mass. At all sites, the estimated crustal material represented only a minor fraction of the total mass, ranging from only 0.3 to 1.2 $\mu g/m^3$ or about 2% to 6% of the measured mass. The coarse particle data collected by the VAPS, however, indicated high coarse particle loadings in Phoenix (41% coarse/PM10 ratio) as opposed to the east coast sites where the coarse/PM10 ratio was around 20%. In fact, at Phoenix, the coarse/PM10 ratio exceeded 50% on three occasions, while at the east coast sites the ratio only exceeded 30% once.

The sum of the components are compared to the measured mass in Table II-6 for the FRM samples collected at each site. Except for Phoenix, it appears that within the error of the measurements the sum of the components accounted for the measured mass. In actuality, there is likely an over accounting of mass as the water associated with the particles has not been included in the sum of the components. At Phoenix, the difference between the sum of the components and the measured mass is even larger. Over estimates of the measured mass at all sites may be due to the use of collecting and measuring the components of PM mass on different filter media to allow for chemical characterization of the mass (i.e., potential positive artifacts associated with using a quart-fiber filter such as the filter collecting HNO_3 or gas phase semi-volatile organic material) or the use of an acid denuder in the Teflon filter channel as opposed to the other channel that did not use a denuder. For the latter, it is possible that 1) particles are being lost in the denuder (reducing the measured mass), 2) there is a shift in the NH_4NO_3 equilibrium due HNO_3 free air are passing over the Teflon filter during sampling (reducing nitrate concentrations on the filter, thus reducing the measured mass), 3) another reason still to be established.

Results presented in this section indicate that the sampling locations used in this study met the objective of stressing the samplers with different chemical and meteorological ambient atmospheres. As anticipated, Rubidoux had high nitrate with moderate to high carbon, Phoenix had the highest crustal material with high organic material and moderate nitrate, Philadelphia and RTP had high sulfate, RTP had low nitrate as well as the lowest overall concentrations for PM. The only unexpected result, relative to past measurements, was the relatively high concentration of nitrate at Philadelphia. However, most past measurements in the east have occurred during summertime conditions, when the NH_4NO_3 equilibrium would be shifted to the gas phase. During the winter, under conditions of this experiment, the equilibrium would be shifted to the particle phase, assuming sufficient ammonia is available (see for example, Russell et al. 1983; Solomon et al. 1992; Hering and Cass, 1999).

Volatilization of Aerosol Nitrate

Ammonium nitrate in air exists in dynamic equilibrium with nitric acid and ammonia (Russell et al. 1983). This equilibrium is dependent on temperature, relative humidity, and the ambient concentrations of nitric acid and ammonia. When collecting on a filter, this equilibrium also is dependent on the pressure drop across the filter (face velocity or flow rate for filters that are the same size) and the air temperature that exists in the sampler around the filter (Hering and Cass, 1999). For the chemical speciation samplers used in this study, aerosol nitrate, with minimum bias, is measured either directly or by the sum of nitrate measured on two filters. For reference, see Figures I-1 to I-5. The direct method, used by the Andersen, MetOne, and IMPROVE samplers, uses a reactive filter (nylon) behind either a MgO coated annular denuder (MetOne, Andersen) or a Na_2CO_3 coated annular denuder IMPROVE (see Figures I-1, I-2, and I-4). The nylon filter is an efficient sink for HNO_3; and therefore, aerosol nitrate. The nylon filter is extracted and nitrate is determined by ion chromatography. In the second approach, used by the URG and VAPS samplers, aerosol nitrate is collected by a two-stage filter pack located downstream of a Na_2CO_3 annular denuder. The two-stage filter pack consists of a Teflon filter followed by a nylon filter. The front filter collects particles, while the nylon backup filter collects nitrate that has volatilized from the Teflon pre-filter (see Figures I-3 and I-5). Historically, the Teflon and nylon filters in a filter pack of this type would each be extracted separately and analyzed for nitrate by ion chromatography. The sum of the measured nitrate on the Teflon and nylon filter should be equivalent to the nitrate measured on just the nylon filters in the direct method. However, in the design used in these two speciation samplers, the Teflon filter is analyzed by vacuum XRF. It was believed, and subsequently proven, that aerosol nitrate, assumed to be in the from of ammonium nitrate, would be lost during the XRF analysis (see discussion below). Therefore, in this study, nitrate was measured on the quartz-fiber filter collected simultaneously and also analyzed for OC. This nitrate was added to the nitrate measured on the back-up nylon filter.

Volatilized nitrate (NO_3V) is determined in a similar manner as aerosol nitrate, but the direct method now applies to the URG and VAPS samplers. For these samplers, NO_3V is measured directly from the nylon back-up filter (see Figures I-3 and I-5). For the other samplers (Andersen, MetOne, and IMPROVE), NO_3V is determined as the difference between nitrate measured on the nylon filter behind the denuder and nitrate measured on the Teflon filter (see Figures I-1, I-2, and I-4). Table II-7 presents the average volatilized nitrate concentrations for each site by sampler as measured under the conditions of this study. Also given are the average temperatures for each site over all study days, as well as the average maximum temperature for all sampling days. For reference, average nitrate over all samplers and periods at a given site is included with the number of samples (n) in the average. Finally, nominal flow rate data are provided for the channels where volatilized nitrate concentrations were determined.

As shown in Table II-7, absolute concentrations of NO_3V measured on each of the samplers at a given site were similar with the most variation observed at Rubidoux. On the average, volatilized nitrate only exceeded 1 $\mu g/m^3$ at Phoenix, where average and maximum temperatures were higher then at the east coast sites, although the same as at Rubidoux. However, volatilization is likely less at Rubidoux due to the large amounts of ammonia transported to that site from the up-wind dairy farms (Russell et al. 1983; Solomon et al. 1988; Solomon et al. 1992). Absolute values at Phoenix were on the order of 1.5

µg/m^3; however, that represented about half of the total particle nitrate measured. Relative to total particle nitrate, less then 10% of the nitrate was volatilized from Teflon filters at Rubidoux (note, Rubidoux has extremely high ammonia concentrations) and Philadelphia, where the coolest temperatures were observed. At RTP, about half of the total particle nitrate was NO_3V; however, nitrate levels in general were low at RTP (average of about 1 µg/m^3) so there is greater uncertainty in the data.

Flow rates ranged from 6.7 lpm to 22.7 lpm through the Teflon filters where nitrate was measured. No apparent affect due to flow rate (face velocity or pressure drop as all samplers use the same diameter and type of filter in this analysis) can be observed in the data for NO_3V. however, values are low and the uncertainty is likely too high to be able to observe a meaningful trend.

Finally, an estimate of $PM_{2.5}$ mass is provided in Table II-7 for comparison to the amount of NO_3V. The ratio of NO_3V to $PM_{2.5}$ mass also is given. As can be seen, under the conditions observed during this study, volatilized nitrate represented only a small fraction of the total $PM_{2.5}$ mass at all sites, ranging from less than one percent at Rubidoux to about eight percent at Phoenix, where the highest absolute values were observed.

Statistical Analysis

In this section, data are presented and described in several ways to provide the reader flexibility in interpreting the data beyond what we present. Data are presented as means, in time series, regressions relative to the FRM, differences relative to the FRM, and with the application of the t-test. The entire data base is given in tabular form in Appendix D and D1, time series in Appendix E, scatter plots with trend lines in Appendix F, and absolute and percent differences in Appendix G.

Means of $PM_{2.5}$ Mass and Major Chemical Components

Average concentrations (in µg/m^3) for all samplers, at all sites, for $PM_{2.5}$ mass and the major components of $PM_{2.5}$ (sulfate, nitrate, ammonium, EC, and OC) as well as Si, K, Ca, Fe, and Zn are given in Table II-8. Means are calculated only for sample sets for a given species and site when valid data were available on all samplers at that site, thus, for the FRM, there are fewer values in the averages in Table II-8 then in Table II-5.

Explanations of Anomalous Data

Data were reviewed and checked against field and laboratory logs. Where problems were indicated in the logs, the data were removed or adjusted as indicated. Thus, data that were identified due to known physical problems with the samplers or with the chemical analysis (see Table II-4 and Appendix C) were removed from the data. In a number of cases, filters were re-analyzed to validated or invalidate suspect data if no physical reason could be identified. Other inconsistent data (i.e., data that appears as an outlier from the bulk of the data) remain in the data set, as no direct reason could be established to indicate it as invalid. Detailed flow audit results indicate very few problems as described earlier. The exceptions include five cases where the indicated flow on one channel of the Andersen sampler differed from the audit value by more then 10 percent; one case where one of the FRM samplers differed by more then 10 percent; and two cases where one channel of the IMPROVE differed form the audit value by more then 10 percent. Of these, only three values differed by more then 15 percent.

The shaded data in Table II-8 indicate average values that are inconsistent with the corresponding values obtained by the other samplers. Reasons for these inconsistencies for most of the data are given below. All data presented in this report are validated to Level 2b, that is, multi-variate analyses of the data have been conducted.

This section attempts to explain or at least suggest possible reasons for some of the inconsistent data remaining in the database that is presented in this report. It is important to clarify these points before moving on to the rest of the statistical analysis sections to help explain the results. The entire data base is given in Appendix D for repeat 1, with replicate data at the Rubidoux site given in Appendix D1.

Mean values presented in Table II-8 for $PM_{2.5}$ mass for the MetOne sampler at Rubidoux and Phoenix appear to be high. This is believed to be due to the passage of coarse particles through the spiral inlet at relatively high coarse particle loadings (see Figure II-2 and Table II-6 for coarse particle concentrations observed at each site). This also is illustrated in the data for Si, Ca, and Fe, which are species typically associated primarily with soil dust and in the coarse particle mode of the atmospheric aerosol (Chow et al. 1996). Silicon, Ca, and Fe are considerably higher for the MetOne at these sites then for the FRM, confirming coarse particle penetration. Recent test by Peters et al. (2000) indicate that the efficiency curve of the Spiral Impactor is somewhat more shallow than the FRM and may experience particle bounce problems for large particles. As a direct result of this 4-City study, MetOne has replaced the spiral inlet with a sharp cut cyclone (BGI) (Merrifield, personal communication) and results of a study conducted by MetOne of the new inlet compared to the FRM are presented in Appendix H. Peters et al. (2000) included the BGI sharp cut cyclone in their evaluation as well, and the efficiency of the cyclone was much closer to that of the FRM (see Appendix I for a draft of Peters et al. 2000).

At Rubidoux, $PM_{2.5}$ mass by the URG sampler seems to be high relative to the FRM as well. Looking at individual values, there appears to be a consistently high bias at the higher mass concentrations, with lower concentrations being essentially equivalent. This difference needs to be investigated further, because it was not observed at the other sites. The VAPS sampler at Rubidoux also appears to be high relative to the FRM, Andersen, and IMPROVE samplers. As explained above, the collection jet for the VAPS was left out after the first sample, thus, both the fine and coarse particle legs of the VAPS essentially collected PM_{10}. This did not result in a large bias for all species, just for nitrate and the crustal related elements (Si, Ca, and Fe). This is reasonable as most of the other species are primarily observed in the fine particle mode. Note, the same observation is true for the MetOne sampler, verifying that under the conditions of this study, $SO_4^=$, NH_4^+, EC, OC, and most of the nitrate are primarily found in the fine particles.

The mean elemental carbon concentration reported for the primary IMPROVE sampler at Rubidoux appears to be low. This is due to low values relative to the FRM and the collocated URG sampler for sampling periods from1/15/99 to 2/2/99. The replicate sampler concentrations are more in line with the other samplers at Rubidoux, with an average value of 2.7 ug/m3. It is possible that a leak occurred during sampling that was not corrected until the mid-study audit, however, the audit results are well with in 10 percent, the audit criteria for sampler flow rates. The data remain in the data base as valid data.

The mean organic carbon concentration reported in Table II-8 for the primary Andersen sampler at Rubidoux are high relative to the other samplers. All individual values for that sampler are high, while the replicate appears to in line with the other samplers during all sampling periods. Quality assurance checks indicated that the flow rate reported by the sampler was a factor of about 2 lower then the measured audit flow rate. Andersen Instrument Company (W. Davis, personal communication) has subsequently noted a problem with the reported indicated flow and has modified (upgraded) their system accordingly. Validation will occur during the Atlanta field program this August. The replicate OC data were used in place of the primary samplers OC data. The higher value for OC by the Andersen sampler at Phoenix appears to be due to a systematic bias. Audit data indicate the indicated flow rate was high, therefore, the concentration would be low by ten percent.

High crustal related trace elements (Fe, Si, and Ca) for the VAPS samplers at Rubidoux and Phoenix suggest that the cutpoint (slope and 50% collection efficiency) of the VAPS sampler is not as efficient as the other samplers. By design, the WINS impactor associated with the FRM and used in the URG speciation sampler have steeper slopes then the VAPS virtual impactor (Peters and Vanderpool, 1996). Additional studies are needed to confirm if the slope in the efficiency curve for the VAPS virtual impactor is the reason for the higher values for the crustal related trace elements at these sites where there was significant coarse particle loadings, relative to Philadelphia and RTP.

Comparison of Means Among Samplers

Mean values for $PM_{2.5}$ mass and the major chemical components are presented in Table II-8 by species, site, and sampler to allow for comparison of individual species among each of the samplers and across sites. Means are calculated pair-wise when all samplers reported a value and the first two days were not included in the average as they were considered to be the shake down period at each site. Thus, the number of samples in the average is somewhat lower than the 20 attempted. It is readily apparent, with the exceptions mentioned above and highlighted in the table, that all the samplers agree within reasonable expectations (based on the precision data) with each other; although real differences among the samplers exist for organic carbon and nitrate. Mass for example ranging from 10 to 20 $\mu g/m^3$ typically only has absolute differences among the samplers of about 1 $\mu g/m^3$, excluding the few exceptions noted above, i.e., the VAPS, which uses a virtual impactor and the MetOne, which used the spiral inlet that has subsequently been shown to allow coarse particle penetration (Tom Merrifield, MetOne, personal communication). Differences for most of the other major components (sulfate, ammonium, and EC) are on the order of a few tenths to 0.5 $\mu g/m^3$ and typically on the order of 10 to 20 percent for most species. Nitrate and OC appear to be the most variable with differences in the average values ranging from 1-3 $\mu g/m^3$ and 1-4 $\mu g/m^3$, respectively. However, the IMPROVE sampler tends to produce lower ammonium values on average at all sites then the other samplers, although it is not a large practical difference. This may be due to attempting to collect a basic substance on a basic material; ideal for collecting and maintaining acidic species, but not basic species, such as ammonia, one of the volatilization products of ammonium nitrate. Differences observed for OC will be discussed below in the Organic Carbon section (Section F, Organic and Elemental Carbon). Nitrate tends to be higher at all four sites for the URG and VAPS sampler and low for the IMPROVE sampler at Phoenix.

Reasons for these differences will be discussed below under the nitrate section (Section E, Aerosol Nitrate). Trace element concentrations are typically within 0.1 µg/m^3 or less. This agreement and the effect of potential outliers in the data will be seen more clearly in the sections that follow.

Comparison To Performance Criteria

EPA's Expert Panel on Chemical Speciation met in May 1999 to review the draft Guidance Document for Chemical Speciation (EPA 1999) and provide comments on results from the Chemical Speciation Sampler Evaluation Study described in this report. The Expert Panel provided recommendations in June 1999 (Koutrakis 1999) and a final report in August 1999. Recommendations for the Chemical Speciation Sampler Evaluation Study included suggested performance criteria by which to judge the relative performance of the individual samplers on a species-by-species basis relative to a sampler designated as the relative reference. Performance criteria were given for mass, sulfate, nitrate, and ammonium. Performance criteria for OC and EC were not recommended due to the poor understanding of how to collect OC with minimal bias. Performance criteria were not established for trace elements. However, results from this study should help to define performance criteria for future studies and uses of the speciation samplers.

The expert Panel established the following performance criteria: for mass, particulate nitrate, and ammonium ions, the ratio of the test sampler to the relative reference should be 1 ± 0.1 with a linear regression correlation coefficient (R^2) of 0.9; while sulfate should have a ratio of 1 ± 0.05 and a R^2 of 0.05. The precision data (Table 2c) suggest the performance criteria established by the Expert Panel is, in general, reasonable. However, a ratio of 1 ± 0.15 might be more reasonable for particle nitrate and organic carbon. Based on the precision data in Table 2c, performance criteria for the other species could be suggested and would be in the range of 1 ± 0.15 for OC, EC, K, Ca, Fe, Zn, while Si and Mn might have criteria in the range of 1 ± 0.25.

Table II-8b presents the ratio of each speciation sample relative to the FRM for all major species and most trace species. OC is given relative to the VAPS OC measured on a quartz-fiber filter behind the XAD denuder. In general, the Expert Panel's performance criteria were obtained for the four EPA test samplers (Andersen, MetOne, IMPROVE, and URG) at Philadelphia and RTP, where the coarse particle loadings were low, temperatures were low, or concentrations were low; although a few exceptions are noted for nitrate and ammonium ion. The URG samplers exceeded the performance criteria for mass, sulfate, particulate nitrate and ammonium ion in either or both Phoenix and Rubidoux; although for sulfate the ratio was only 1.06 and likely well within acceptable error of the 5% performance criteria. Positive bias was indicated for mass, sulfate, and particle nitrate and negative bias for ammonium ion. The MetOne sampler exceeded the performance criteria for mass and sulfate at Phoenix and Rubidoux and for ammonium ion at Phoenix; although the MetOne was acceptable for nitrate at Phoenix, suggesting an individual problem at Phoenix for ammonium. The ratio for the IMPROVE sampler was low at all sites for ammonium and exceeded the performance criteria at Rubidoux, Phoenix, and Philadelphia.

Given the performance criteria suggested above for the other species, the data are mixed with samplers meeting the criteria at some sites for one species, but not for another. However, in general, most ratios fall within 20% of 1 for all species and samplers with a few exceptions. For example, OC exceeds even this criteria at most sites and for most samplers. However, as discussed below, this is likely due to differences in face velocity through the filter or pressure drop across the filter. As well, crustal related elements far exceed the criteria for the MetOne sampler, due to the inlet/fractionator problems noted earlier.

Time Series Analysis

Time series of all the data are given in Appendix E with examples given in Figure II-3a-i for mass, sulfate, nitrate, ammonium, OC, EC, Si, Ca, and Fe. These species were chosen as they represent the major components of the $PM_{2.5}$ mass and the indicators for crustal material (Si, Ca, and Fe) typically associated with coarse (>PM2.5 um) particles. Prior to this, results from the VAPS sampler at Rubidoux have been included to show the identified problem with that sampler. For the time series analysis, the VAPS data at Rubidoux have been removed. At this point, it was our intention to remove the data for the first two days of sampling, as these were considered shake down periods, however, the first two days of data remain in the time series plots for mass, sulfate, nitrate, and ammonium, but have been removed from the plots for the other species. Thus, the reason for the different sample numbers in the time series plots. The first two days of data for all the species have been removed for analyses that follow (i.e., regression analysis, difference analysis, and t-test) for all species.

In examining the time series plots it is important to take note of the range of concentrations observed at each site, as there is considerable variability among the sites, as noted earlier in the discussion about the means. $PM_{2.5}$ mass exceeded the 24-hour $PM_{2.5}$ standard of 65 µg/m3
only once during the study at Rubidoux.

The time series plots show generally good agreement among the samplers for the major species, noting the exceptions mentioned earlier under the discussion of the means. In general, data for a given site and species tend to increase and decrease together; although at some locations and for certain species there is considerable scatter among the samplers (e.g., nitrate at Phoenix and the OC data at all sites). A more detailed discussion of how the samplers compare and the relative biases observed among the samplers is given in the next section on regression analysis.

Regression Analysis

Regression analysis, slopes, intercepts, and correlation coefficients were obtained for each species and sampler against the FRM. Results of this analysis for all sites and species are illustrated in scatter plots in Appendix F with examples given in Figure II-4a-i for mass, sulfate, nitrate, ammonium, OC, EC, Si, Ca, and Fe. These species were chosen as they represent the major components of the $PM_{2.5}$ mass and are indicators of crustal material (Si, Ca, and Fe). The scatter plots include a regression line through the data, where the intercept is allowed to float (i.e., not set to zero). Table II-9 provides a complete listing of the slopes, intercepts, and correlation coefficients (square root of the R^2 value given) for all species (excluding As and Pb), sites, and samplers against the FRM and their associated standard errors. The first two days of data have been removed from all regression analyses, as explained earlier, since those days were considered the shake down period. As a reminder, the VAPS data at Rubidoux likely represent PM_{10} rather than $PM_{2.5}$, since the acceleration nozzle was not placed back into the sampler after the first sampling period.

A gross examination of the regression plots in Figures II-4a-i and in Appendix D show that the samplers are, in general, providing similar data, where the slopes are parallel, reasonably closely packed, and scattered around the 1:1 line. Regression statistics shown in Table II-9 also confirm the generally good overall agreement with the majority of the slopes in the range from 0.8 to 1.2 and R^2 values greater then 0.8 and even 0.9. Exceptions to this follow the discussion presented in the sections above, that is, there are a few known problems with sampler operations and there are a few data points that are either significantly above or below the trend line.

Typically lines that are not parallel with the group on a given plot have one or two points that are relatively far from the trend line, and if these data points that are at high or low concentration they greatly influence the slope, intercept, and correlation coefficient. These “inconsistent” data points have been investigated thoroughly, including re-analysis of filters or extracts, and those that remain are considered to be valid data, i.e., no explanation can be found to invalidate the data. The following provides brief comments on each of the species presented in Figure II-4a-i. Comparisons are made to the 1:1 line (not shown) of the speciation samplers to the FRM, since volatilized nitrate appeared to represent only a small fraction of the nitrate collected, with the exception of Phoenix, where about half of the nitrate was measured as volatilized nitrate. Similar data are not available for OC; although one would expect more volatilization in the locations with higher temperatures, Phoenix and Rubidoux, then at RTP and Philadelphia, the latter which had the coolest temperatures (see Table II-7 for average and average maximum temperatures observed during sampling days). Comparisons are made to FRM, since it is a well characterized aerosol sampler with a sharp cutpoint and under wintertime conditions, volatilization should be minimal.

Mass

In general, and as expected from the time series results, the trend lines are tightly packed and parallel with and scattered around the 1:1 line. A few of the trend lines are noticeably separated from the others, being above the 1:1 line. This is the case for the URG and MetOne mass results at Rubidoux, the MetOne mass results at Phoenix, and the for the VAPS at Philadelphia. Audit results for the URG were within 5 percent for all audits, however, sulfate was also high, suggesting a small bias in the reported flow rates. The MetOne sampler is high at all sites, and noticeably high at Rubidoux and Phoenix due to the reasons indicated earlier (see section: **Means of $PM_{2.5}$ Mass and Major Chemical Components**).

Sulfate

Regression analysis of the sulfate data shows good agreement among the samplers. Within day variations among the samplers are on the order of a few tenths of a $\mu g/m^3$, lines are, in general, parallel and scattered about the 1:1 line. This suggests that the quality assurance and quality control objectives were achieved in monitoring and validating flow rates and chemical analysis, at least for sulfate. It also suggests that differences seen in what are typically considered coarse particle species (Fe, Ca, Si), are due to the differences in the collection efficiency of the inlets, as has been identified for the MetOne sampler and is suggested here for the VAPS sampler, which uses a virtual impactor to size fractionate PM in to a fine (<2.5 um) and coarse (2.5-10 um) size ranges. At Rubidoux, Philadelphia, and RTP the reported concentrations among the samplers appear mostly random with no one sampler showing a systematic bias. At Phoenix, sulfate concentrations are lower then the other sites (range is from 0.2 - 2 µg/m3) and while there looks to be more variability, the overall range (y-axis) is about one fourth the other sites. In general, differences among the samplers, on a day-to-day basis, are on the order of a few tenths of a µg/m^3, and certainly small compared to PM$_{2.5}$ mass, and even to sulfate as observed in the figures.

Nitrate

The variability in nitrate, as measured by the denuder/filter pack method is somewhat larger than sulfate at Phoenix and RTP as well, the variability for nitrate is larger at Phoenix and RTP than at Rubidoux and Philadelphia. The highest concentrations of nitrate were observed at Rubidoux and the lowest at RTP, thus, it is important to note the range of concentrations given on the y-axis when looking at these plots. Variability among samplers for a given day range from a few tenths of a µg/m^3 at low nitrate concentrations to about 3 µg/m^3 at mid-range concentrations, and about 7 µg/m^3 on the highest sampling day (maximum FRM nitrate was 38 µg/m^3, observed at Rubidoux). At Rubidoux, the URG and MetOne are reporting slightly higher concentrations (2-3 µg/m^3) relative to a 1:1 line, while the other samplers are slightly below by about the same amount. At Phoenix and RTP, the VAPS and URG samplers are reporting nitrate concentrations higher then the 1:1 line (also seen in the means data, Table II-8a, means differ by about 30% - 50% among samplers at these sites), while the IMPROVE sampler is slightly below the 1:1 line relative to the FRM. However, audit flow rates for the IMPROVE sampler were about 12 percent high relative to the indicated flow rate, possibly accounting for at least part of the discrepancy.

These differences can be accounted for, in general, by the different methods used by the speciation samplers for collecting aerosol nitrate. Nitrate can be determined directly on either Teflon or quartz-fiber filters, or using the denuder/filter pack methods, one a direct measurement on a nylon filter behind a denuder, the other requiring the sum of nitrate measured on a nylon filter behind a denuder and Teflon filter plus nitrate on from a parallel quartz-fiber filter. Volatilized nitrate also is determined differently, depending on how particle nitrate is determined. A more careful examination of nitrate measured by these different methods is given below (Section E, Aerosol Nitrate).

Ammonium

Regression plots for ammonium ion are given in Figure II-4d. In general, the variability in these data tend to follow a similar pattern to nitrate, with the exception that ammonium measured by the IMPROVE sampler tends to result in the lowest slopes at each site (Table II-9 and Figure II-4d). This was also observed in the comparison among the means (Table II-8a). It is suggested here, as discussed earlier, that the nylon filter may not be the best medium for collecting ammonium, in particular, ammonium associated with ammonium nitrate. The use of the nylon filter, with a basic pH, allows HNO_3 to be recaptured when volatilized after collection; however, ammonium would not be recaptured and lost from the measurement. In fact, results here suggest the use of a nylon filter it may even enhance the loss of ammonium from the filter.

Organic and Elemental Carbon

Organic carbon concentrations range from about 3 to 9 µg/m^3 on average over all sites, while elemental carbon concentrations range from about 1 to 4 µg/m^3 (see Figures II-4d and II-4e and Table II-8). Variability of OC and EC at all sites was large relative to these averages and often approaching 6 - 8 µg/m^3 for OC and 2 - 3 for EC. However, as will be discussed later, the measured concentrations of OC are a function of the face velocity or pressure drop across the filter, or for these samplers because they all used the same size filters, the flow rate. As well, the VAPS sampler had an XAD coated annular denuder designed to remove SVOC in the gas phase (Gundel and Lane, 1999; Gundel et al., 1995) that have been noted to cause positive artifacts for OC (Turpin et al., 1994).

In general, the regression lines for the OC measurements by the speciation samplers relative to the FRM are parallel to and scattered about the 1:1 line; although there is considerable variability among the samplers with parallel, but definitely consistent high or low biases relative to the 1:1 line for all samplers, with the exception of the IMPROVE sampler at Rubidoux. For that sampler, the slope is considerable lower then the other samplers and appears to be due to a series of 5-6 data points at the beginning of the study, after which, the data agree better. The different slope was not observed at the other sites for OC by the IMPROVE sampler; however, a similar slope was observed at Rubidoux for EC, thus, suggesting a potential problem with that module during the beginning of the study. General trends in bias are also observed among the samplers for OC. For example, the OC VAPS regression line was typically the lowest (excluding Rubidoux where the collection cone was missing from the sampler), while the Andersen and MetOne typically had the highest regression line on the plot, while operating at the lowest flow rates among the samplers. The MetOne data however, may be compromised due to the problem noted earlier with the spiral inlet.

Nonetheless, there was considerable variability among the samplers for measuring OC; although much of the variation can be explained due to operational problems and more importantly due to differences in how the samplers operate. The latter is likely due to differences in the face velocity or pressure drop across the collection media in the different samplers or the effect an organic denuder has on removing SVOC with subsequent collection on pre-baked quartz-fiber filters. OC data are discussed more fully later in this report (Section F, Organic and Elemental Carbon).

Elemental carbon, a stable species like sulfate, shows somewhat less variability among the samplers then OC, but the variability is still somewhat larger then for sulfate. In general, the regression lines are parallel to the 1:1 and reasonably closely packed at Phoenix, RTP, and Philadelphia; although for Philadelphia the regression line for the Andersen sampler is not parallel due to one high point at low FRM concentrations and one low point at high FRM concentrations. Validation of the data, including re-analysis of the samplers suggested these data to be valid. Other data from the Andersen fall close to the 1:1 line. At Rubidoux, a series of low points for the IMPROVE sampler add considerably to the observed variability at that site. For the IMPROVE sampler, as noted earlier, the data for the first 5-6 days of the study appear low, relative to the other samples, and then for the remainder of the study agree much better. This is also true for the OC data; although it is not as noticeable with the OC data due to the additional scatter in the plot. However, the EC concentration data for the IMPROVE samplers at the other sites show better agreement. The best agreement was observed at RTP, where the lowest EC concentrations were observed. EC data will have to be more carefully studied to determine if the variability is due to the design of the samplers, operations by site operators, variations in the laboratory analysis, or some other reason.

Trace Elements

The trace elements measured as part of this experiment are non-volatile and would be expected to agree well among the samplers, and in general they do. Trend lines for trace elements are typically clustered with parallel slopes; although there are a number of single data points significantly away from the 1:1 line that sometimes skew the slope and intercept of the regression line, as well there are the exceptions noted earlier. For example, the crustal related species (Si, Fe, and Ca) are skewed high for the MetOne sampler due the bias noted with the inlet of that sampler.

T-TEST Results

The sample collection schedule at the four sites was designed to permit an analysis of variance (ANOVA) to be conducted on the results. The plan was to have a single data set and to conduct ANOVA on it on a site-by-site and analyte by analyte basis using the following linear model to establish the comparability of the samplers:

$$y_{ijk} = u + D_i + L_j + S_k + DL_{ij} + DS_{ik} + LS_{jk} + DLS_{ijk}$$

where:

y = Analyte

Di = Days with associated degrees of freedom equal to D - 1.

Lj = Locations with associated degrees of freedom of L - 1.

S_k = Samplers with associated degrees of freedom of S - 1.

DL_{ij} = The interaction between days and locations.

DS_{ik} = The interaction between days and samplers.

LS_{ik} = The interaction between locations and samplers.

DLS_{ijk} = The three way interaction term (used to estimate overall experimental error).

The results from the ANOVA would be used to test the following hypotheses.

T There will be no statistical difference between the $PM_{2.5}$ mass concentrations measured by the FRM-Teflon filter and the Teflon filters on the other samplers.

T There will be no statistical difference between the FRM-Teflon filter sampler, the VAPS sampler, and each speciation sampler for concentrations of trace elements (by atmospheric pressure XRF).

T There will be no statistical difference between the FRM-quartz-filter-equipped sampler, the VAPS sampler, and each speciation sampler for nitrate, ammonium, and sulfate (by ion chromatography).

T There will be no statistical difference between the FRM-quartz-filter-equipped sampler, the VAPS sampler, and each speciation sampler for OC and EC (by thermal optical reflectance).

At the completion of the Level 1b data validation, it was obvious that there were a large number of missing values and that there were large variations in the concentrations measured for many of the analytes at the four sites. These factors made it impractical to conduct the planned ANOVA, so instead, a paired t-test (alpha = 0.05) approach was used to determine whether two samplers were statistically similar. Based on the large numbers of values below five times the MDL, it also was decided to exclude As, Cu, Pb, and Mn from this statistical analysis.

Results from the Paired T-Tests

Presented below are the results from those paired t-tests where the FRM value was used as the reference standard. Although the FRM, Andersen, IMPROVE, Met One, and URG samplers were operated in duplicate at Rubidoux, only the value from each primary sampler was used for the t-test.

The results are presented in tabular form in Tables II-10a through II-10e for each sampler (a-e) on a site-by-site, analyte-by-analyte basis using the following parameters:

X Actual P-value. P-values less than 0.05 mean that the FRM and the speciation sampler's results are statistically different at the site for the analyte tested.

X Statistical decision made based on the P-value. "Y" means the two results for the FRM and speciation sampler are statistically the same and "N" means they are statistically different.

X The number of times the FRM value was larger than the corresponding speciation sampler value (numerator) compared to the total number of differences used in the paired t-test for that site/analyte (denominator). Appendices G-1 and G-2 provide a complete listing absolute and percent differences between the FRM and each speciation sampler by site and sampling period. These data were used to calculate the above ratio.

Besides the t-test, an ANOVA was conducted using only the particle nitrate data from the four speciation samplers. This ANOVA was conducted for the following reasons. First, the speciation samplers were designed to provide an accurate measure of particle nitrate concentration, whereas, the FRM was not. Second, the particle nitrate concentrations measured at a site did not vary substantially across all the sampling runs. Third, except for the URG sampler at site 1, the particle nitrate data set was reasonably complete, i.e. there were few missing values.

The sampling results for the first two days at each site were excluded from the t-tests and the ANOVA because these were considered to be sampler shakedown/operator training days. The decision to exclude the first two days from the statistical analysis was made before the first samples were taken.

Overall, there appears to be no consistent pattern in the T-test results presented in Table 10. This is likely due to the reasonably high precision obtained by these samplers and due to the high correlations among the samplers. Note, Table II-2c presents the sample precision, but the mean precision is about 4 times smaller (n = 14 or 18 in most cases). Below is a brief discussion on a sampler-by-sampler comparisons relative the FRM.

Paired T-Test Results for FRM and Andersen Samplers

Table II-10a presents results from the paired t-tests for the FRM and Andersen samplers. The Andersen was the only speciation sampler that produced $PM_{2.5}$ mass concentration values that were statistically equivalent to those of the FRM at all four sites. The only other analytes that were two samplers were equivalent at the four sites are S (by XRF) and Zn. It is interesting to note that the two samplers are different for sulfate (by IC) at site 2 (P value = 0.0001) and site 3 (P value - 0.0028), despite being statistically equivalent at these sites for S by XRF. This anomalous situation might be attributable to analytical imprecision at the low sulfate concentrations measured. Table II-10a also shows that at sites 1, 2 and 3, the Andersen sampler consistently produced lower particle NO_3^- and NH_4^+ values and higher OC values than the FRM.

Paired T-Test Results for FRM and MetOne Samplers

Table II-10b presents the results from the paired t-tests for the FRM and the MetOne samplers. Particle nitrate was the only analyte for which the two samplers produced statistically equivalent results at the four sites. The $PM_{2.5}$ concentrations and the Si, K, Ca and Fe concentrations measured by the two samplers were statistically different either at all four sites (K, Ca, Fe) or at three of the four sites ($PM_{2.5}$, Si). The MetOne produced $PM_{2.5}$, Ca Si, K, and Fe concentrations at the four sites that were consistently larger than those from the FRM sampler (with the exception of $PM_{2.5}$ mass at Site 3). These results indicate strongly that the sampler inlet did not effectively remove coarse particles, as discussed earlier. For the other analytes the agreement between the two samplers were inconsistent across sites and analytes.

Paired T-Test Results for FRM and IMPROVE Samplers

Table II-10c presents the results from the paired t-tests for the FRM and the IMPROVE samplers. The two samplers produced statistically equivalent results at all four sites for only three analytes: S (by XRF), K, and Zn, but also produced results for three other analytes (NH_4^+, OC, and EC) that were statistically different at all four sites. The statistical equivalence for the other analytes was highly variable across the sites. A strong negative bias existed at all sites for the IMPROVE sampler for sulfate by IC, S by XRF, particle nitrate, ammonium, OC, and EC, and a consistent positive bias exists for the sampler for Si, Ca, and Fe at sites 1 and 2, where there were significant coarse particle concentrations. This may suggest a positive bias for coarse particle penetration relative to the FRM for the IMPROVE sampler.

Paired T-Test Results for FRM and URG Samplers

Table II-10d presents the paired t-test results for the FRM and URG samplers. This sampler suffered from a variety of operational problems at Site 1, which resulted in a large number of samples being lost or declared invalid. From a statistical point of view, the performance of this sampler with respect to the FRM was poor. This was unexpected since the URG sampler closely matches the FRM with respect to its design and flow operation. Zn was the only analyte where the URG yielded results that were statistically equivalent to the FRM at all four sites. Otherwise the statistical equivalence between the FRM and URG samplers varied inconsistently from site-to-site and analyte-to-analyte. It is likely that the mechanical problems associated with the specific URG samplers used in this study and not the design of the sampler itself was the cause of the poor agreement between the FRM and the URG sampler.

Paired T-Test Results for the FRM and VAPS Samplers

Table II-10e presents the paired t-test results for the FRM and the VAPS sampler. As noted earlier in this report, the VAPS sampler's virtual impactor was not correctly assembled at Site 1 but was included in the analysis to illustrate that point as well as for species, such as sulfate that are not affected by a cutpoint greater than 2.5 µm. S by XRF and Zn were the only analytes for which the two samplers produced statistically equivalent results at all four sites. For all the other analytes, the statistical equivalency of the results differed from site-to-site. Mass and the trace elements showed a consistent negative bias relative to the FRM, while the other species showed a consistent positive bias.

Results from the ANOVA on Particle Nitrate Data

The ANOVA was done on a site-by-site basis. At Rubidoux ANOVA involved 51 concentration values covering 14 days of sampling, at Phoenix ANOVA involved 67 concentration values covering 18 days of sampling, at Philadelphia ANOVA involved 71 concentration values covering 18 days of sampling, and at Research Triangle Park ANOVA involved 67 concentration values covering 18 days of sampling. The results of the ANOVA are presented in Table II-11 in terms of the mean concentrations and the number of values (in parentheses) used in calculating the mean. The last column in Table II-11 identifies the samplers that are statistically equivalent, that is, samplers within parentheses are statistically equivalent. For example, at Phoenix, the means for the Andersen and the IMPROVE samplers are statistically equivalent as are those for the Andersen and MetOne samplers. Note, however, that the means for the IMPROVE and MetOne samplers are not statistically equivalent. Only the Andersen and the IMPROVE samplers apparently had statistically equivalent results across all four sites for nitrate.

Aerosol Nitrate

As discussed above, aerosol nitrate as well as volatilized aerosol nitrate were determined by several methods, and there appears to be differences in the nitrate concentrations reported by those different methods. Tables II-12a through II-12c present data by sampler type and on a site-by-site basis for nitrate measured by the different methods employed in this study. Sulfate data are presented in Table II-12d, for comparison to a stable species, not influenced by volatilization. Tables II-13a through II-13d present similar data, however like methods are averaged, as well, the ratio of the methods are given to indicate the relative difference between methods.

The data in Table II-12a represent nitrate concentrations measured directly on Teflon and quartz-fiber filters without a preceding denuder. The data in this table suggests a difference between the two filter types for collecting aerosol nitrate. Chow (1995) indicates that both Teflon and quartz-fiber filters are suitable for the collection of nitrate, that is, both experience similar negative and positive artifacts. However, they are similar for quartz-fiber filters that have not been pre-treated (heated to 900 C) for OC collection, as is the case in this study. Apparently, heating the quartz-fiber filter reactivates it and allows it to adsorb gas phase nitrogen species (e.g., HNO_3). Table II-13a shows the average of nitrate measured on Teflon filters, quartz-fiber filters, the difference (Q-T), and the ratio of the quartz-fiber filter nitrate results to those measured on the Teflon filter. Ratios range from about 1.2 at Philadelphia, where temperatures are sufficiently cold to maintain the ammonium nitrate in the aerosol phase (no HNO_3 available to react with the quartz-fiber filter), to about 1.8 at Phoenix and RTP, where higher temperatures were observed as well as the likely hood of lower ammonia concentrations relative to Rubidoux, thus the possibility of HNO_3 available to react with the quartz-fiber filter. Absolute differences between nitrate concentrations measured on the quartz-fiber filter and the Teflon filter range from about 0.2 µg/m^3 at Philadelphia to 1.0 µg/m^3 at Phoenix, in a similar pattern to the ratio.

As described above, particulate nitrate was measured either directly on a filter behind a denuder or indirectly by summing two filters. Table II-12b summarizes these data by method or sampler. Once again, samplers that use a quartz-fiber filter (the indirect method) appear to measure more particulate nitrate then the direct method, which does not use a quartz-fiber filter. Table II-13b provides average data for the two methods. The ratio of the indirect to the direct method ranges from 1.1 to 1.5 and each value is slightly lower then the corresponding ratio in Table II-13a; although their associated standard deviations suggest there is likely no difference. However, absolute differences (Indirect - Direct Methods, where the indirect method includes the use of nitrate measured on a quartz-fiber filter) are slightly larger then the differences observed for nitrate measured on the quartz-fiber filter and the Teflon filter (Table II-13a). This suggests another factor also is involved causing the apparent difference between these methods. Hering (Aerosol Dynamics, Berkeley, CA, personal communication) suggests there may be a small positive bias, possibly due to the adsorption of other nitrogen containing compounds (e.g., NO_2), when using Na_2CO_3 coated denuders with nylon filters relative to using Na_2CO_3 impregnated filters with a Na_2CO_3 coated denuder. However, the IMPROVE sampler shows a trend opposite that of the URG and VAPS; however, it operates at a higher flow rate. A potential positive bias has been observed in this study using the indirect method to measure particulate nitrate if that method used a pre-heated quartz-fiber filter to obtain particle nitrate concentrations.

Volatilized nitrate concentrations measured by each method or sampler are given in Table II-12c. The IMPROVE value was obtained relative to the FRM, since nitrate was only measured on the nylon filter in that sampler. In determining volatilized nitrate, the quartz-fiber filter is not used by any sampler, thus eliminating that variable from the uncertainty in the measurement. In general, there is no consistent difference observed among the different samplers or methods. Table II-13c presents the averaged data by method. The standard deviation of the average ratio at all four sites either exceed the average or encompass 1, suggesting no difference can be distinguished for volatilized nitrate by these two methods. On the other hand, the higher variability at Phoenix vs Philadelphia (similar concentration ranges) may be due to how nitrate is measured and the amount of nitrate volatilized or in the gas phase as nitric acid.

Finally, to confirm that the differences are due to the method of collection, direct vs indirect, Teflon vs quartz-fiber filters, data are presented by sampler in Table II-12d for sulfate as measured on either Teflon or quartz-fiber filters. There is no difference between the use of the two filter types for determination of aerosol sulfate. Table II-13d provides summary averages of the data in Table II-12d. There is no difference between the two filter types, and the ratio at Rubidoux being different then one is due to rounding errors, all ratios were within 5%.

Given the above discussion, there is an apparent positive bias when measuring nitrate on a quartz-fiber filter that has been heat treated for carbon analysis. Therefore, it is recommended that a different approach be used for the determination of particulate nitrate on those samplers that may use the quartz-fiber filter in their determination of nitrate.

Organic and Elemental Carbon

Denuded vs Non-Denuded Organic Carbon Results

The $PM_{2.5}$ Chemical Speciation Evaluation Study collected particulate carbon on quartz-fiber filters from one sampler with an XAD denuder and five samplers without an XAD denuder. Data from Phoenix were selected for this analysis because the Phoenix samples included an additional IMPROVE sampler that used 25 mm quartz filters. Samples from the SASS were not included in this evaluation due to potential carbonate contamination from soil, since the inlet allowed particles greater than 2.5 µm to enter the inlet. The range of filter face velocities was from 11 to 104 cm/sec. Thermal Optical Reflectance carbon concentrations were used to evaluate the effect of using the XAD denuder and to investigate the differences in OC concentrations between the samplers.

Denuded and non-denuded samples were first compared using both the carbon fractions from TOR and the mass concentration of OC, EC, and TC. Figure II-5a shows the average percent of OC for OC1, OC2, OC3, OC4, pryrolized carbon; and the average mass concentrations for OC, EC, and TC (EC + OC). Five samplers were used for the non-denuded average and 1 sampler was used for the denuded sampler average. Seventeen 24-hour samples were used to calculate the average for each sampler. Figure II-5b shows the average percentages and masses for the denuded sampler with a 15 liter per minute (lpm) flow rate (21.1 cm/sec face velocity) and the non-denuded samplers with 16.7 lpm flow rate (23.6 cm/sec face velocity). The OC1 mass percent was less for the denuded samples in both Figures II-5a and II-5b. OC3 shows an increase for the denuded samples and little difference for OC2 and OC4. Differences in the OC3 concentrations may be due to the shape of the cutpoint for the VAPS compared to the other samplers. Organic carbon concentrations for the denuded sample were less than the non-denuded sample and the EC concentrations were similar. The differences in the OC concentrations are due to a combination of reduced positive artifact and a potential increase in the negative artifact or stripping of volatile organic compounds from the collected particles.

The impact the denuder has on the collection of OC, under the conditions of this experiment, can be seen in Figure II-6, where OC concentrations are plotted for the FRM sampler and the VAPS samplers against $PM_{2.5}$ mass. The VAPS sampler used a denuder in front of the quartz-fiber filter, whereas the FRM sampler did not use a denuder. Except for Rubidoux, the regression lines of the two samplers are parallel, but the FRM OC regression lines are offset high indicating a positive artifact in the method relative to OC collected on a quartz-fiber filter behind a denuder. This assumes both filters have similar negative artifacts. At Rubidoux, the VAPS sampler data likely represent PM_{10} rather then $PM_{2.5}$ and should not be considered valid data for OC or EC.

Figure II-6 also provides an estimate of the magnitude of the positive artifact for OC. Once again, at zero $PM_{2.5}$ mass the OC measured at Phoenix and Philadelphia by the FRM have intercepts of between 1-3 µg/m^3, except at RTP, where it is closer to about 0.2 µg/m^3. OC by the VAPS sampler has near zero intercepts, except at Rubidoux as just explained, suggesting that the use of the denuder provides a more suitable estimate of OC, at least relative to what is measured on a Teflon filter, i.e., assumes similar negative artifacts, which are likely minimized since this was a wintertime study. Differences RTP and the other cities may be due to the mix of OC compounds present in the atmosphere during sampling, as RTP is a more rural location then the sites in Philadelphia or Phoenix.

Face-velocity effects were investigated using the ratio of the non-denuded to the denuded samples. Figures II-7a and II-7b show the relationship between filter face velocity and the OC and EC concentrations, respectively. Denuded OC1 to non-denuded OC1 ratios range from 9.7 at 11 cm/sec to 4.8 at 104 cm/sec. The 95 percent confidence intervals show that the ratios have a fair amount of scatter at each face velocity. EC2 and EC3 concentrations show a increase that may be due to the $PM_{2.5}$ collection efficiency of the VAPS as compared to the RAAS. The effect of face velocity is shown strongest in the lowest temperature carbon fraction determined by TOR (OC1). This fraction may represent positive artifact that is due to SVOC that boil in the range of 120 C. Additional experiments, like those conducted in Seattle, with back-up XAD impregnated quartz filters will help in the interpretation of these data (Phase II of the evaluation of the chemical speciation samplers, Mitchell, EPA, ORD, personal communication) .

Comparison between TOR and TOT for OC and EC in $PM_{2.5}$

Carbon in atmospheric particles typically represents a large fraction (25 – 50%) of the $PM_{2.5}$ mass. Two methods are used currently for the analysis of particulate carbon: Thermal Optical Transmission (TOT - NIOSH Method 5040) and Thermal Optical Reflectance (TOR). These two methods both quantify carbon by heating filters and volatilizing the carbon that is oxidized in a granular bed of MnO_2, reduced to CH_4 in a Ni methanator, and quantified as CH_4 with a flame ionization detector. The TOT and TOR methods use different temperature programs and use different techniques to correct for the formation of pyrolysis products. These differences result in an operational definition of OC and EC by each method and while total carbon values are typically the same, the split between OC and EC are different, which usually results in a higher observed EC fraction by the TOR method. To better understand this difference, the TOT and TOR methods were compared using samples from the Chemical Speciation Monitor Evaluation Field Study. Additional wood smoke, and diesel exhaust samples were also included in the evaluation. Appendix J provides a more detailed description of the TOR and TOT methods comparison.

Both source and ambient wood smoke samples were evaluated. Thermal Optical Reflectance EC was on average 175 percent greater for a triplicate analysis of the smoldering wood smoke source sample. Measurement precision was similar for both techniques with a coefficient of variation (CV) of 21 and 23 percent for TOT and TOR, respectively. Spokane ambient wood smoke samples showed a lower difference in the EC concentrations with a ratio of TOR EC to TOT EC of 1.21.

A diesel truck source sample also was evaluated in triplicate. The TOR method EC and TC were 30 and 7 percent higher than the TOT method, respectively. TOR TC was 7 percent higher than the TOT TC. The CV for TOR EC (4 percent) was higher than the TOT EC (CV = 1 percent); however, both CV values are small compared to the differences between the methods for EC. The diesel truck exhaust was spiked with 10 µL of Trona solution, a sodium carbonate ore containing both carbonate and bicarbonate. The solution contained 10.16, 0.50, and 10.65 µg as C of OC, EC, and TC, respectively. Neither analysis show an increase in the amount of EC measured, while the TOR method showed a decrease in EC from 6.07 to 4.05 $\mu g/cm^2$. The TOT technique quantifies CC as part of the routine analysis and gave a value of 10.3 $\mu g/cm^2$ for CC. TOR showed an increase in OC as opposed to an increase in EC.

Samples were selected from the Phoenix (20) and Philadelphia (20) that represented a range of loadings. Six days with a range of concentrations were selected from the co-located VAPS with an XAD denuder, the IMPROVE sampler, and the Anderson RAAS. The VAPS, IMPROVE, and RAAS sampled 21.6, 32.8, and 10.5 cubic meters of air through a 47 mm quartz-fiber filter, respectively. The use of the different sample flow rates provided an average TC loading of 18.41 $\mu g/cm^2$ and wide range of TC loadings (4.77 to 41.78 $\mu g/cm^2$). The average EC, OC, and TC concentrations were significantly different (p # 0.001) when the TOR and TOT methods were compared using a paired t-test and the Wilcoxon Signed Rank Test. Linear regressions were used to evaluate the linear relationship between TOR and TOT in Phoenix and Philadelphia. Slopes for EC, OC, and TC were not significantly different for each city, and the intercepts were not significantly different from zero. Overall relationships between TOR and TOT ($\mu g/cm^2$) were TOR OC = TOT OC * (0.91 ± 0.02 (SE)) +(0.00 ± 0.35(SE)), r^2= 0.98; TOR EC = TOT EC * (1.94 ± 0.08) - (0.22 ± 0.31), r^2= 0.93; and TOR TC = TOT TC * (1.11 ± 0.02) - (0.07 ± 0.32), r^2= 0.99.

Two conclusions can be made based on this methods comparison: $[TOR]_{EC} > [TOT]_{EC}$, and $[TOR]_{TC} > [TOT]_{TC.}$ These conclusions are based on source and urban samples. Additional samples from non-urban locations need to be evaluated to determine if the association is the same for urban motor-vehicle dominated and non-urban biogenic/secondary aerosol samples.

Loss of Nitrate During Vacuum XRF Analysis

The analysis protocol for the FRM, URG, and VAPS samplers require mass, XRF, and ions analysis to be performed on the same Teflon filter. Due to the potential loss of ammonium nitrate from filters during vacuum XRF, nitrate, sulfate, and ammonium were determined on the quartz-fiber filter in these samplers. However, the observed positive artifact noted above with the quartz-fiber filter for nitrate required us to re-examine the use of the Teflon filter that has been used for XRF analysis in those samplers for ions analysis. Paired Teflon filters (same fow rate, and usually in parallel lines in the same sampler) were chosen for this analysis. One filter was analyzed directly for nitrate and sulfate, the other, having been analyzed for atmospheric XRF was analyzed also by vacuum XRF followed by determination of nitrate and sulfate on that filter. Another set of filters, analyzed only by atmospheric pressure XRF, also were analyzed for nitrate and sulfate to see the effect of just atmospheric pressure XRF on the potential loss of nitrate. The latter data are not yet available.

Table II-14 presents data for the loss of nitrate from Teflon filters as a result of XRF analysis. On the average, about 40 ± 16% of the nitrate was lost during XRF analysis. Also presented in the table are results for sulfate on the same filters. No sulfate was lost during the analysis. Figure I-8 is a scatter plot of the nitrate loss data as a function of the original nitrate concentrations. Data below original nitrate levels of 500 ug/filter are grouped along one regression line with a correlation coefficient of 0.851. On the other hand, data above 500 ug/filter fall well below the less than 500 ug/filter regression line. These higher concentration data points may have lost less nitrate because of the nitrate present on the filter may have been non-volatile {NaNO3, or metal$(NO_3)_X$}, rather then NH_4NO_3 (e.g., Eldering et al. 1991). Two of the three data points occurred on January 18th when Ca and Fe were near their highest levels during the study. Sodium values were not measured.

These data indicate that filters used for vacuum XRF analysis can not be used for nitrate analysis; although they can be used for sulfate analysis. One would also assume that the ammonium ion results i.e., ammonium associated with NH_4NO_3, also would be biased low as a result of vacuum XRF.

Field Experience with the Speciation Samplers

The overall objective of the chemical speciation sampler evaluation study was to characterize their field performance under a range of atmospheric chemical, meteorological, and operating conditions. While the primary evaluation criteria used to judge sampler performance was each sampler's ability to representatively collect and provide equivalent chemically speciated atmospheric fine particulate matter, each sampler's ease of use, reliability, and field worthiness also were evaluated. For this reason, site operators were instructed to record their daily experience with sampler setup and routine operation. At the completion of the field sampling component of the overall study, a four-page field operations survey was developed and distributed to allow site operators to document their overall experience with each of the samplers. Evaluation criteria included ease of sampler installation, audits and calibrations, programming, filter holder exchange, sampler maintenance, and data retrieval procedures.

Review of the daily site operations records and completed surveys revealed problems with each of the speciation samplers as well as the collocated $PM_{2.5}$ FRM samplers. Some problems were particular to individual instruments of a given design at a given site and were typically associated with sampler construction, handling, setup, or operation, rather than sampler design. Other problems were associated with design, and thus, all samplers of that type were affected.

A summary of the site operator's surveys is presented in Table II-15, while Table II-4 details noted problems or deficiencies with each sampler as recorded from the daily field data sheets. A descriptive summary of each sampler's field performance is listed below.

Andersen RAAS

The Andersen sampler was judged to be relatively straightforward to unpack and setup in the field; although one site operator indicted that its main module weighed more than other sampling modules. The ease of setting up the sampler in the field was judged to be good. The sampler is capable of being temperature, pressure, and flow calibrated in the field and calibration procedures were judged to be average to good. Good to excellent ratings were received for conducting the manufacturer's temperature, pressure, and flow audit procedures. Few problems were noted during programming or retrieving pertinent data after each sampling event.

At the Rubidoux site, the Andersen sampler lost the temperature, pressure, and flow calibrations on two occasions requiring complete re-calibration of the instrument. The Rubidoux site operator also noted a slight water intrusion problem following a rain event and indicated occasional drifts in reported internal cabinet temperature. Two particular design problems were identified by each of the five site operators. First, the sampler's indicated flow rate was difficult to calibrate due to electronic drifts in the flow sensor response. Fluctuations in the indicated flow rate of each Andersen channel were observed throughout the study at each of the four sites and caused uncertainties in overall volume sampled. The second design problem observed by all site operators was the tendency for o-ring seals to fall out during installation and removal of filter holders. This latter problems made routine filter holder exchange awkward and raised concerns regarding potential sample contamination.

Met One SASS

The Met One speciation sampler was judged to be relatively easy to setup in the field and could be accomplished by one person, with an overall rating for installation of good to excellent. The sampler's response to ambient temperature, pressure, and flow rate only can be calibrated by the factory and cannot be adjusted in the field. The manufacturer's procedures for auditing these quantities was rated as good to excellent. Few problems were noted during exchange of the sample canisters in the field. No problems were noted with post-sampling data retrieval.

Some problems were encountered during laboratory disassembly of the Met One canisters. Specifically, collected filter samples were sometimes difficult to remove without damaging or contaminating the sample. Occasional field problems were noted regarding failure to start as programmed or with sampler premature shut-downs. These events were intermittent and varied by sampling site. One operator experienced sharp edges on the sampler's upper and lower inlet shroud. The sampler's screen was noted to be difficult to read in bright sunlight.

URG MASS

The URG sampler generally received favorable ratings regarding ease of field installation and initial setup. Ambient temperature, pressure, and flow rate response for the URG sampler can be calibrated in the field and the manufacturer's instructions for conducting these calibrations received average to good operator responses. Programming and its reliability received excellent ratings. Responses regarding sample exchange and data retrieval were rated as good.

The high pressure drop though the MASS 400 filter holder system exceeded the ability of the unit's flow control system and resulted in low initial flow rates at all sites. Addition of a second air pump to each flow system by the manufacturer effectively resolved the flow performance problem. Filter holder temperature flags were often encountered at the Rubidoux and Phoenix sampling sites. Contact of threaded Teflon components with threaded aluminum components in the MASS 400 resulted in damage to Teflon filter holders.

IMPROVE

Site operators noted that setup of the IMPROVE sampler was generally more cumbersome and required more time than the other speciation samplers. Unlike most of the other speciation samplers, the IMPROVE does not provide ambient temperature or pressure measurement. Calibration of system flow rates in the field were judged to be average to good and sampler programming was judged to be average. Ease of exchanging filter holders in the field was rated as average to good.

Field reliability problems with the IMPROVE sampler were experienced at all four sites with most problems relating to faulty timers, solenoids, and pumps. A slight water intrusion problem was noted at RTP following two significant rain events.

VAPS

Installation and setup of the VAPS sampler was judged as average by operators at each site. Like the IMPROVE sampler, the VAPS provides no measurement of ambient temperature and pressure, so these parameters could not be calibrated nor audited in the field. The ease of the flow calibration and flow audit procedures were both rated as average. Fair to average ratings were received regarding exchanging of field samples and ease of data retrieval from the sampler.

Problems encountered with the VAPS were typically ones of programming and failure of the sampler to properly shut down at the specified time. All site operators experienced problems with o-rings and virtual impactor receiving tubes falling out during filter holder installation and removal.

FRM

Three different FRM models were used during the Four City study so comments received are primarily sampler-specific. In general, however, the FRM samplers were judged to be relatively straightforward to install and setup in the field. Manufacturer's procedures for calibration and auditing of temperature, pressure, and flow rate sensors were generally judged to be good. Sampler programming and its reliability were rated as good to excellent. Data retrieval from each sampler was judged to be good.

Specific problems encountered with the FRM were normally sampler specific and included problems with pump failures, water intrusion, and failure to initiate the programmed sampling event.

Sampler Costs and Related Spare Parts

Table II-16 lists each sampler used in this study and parts needed to operate the samplers on a 1 in 6 day schedule. To operate the samplers on a more frequent schedule would require multiples of each based on shipping and filter changing schedules. Operational costs for each of the speciation samplers was considered to be essentially equivalent.

DISCUSSION

Expectations

The speciation samplers were designed to minimize sampling artifacts during the collection of atmospheric particulate matter, and thus, provide an improved estimate of the $PM_{2.5}$ actually present in the atmosphere, relative to the FRM. As stated in the introduction, for stable species, such as, sulfate and the trace elements measured here, we would expect good agreement (approaching the precision for that species) between the FRM and the chemical speciation samplers. This of course assumes the inlets of the samplers are performing in a manner similar to the FRM. This was recommended highly by the PM Expert Panel (Koutrakis, 1998).

For aerosol species in dynamic equilibrium with their gas phase counter parts (i.e., NH_4NO_3 and semi-volatile organic compounds) we would expect agreement between the FRM and the speciation samplers under some conditions, but not under others. This is because these equilibrium processes are dependent on temperature, relative humidity, pressure drop across the collection substrate (proportional to flow rate with filters of the same diameter), and the concentration of the precursor gases. The latter is especially true in the case for NH_4NO_3 in equilibrium with nitric acid and ammonia (Russell et al. 1993, Hering and Cass, 2000), as they need to react to form aerosol, as opposed to just condensing as might be the case for many of the SVOC. Since diffusion denuders and reactive sorbents were not used to remove gas phase species or to efficiently collect SVOC, respectively, we would expect there to be differences among the samplers for the measurement of OC as a function of pressure drop across the collection substrate and other variables. On the hand, denuders and reactive filters were used to collect NH_4NO_3, and therefore, we would expect NH_4NO_3 to agree among the chemical speciation samplers for particulate nitrate, but perhaps not with the FRM depending on the conditions stated above.

Before discussing differences among methods it also is important to review the precision results (Table II-2c). Estimated precision, calculated as the coefficient of variation between collocated sampler pairs was within 10 percent for most of the samplers for mass, sulfur, sulfate, ammonium, and potassium. Precision values estimated for the other species, independent of sampler, were within 15 percent, except for OC and EC by the IMPROVE sampler and silicon on all samplers. The latter 3 species had measured precision values greater then 15 percent but usually less then 30 percent. The precision results therefore, provide a lower bound for agreement between the speciation samplers and the FRM and among the speciation samplers.

Major Questions Addressed

As described in the introduction, the primary objective of this study is to determine if there are differences among the three chemical speciation monitors for their ability to estimate concentrations of the chemical components of $PM_{2.5}$ mass found in ambient air. Comparisons also will be made to two historical samplers and to the FRM using these samplers as a relative reference.

There are four questions to be addressed by this intercomparison study with associated hypotheses designed to address the questions. The questions and hypotheses are stated below with responses based on the data provided from this study.

Q1. How well do $PM_{2.5}$ mass and the chemical components of mass agree between the FRM and the chemical speciation samplers tested in this study?

There is generally good agreement between the FRM and the chemical speciation samplers for the measurement of PM.2.5 mass and it chemical components, under the conditions encountered in this study, including meteorological and operating conditions. There are a few exceptions, due to differences in sampler inlets or efficiency of the $PM_{2.5}$ cutpoint. As well, real differences were observed for nitrate and organic carbon. For nitrate the differences appear to be due to the use of pre-heated quartz-fiber filters, and the believed associated positive artifact for nitrate with that filter material. For organic carbon the differences appear to be due to the different face velocities across the quartz-fiber filters used among the samplers. Tables II-8a lists average values for each species and sampler by site, while Table II-8b lists the ratio of the speciation sampler to the FRM for each chemical component by site and sampler. For example, there is excellent agreement for sulfate, suggesting that the quality assurance and quality control objectives were achieved in monitoring and validating flow rates and for chemical analysis, assuming sulfate results are representative of other species. $PM_{2.5}$ mass agree extremely well (with in 5%) at Philadelphia and RTP for all samplers and at Rubidoux and Phoenix for the Andersen and IMPROVE samplers. More variation was observed for the URG and MetOne as explained earlier.

There were individual data points or small groups of data that effectively biased the analysis (see Figures II-3 and II-4). These data have been carefully reviewed and have been validated to Level 2b. Any remaining inconsistencies in the data have been included in the analyses presented here as valid data.

The spiral inlet of the MetOne Sampler produced results that were biased high relative to the FRM. The data indicated (e.g., see Tables 8a and 8b) that coarse particles were passing through the inlet to the collection substrate, especially at high coarse particle loadings. This problem has been addressed by MetOne and the spiral inlet has been replaced with a Sharp Cut Cyclone (SCC). Results of preliminary evaluations performed by MetOne of the MetOne sampler with the SCC are presented in Appendix H. Results presented in Appendix H indicate much better agreement with the FRM than the spiral impactor. Subsequently, the spiral inlet has been evaluated with test aerosol in the laboratory and compared to the WINS impactor of the FRM and SCC now used in the MetOne sampler (Peters et al. 2000; given in Appendix I)

More variation was observed among the chemical speciation samplers relative to the FRM for organic carbon than the other major species. Organic denuders and reactive sorbent collectors were not used in this study to minimize negative and positive artifacts in the collection of organic carbon. If the method for collecting OC was identical among the samplers, artifacts would not be an important factor, at least for noting differences among the samplers. However, the samplers operated at different flow rates and used the same size filter for organic carbon, except MetOne, which used a mask over the quartz-fiber filter to achieve the same face velocity as the FRM. Therefore, variations due to pressure drop across or face velocity through the filter were observed (see Figures II-7a and II-7b) and resulted in significant variations for measured OC concentrations among the samplers tested in this study (e.g., see Figures II-3e and II-4e).

More variation was observed among the nitrate at Phoenix then at Philadelphia, even though similar nitrate concentrations were observed at both sites. This variation was partly attributed to the use of pre-heated quartz-fiber filters originally designed for collecting OC and EC for subsequent analysis and temperature differences (Philadelphia was colder). On an absolute basis, variations in nitrate are similar at Philadelphia, RTP, and Rubidoux and on the order of 1 - 3 µg/m^3. Ammonium follows a similar pattern to nitrate.

Variation among the chemical speciation samplers relative to the FRM for trace elements was varied. Sulfur had excellent agreement, typically within 10%, while silicon varied up to a factor of 5 or more, including the MetOne sampler. Excluding the MetOne sampler most differences were within 20-25%, with the highest variations for all samplers being observed at Phoenix, where the highest coarse particle loadings were observed. Similar results were observed for Ca and Fe, species typically associated with the coarse particle size fraction.

Q2. How well can the FRM mass be reconstructed by summing the chemical components measured by the speciation samplers.

Mass balance results only were calculated for the FRM sampler. Mass and trace elements were measured on the Teflon filter, while ions and OC/EC were measured on the quartz-fiber filter as indicated in Figure I-6a. In calculating the mass balance, Si, Fe, and Ca were converted to their oxides and summed to give an estimate of crustal material and organic carbon was multiplied by 1.4 to give an estimate of organic material. Other species were used directly. The sum of the species as defined above accounted for 111, 135, 110, and 108 percent of the mass on average at Rubidoux, Phoenix, Philadelphia, and RTP. Since mass is measured on an inert Teflon filter, where positive artifacts would be minimized, it is likely that this overestimation in calculated mass is due to positive artifacts for OC and nitrate on the quartz-fiber filter. Using data in Table II-13a (Q-T) to represent the positive artifact for OC and regression intercepts from Figure II-6 the estimated corrected mass balance adjusted for potential artifact for both species is 94%, 112%, 101%, and 104% at Rubidoux, Phoenix, Philadelphia, and RTP, respectively. These values are more reasonable, however, they are still lower estimates since Al, Ti, and Mg oxides have not been accounted for in the crustal material estimate (likely less than 1% addition) and water has not been estimated and included. However, past experience suggests that mass balance results of 100±20% is reasonable.

For the speciation samplers one would expect similar results, as there was reasonably good agreement among the speciation samplers and the FRM for mass and its components, as discussed above. As well, the FRM is likely a reasonable surrogate for the speciation samplers because 1) this was a wintertime study and artifacts due to volatilization would be minimized, 2) the positive artifact observed for nitrate, as measured on the quartz-fiber filter, resulted in similar particle nitrate concentrations between the FRM and the speciation samplers, and 3) the fact that OC was measured by the FRM at the standard face velocity of 16.7 lpm. The major difference between a calculated mass balance for the speciation samplers relative to the FRM would be due to organic material as the OC measurement continues to have both positive and negative artifacts that are a function of the sampler design parameters (e.g., face velocity through the filter) and for nitrate for the samplers where particulate nitrate includes nitrate measured on a quartz-fiber filter.

Specific Hypotheses Related to Questions Q1 and Q2

The following hypotheses are related to reconstructing the measured FRM mass. For each of these hypotheses, the concentrations, on a species-by-species basis, from each of the speciation samplers is compared to the respective concentration from the FRM. The concentrations from the speciation samplers are not compared to each other. The specific hypotheses and brief statements regarding those hypotheses are given below:

1. *$PM_{2.5}$ mass concentrations on the FRM Teflon filter measured by the gravimetric method are compared to $PM_{2.5}$ mass concentrations as measured on the Teflon filters in the chemical speciation samplers by the gravimetric method. The hypothesis is that the mass concentration from each of the speciation samplers is not statistically different from the mass on the FRM filter. The next eight hypotheses delve further into understanding why the mass concentrations do or do not compare favorably.*

   Tables II-10a through II-10e provide results of the paired t-test for all samplers and all species measured in this study. Mass concentrations obtained by the speciation samplers are equivalent for the Andersen sampler at all sites, while the other samplers are equivalent to the FRM mass at some sites, but not others. However, while there are statistical differences at alpha equal to 0.05, the differences are small in absolute concentrations, for samplers operating properly, and are within expectations based on the precision obtained from collocated samplers (Table II-2c). The reason for these inconsistencies is due likely to differences in the inlet collection efficiency (slope and cutpoint) of the samplers for $PM_{2.5}$. The only unexplained exception is mass measured by the URG sampler at Rubidoux. This sampler reported an average mass concentration that was more then 30 percent greater then that report by the FRM (see Tables II-8a and II-8b). The major species are high on the URG sampler relative to the other samplers at Rubidoux (excepting the MetOne), as opposed to having a few data points that are at an extreme value (see Figures II-3 and II-4). Trace elements associated with crustal material are not high on the URG sampler relative to the other samplers at Rubidoux and these were measured on the same Teflon filter as the mass. In addition, comparable results among the URG sampler and the other samplers were observed at Phoenix, where coarse particle concentrations were similar to Rubidoux, therefore, it is likely that the relatively high mass concentrations observed at Rubidoux for the URG sampler were a problem only with that particular URG sampler and the composition data do not provide the answer as they did for the MetOne sampler.

2. *$PM_{2.5}$ trace element concentrations or groups of elements on the FRM Teflon filter as determined by XRF are compared to trace element concentrations or groups of elements on the Teflon filters in the speciation samplers as determined by XRF. The hypothesis is that there is no statistical difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since these species are stable.*

   Statistical differences were found for all trace elements (Si, K, Ca, Fe, and Zn) at most locations for the MetOne sampler as expected due to the inlet problem. The other samplers had mixed results. However, even though the samplers were not equivalent (at alpha = 0.05) to the FRM, in all cases, the differences on the average are usually small in absolute concentrations (see Table II-8a) (except for the MetOne) and are reasonable based on the precision obtained from collocated samplers (Table II-2c).

3. *$PM_{2.5}$ sulfate concentrations on the FRM quartz-fiber filter are compared to sulfate concentrations on the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since sulfate is a stable species.*

   Statistical differences were found for sulfate for all samplers at one or two of the sites; although there is no consistent pattern among the sites and samplers. However, the differences on the average are usually small in absolute concentrations (see Table II-8a) and relative to the FRM (see Table II-8b) and are reasonable based on the precision obtained from collocated samplers (Table II-2c).

4. *$PM_{2.5}$ ammonium concentrations on the FRM quartz-fiber filter are compared to ammonium ion concentrations on the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations may not be comparable since ammonium is volatile when in the form of ammonium nitrate.*

   While manufacturers went to great trouble to develop samplers that minimized sampling artifacts for nitrate, no designs included collecting ammonium with minimal artifacts. Therefore, one would expect ammonium to agree with the FRM. However, the t-test (alpha = 0.05) indicated significant differences at most sites for the Andersen, IMPROVE, and URG; the MetOne sampler is statistically different only at Phoenix. For the collection of ammonium, based on the averages (see Table II-8a) and the data presented in Tables II-10a-e, there appears to be a trend with quartz-fiber filters reporting the highest ammonium concentrations, then Teflon, with nylon filters reporting the lowest averages and having the largest differences relative to the FRM. In some cases, these differences are as great as 50% relative to the FRM ammonium concentrations; however, relative to $PM_{2.5}$ mass the differences are small. It is possible that the IMPROVE sampler reports lower ammonium concentrations than the others due to enhanced volatilization of ammonium from the basic nylon filter, i.e., NH_4NO_3 that volatilizes after collection on the nylon filter efficiently collects the HNO_3, but not the NH_3.

5. *$PM_{2.5}$ nitrate concentrations on the FRM quartz-fiber filter are compared to nitrate concentrations on the Teflon (RAAS, SASS), quartz-fiber (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypotheses is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since the collection of nitrate on these filters should all be biased by the loss of nitrate due to volatilization, with the exception of the IMPROVE.*

> The data presented in Table II-13a, indicate a difference, on average, of up to 1.0 µg/m^3 for nitrate measured on the Teflon filter relative to the quartz-fiber filter with the latter being consistently higher, under the conditions observed during this study. The difference is likely due to a positive artifact associated with the quartz-fiber filter, which was pre-treated for carbon analysis, i.e., heated to reduce carbon levels on the filer. This assumes that quartz-fiber and Teflon filter media have similar losses due to volatilization, which is apparently true for quartz-fiber filters that have not been pre-heated (Chow 1995). Nitrate concentrations obtained from the nylon filter on the IMPROVE sampler were not included in the analysis.

6. *$PM_{2.5}$ nitrate concentrations on the FRM quartz-fiber filter are compared to nitrate concentrations on the nylon (RAAS, SASS, IMPROVE), or quartz+nylon (MASS, VAPS) filters in the speciation samplers. The hypothesis is that the nitrate from each of the speciation samplers is greater than or equal to the nitrate on the FRM quartz-fiber filter, due to negative artifacts anticipated collecting nitrate on a quartz-fiber filter in the FRM. This addresses questions about the amount of nitrate volatilized from the FRM Teflon filter.*

> The paired t-test indicated statistically equivalent results for particle nitrate between the MetOne sampler and the FRM, while mixed results were observed at the other sites for the other samplers. The URG samplers reported consistently high nitrate concentrations relative to the FRM as well as the VAPS sampler (see Tables II-10a - II-10e), mentioned here because the VAPS and URG used similar methods for measuring nitrate. Table II-13b compares the two methods for particulate nitrate. On the average, the direct method (nitrate measured on a nylon filter directly behind a denuder) is consistently lower then the indirect method (requires the sum of two filters, a nylon behind a denuder and Teflon filter and a quartz-fiber filter in parallel) for particulate nitrate. The absolute differences are larger than the difference due to using the quartz-fiber filter, suggesting another reason for the difference, other then just the positive artifact observed on the quartz-fiber filter for nitrate.
>
> Volatilized nitrate was a low fraction (on average < 10%) of the total nitrate at all sites except Phoenix, where it represented about 50% of the total nitrate on average. Absolute values of volatilized nitrate were less than 0.5 µg/m^3 at Rubidoux, Philadelphia, and RTP, and around 1.3 µg/m^3 at Phoenix. On the average, differences between the FRM, Andersen, IMPROVE, and MetOne were typically about 10%, with larger differences observed between these samplers and the URG and VAPS. Differences between the direct and indirect methods for determining volatilized nitrate were on the average, small (< 0.2 µg/m^3) (see Table II-13c); although, on average, the direct measurement was higher than the indirect at all sites.

7. *$PM_{2.5}$ elemental carbon (EC) concentrations on the FRM quartz-fiber filter are compared to EC concentrations on the quartz-fiber filters from the chemical speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since elemental carbon is stable.*

> Mixed t-test results were observed for EC across the sites and samplers as seen in Tables II-10a-e. In general, the FRM reported higher EC concentrations then the speciation samplers as indicated in Tables II-10a-10e and Table II-8b. However, the differences were usually small (10-20%) on an absolute basis and reasonable based on the precision results obtained by collocated sampling at Rubidoux (see Table II-2c).

8. *$PM_{2.5}$ organic carbon (OC) concentrations on the FRM quartz-fiber filter are compared to OC concentrations on the quartz-fiber (MASS, RAAS, SASS, IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that of the FRM. These concentrations should be comparable since as designed they all potentially experience similar negative or positive artifacts.*

> Statistically different OC concentrations relative to the FRM were reported for the Andersen, IMPROVE, and URG sampler at nearly all sites. The MetOne sampler was only different from the FRM at RTP. Differences and variability were larger for the OC data then for many of the other species. As discussed earlier, the measurement of OC by the speciation samplers also is dependent on the face velocity of air being pulled through the filter (see Organic and Elemental Carbon; Denuded vs Non-Denuded Organic Carbon Results). This resulted in larger (10-30%) differences between the averages for OC measured by the speciation samplers and the FRM then for the other major species. The scatter is illustrated in Figures II-3e and II-4e. The face velocity effects can be seen in Figures II-7a and II-7b.

9. *$PM_{2.5}$ OC concentrations on the FRM quartz-fiber filter are compared to OC concentrations on the quartz filter following an oversized XAD denuder from the VAPS speciation sampler and from channel 5 on the SASS sampler. The hypothesis is that OC on the FRM will be greater than OC collected by the VAPS or SASS denuded channels if there are positive artifacts or less than the VAPS and SASS denuded channels if there are negative artifacts. No difference would be inconclusive.*

> The SASS denuder was never installed in the samplers, as it was found to be to brittle. A modified honeycomb denuder will be used in Atlanta. Paired t-test analysis was not performed for this comparison. However, it is evident from the other analyses that lower OC concentrations were measured using the VAPS with the XAD diffusion denuder then without the denuder for OC concentrations measured on all other samplers. Results suggest (see Figure II-6) that the VAPS denuder is at least eliminating partially the positive OC artifact OC positive artifacts, relative to the FRM appear to account for up to 3 µg/m^3 under the conditions observed during this study. No information is available on OC negative artifacts from the experiments conducted here.

Q3. How well do the measured concentrations from the various speciation samplers agree?
On the average, the chemical speciation samplers produced results for mass and the chemical components of mass that agree within reasonable expectations based on the precision estimates obtained from collocated samplers, that is, to within 10-30 percent depending on the species. However, real differences exist among the samplers for organic carbon and nitrate. Removing the biases associated with those measurements will provide even better agreement for those two species. Paired t-test analysis supports this finding on the average. Differences greater then 30 percent were observed in some cases for the trace elements, which may be important for receptor modeling, but not for reconstructing $PM_{2.5}$ mass. A number of exceptions have been noted and reasons for those exceptions are described in the previous sections.

Q4. What are the causes of the differences among the speciation samplers for measured concentrations of mass and the components of mass if they exist.
This has been explained in the previous sections, with regard to mass, nitrate, and organic carbon. However, there are subtle differences among the samplers that would be beneficial to explain. As well, the samplers are all designed slightly different and it would be useful to examine more carefully those differences on their ability to obtain reliable and consistent chemical speciation data.

Specific Hypotheses Related to Questions Q3 and Q4

The following hypotheses compare the concentrations of the chemical components measured on the chemical speciation samplers to each other to address why there are differences among measured concentrations, if they exist. For each of these hypotheses, only the concentrations from the speciation samplers are compared, excluding the FRM, except for the first hypothesis, which will include the FRM in the analysis.

The following hypotheses were addressed in the above section when comparing the speciation samplers to the FRM. There are subtle differences, i.e., speciation samplers show more variability among themselves for nitrate and carbon, than relative to the FRM. This is typically due to the samplers showing a consistent bias rather than a random bias relative to the FRM, i.e., one sampler is usually high relative to the FRM, while another is usually low. Once again, from a practical standpoint and for most species, the differences are usually small and reasonable given the measured precision estimates obtained from collocated sampling. However, there are real differences observed for organic carbon and nitrate that need to be addressed to reduce the variability among the samplers as differences as high as 1-3 µg/m^3 are observed on average for nitrate and 1-4 µg/m^3 are observed for organic carbon.

1. *$PM_{2.5}$ mass and chemical composition as determined according to the manufacturer's guidelines. The hypothesis is that all species of interest are comparable among the chemical speciation samplers when concentrations are determined according to manufacturer's guidelines.*

> As noted above, on the average the concentrations of the species measured by the chemical speciation samplers when operated according to the manufacturer's specifications agree within reasonably expectations for most species, based on the observed precision estimates obtained from collocated sampling. Organic carbon showed more variability among the samplers, and relative to the FRM, two samplers tended to be high while two tended to report lower OC concentrations. Thus, differences among the samplers for OC is somewhat larger then when

comparing their values to the FRM. This variation can be seen in Figure II-3e and II-4e. These differences are in part due to a combination of positive and negative artifacts that have been shown to occur during sampling and perhaps sample storage (Eatough et al. 1989; McDow and Huntzicker 1990; Turpin et al. 1994).

Results shown in Figure II-7a and II-7b indicate the significant impact that face velocity through the filter or pressure drop across the filter has on the measured OC concentrations. Differences among the chemical speciation samplers also were noted for aerosol nitrate and were most pronounced when volatilized nitrate was a large fraction of the total nitrate (i.e., about 50% vs 10% in this study). These differences resulted in a consistent bias among the speciation samplers relative to the FRM and to each other with the URG and VAPS sampler typically reporting nitrate concentrations higher then the FRM and the Andersen and MetOne typically reporting concentrations lower then the FRM. It is believed these differences are due to the methods used to collect aerosol nitrate. Two factor have been identified. First, the use of the pre-heated quartz-fiber filter in the URG, VAPS, and FRM samplers and its associated positive bias, and secondly, the direct vs indirect methods for collecting particulate nitrate.

However, based on the data presented here and the fact that there are no reference standards for OC or nitrate, we are unable to indicated which sampler is providing more accurate results. However, the data do indicate real differences between organic carbon and nitrate concentrations among the samplers, both most likely due to positive artifacts for their respective species.

2. *$PM_{2.5}$ mass concentrations by gravimetric method on Teflon filters are compared among the samplers. The hypothesis is that there is no difference in these masses.*

On average, when the samplers are operating correctly, they appear to be reporting similar $PM_{2.5}$ mass concentrations. For MetOne this condition is based on results obtained for that sampler using the sharp cut cyclone, rather then its original design tested here using the spiral inlet (see Appendix H). The one exception to this is the URG sampler at Rubidoux. Examination of the composition data failed to reveal the cause of this difference.

3. *$PM_{2.5}$ elements (individually or in groups) from the Teflon filters as measured by XRF are compared among the samplers. The hypothesis is that there is no difference in these concentrations as these elements are stable during sampling and analysis.*

In general, there was good agreement among the samplers for trace elements, with the exception of MetOne, due to the spiral inlet apparently allowing coarse particles to penetrate to the filter. More information is given above in No. 2 under Specific Hypotheses Related to Questions Q1 and Q2.

4. *$PM_{2.5}$ nitrate concentrations from the nylon (RAAS, SASS, IMPROVE) or Teflon+nylon (MASS, VAPS) filters are compared among the samplers. The hypothesis is that there is no difference in these concentrations.*

Real differences are seen among the speciation samplers for particle nitrate. The differences appear to be due to the use of pre-heated quartz-fiber filters, used for organic carbon analysis, and differences among how the denuder/filter pack arrangements are used in the samplers. More detail is given above in No. 6 under Specific Hypotheses Related to Questions Q1 and Q2 and No. 1 under Specific Hypotheses Related to Questions Q3 and Q4.

5. *$PM_{2.5}$ sulfate from the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that there is no difference in sulfate concentrations as sulfate is stable during sampling and analysis. We will also look at sulfate estimated from XRF sulfur (S X 3 equal to sulfate) to see how well XRF sulfur estimates sulfur determined by IC from both Teflon or quartz filters.*

As discussed above, no differences are observed for measured concentrations of sulfate among the samplers. More details are given above in No. 3 under Specific Hypotheses Related to Questions Q1 and Q2.

Comparison of sulfur by XRF times three (S*3) to sulfate by IC showed excellent agreement among all samplers. Ratios of S*3/Sulfate were 1.08 ± 0.13; 1.06 ± 0.10; 0.99 ± 0.08; and 1.06 ± 0.05 at Rubidoux, Phoenix, Philadelphia, and RTP, respectively. These data are indistinguishable from a ratio of 1, thus, XRF sulfur could be used to estimate sulfate, under the conditions that occurred during this study.

6. *$PM_{2.5}$ organic and elemental carbon from the quartz-fiber filters where no denuder is used will be examined relative to each other. Since channel 5 of the VAPS uses a denuder, it will not be included in this hypothesis. The hypothesis is that the concentrations of OC and EC are the same provided no denuder is employed.*

As discussed above, differences in face velocity across the filter (or pressure drop through the filter) resulted in real differences (from 1-4 $\mu g/m^3$ on average) among the measured OC concentrations for these samplers. More details are given in Nos. 7 and 8 under Specific Hypotheses Related to Questions Q1 and Q2 and No. 1 under Specific Hypotheses Related to Questions Q3 and Q4.

7. *$PM_{2.5}$ organic and elemental carbon from quartz filters including speciation samplers where a denuder is used is compared among the samplers. The hypothesis is that samplers that use denuders (i.e., the VAPS) will have lower OC concentrations since the potential for positive artifact due to organic vapors has been minimized. Nothing can be said about negative artifacts. EC should not be affected.*

As described above, the OC measured by the VAPS sampler behind the XAD denuder was consistently lower then the other samplers indicating removal of positive artifact from the air stream. Estimates of this positive artifact were obtained relative to $PM_{2.5}$ mass measured by the FRM (also see Tolocka et al. 2000). Positive artifact for OC ranged from about none at RTP to about 3 $\mu g/m^3$ at Phoenix. Artifact at Rubidoux could not be estimated due to the operational problem with the VAPS sampler at that site. More information is given above in

No. 9 under Specific Hypotheses Related to Questions Q1 and Q2 and No. 1 under Specific Hypotheses Related to Questions Q3 and Q4.

8. *$PM_{2.5}$ ammonium from the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that the concentrations of ammonium are the same for all speciation samplers as all potentially suffer from negative artifacts.*

> Measurement of ammonium ion in the speciation samplers did not include a method to minimize artifact due to volatilization of ammonium nitrate. Variability among the samplers was on the order of 0.5 µg/m^3 or less. In general, the IMPROVE sampler was slightly lower then the other samplers, likely due to the use of a nylon (basic pH) filter to collect a basic gas (NH_3 after dissociation of NH_4NO_3), while HNO_3 would be collected efficiency by the nylon filter. More detail is given above in No. 4 under Specific Hypotheses Related to Questions Q1a and Q1b.

9. *Ammonium nitrate equilibrium is a function of temperature and relative humidity and thus, nitrate and HNO_3 concentrations will be compared as a function of temperature and RH to determine if these factors bias sample collection. The hypothesis is that there is not difference in the samplers as a function of temperature or RH.*

> Due to resource limitations, HNO_3 data were not obtained from the VAPS Na_2CO_3 denuder. Therefore, this hypothesis can not be fully evaluated. However a partial response is given in No. 6 under Specific Hypotheses Related to Questions Q1 and Q2 and No. 1 under Specific Hypotheses Related to Questions Q3 and Q4.

10. *Crustal related elements are typically associated with particles greater than 2.5 um AD, however, differences in the inlet efficiency or slope of the collection efficiency curves may result in different concentrations of crustal related material being measured by these samplers. The hypotheses is that the crustal related material as determined from summing the oxides of Fe, Ca, and Si are not statistically different among the samplers. If differences are observed relate these differences to the coarse particle mass as measured by the VAPS or by other collocated PM_{10} monitors. Wind speed may also be a variable of interest in this analysis.*

> Significantly higher mass concentrations are reported by the MetOne sampler using the spiral inlet then the other samplers, including the FRM. As stated above, this is due to the spiral inlet allowing particles greater than 2.5 um to penetrate, as well as an efficiency curve that is not as steep as the FRM or Andersen cyclone (Peters et al. 2000; Appendix H; Appendix I) Secondly, the VAPS sampler at sites where high coarse particle loadings were observed, also had higher measured concentrations of crustal related elements relative to the other samplers, except the MetOne. At Rubidoux this is likely due to the operator leaving out the collection jet after the first day of sampling, thus the VAPS collected PM_{10} on both its fine and coarse sampling legs. However, high coarse particle related species also were observed at Phoenix. This suggests that the collection efficiency of the VAPS sampler is not as efficient as the other speciation samplers. This is expected as the slope of the efficiency curve for the VAPS is not as sharp as, for example, the WINS impactor.

In general, the Andersen and IMPROVE samplers consistently reported slightly higher concentrations of Fe, Ca, and Si then did the FRM, while the URG reported slightly lower concentrations. While the differences among the Andersen, IMPROVE, and URG are usually small, and reasonable based on the precision obtained with collocated samplers, they are consistent biases and may be truly representative of differences among the samplers. For example, the Andersen and IMPROVE use cyclones and the efficiency curve for the cyclone is likely not quite as sharp as the WINS. The difference between the FRM and URG may be due to the location of the denuder in the URG sampler, which is placed before the WINS impactor, while the FRM does not have a denuder, but a hollow down tube. Additional evaluations of these fractionators are needed to more thoroughly address this hypothesis.

SUMMARY AND CONCLUSIONS

The purpose of this study was to evaluate, prior to their implementation in EPA's $PM_{2.5}$ Chemical Speciation Network (EPA, 1999), the three chemical speciation samplers now available on the National Sampler Contract. These samplers were compared to two historical samplers, the IMPROVE sampler and the VAPS, as well as to two $PM_{2.5}$ FRM, one operating with a Teflon filter and one with a quartz-fiber filter to allow for determination of the same species as in the chemical speciation monitors. Samplers were operated for up to 20 days during January and February 1999 at four sites around the county: Rubidoux, CA; Phoenix, AZ; Philadelphia, PA; and Research Triangle Park, NC. These sites were chosen to represent different chemical atmospheres and environmental (meteorological) conditions. Rubidoux experiences high nitrate and moderate organic carbon, but low sulfate, Phoenix experiences high coarse particle crustal material, high organic carbon, moderate nitrate, and low sulfate, Philadelphia was chosen since it has high sulfate and low nitrate, while RTP was chosen because it would represent an area near the sampler's limit of detection.

Key findings from the study, separated into Site Characteristics, Operations, Measurement Performance, and Implications include:

Site Characteristics

X Chemical analysis indicated that the four cities chosen for the study met the criteria for different chemical atmospheres (Tolocka et al. 2000).
X Meteorological conditions also were varied with average high temperatures around 70 F in Phoenix and Rubidoux and around 38 F in Philadelphia, where it snowed during parts of the study.

Operations

X All samplers encountered operational or design problems that increased variability among sampler results. Most operational and design issues have been resolved by the manufacturers.
X The MetOne spiral inlet allowed particles greater then 2.5 m to penetrate and has been replaced with a sharp cut PM 2.5 cyclone. Both fractionators have been evaluated in the laboratory (Peters et al. 2000) against the WINS impactor in the FRM.
X Flow indicator problems in the Andersen sampler identified through the audits, invalidated a series of OC and EC data at Rubidoux. Fortunately, replicate data were obtained at that site. This problem has been rectified by the manufacturer.
X Insufficient pump capacity in the R&P 400 sampler invalidated data for the first two days at Phoenix and Rubidoux. This problem was rectified by the manufacturer during the study.
X Tradeoffs exist among the samplers for ease of use, flexibility for sampling, and cost.

Measurement Performance

X Samplers tend to agree well (10-15%on average) for stable species. There were a few exceptions due to differences in inlet collection characteristics.
X XRF sulfur times 3 was statistically equal to sulfate by ion chromatography.

X Differences of ~1-3 µg/m^3 are observed among the samplers for nitrate. Differences appear to be due partially to the use of pre-heated quartz-fiber filters for nitrate vs Teflon filters. Results also suggest differences due to the method for collecting particle nitrate, one of which includes adding the nitrate collected on the quartz-fiber filter to a nylon filter behind a denuder and Teflon filter (i.e., what is termed in this report the indirect method).

X Sulfate measured on Teflon filters agreed well (with 5% or so) to sulfate measured on quartz-fiber filters, suggesting that the differences mentioned above for nitrate between the two filter types was not due to the ability of the samplers to collect fine particles, but to their ability to collect ammonium nitrate.

X Differences of up to 3.5 µg/m^3, on average, are observed among samplers for organic carbon. Differences appear to be due to a positive sampling artifact and are a function of the face velocity across the collection filters as well as other variables. Positive OC artifact was estimated relative to a quartz-fiber filter behind an XAD denuder. Reactive backup filters were not used in this study so no information is available on negative artifacts. Results from Phase II of the study, where XAD and carbon impregnated filters and denuders are being evaluated for efficiency and capacity, should yield considerable insight for better understanding positive and negative artifacts associated with collecting OC on quartz-fiber filters.

X While not definitive, the data suggest a low bias for the collection of ammonium on nylon filters. It is postulated that the ammonia produced from ammonium nitrate volatilization is not efficiently collected by the basic (pH) nylon filter; although it is appropriate for collecting nitrate with minimal bias if a suitable denuder is located up stream of the nylon filter. Further investigation should be conducted to evaluate the efficacy of using a nylon filter to collect ammonium aerosols.

X Results indicate that vacuum XRF can reduce the amount of nitrate on the filter by up to 40%. Therefore, a Teflon filter analyzed for trace elements by XRF should not be used for nitrate analysis; however, sulfate is not affected.

Implications

Nitrate

X Direct measurement of nitrate on a reactive filter (nylon or Na_2CO_3 impregnated) directly proceeded by a diffusion denuder will likely provide the most reliable measure of total particle nitrate. However, denuder coatings and reactive coating should be appropriately matched. This implication is supported by the following two results:

    T Determination of nitrate by a sampling protocol that requires addition of nitrate collected on a pre-heated quartz-fiber filter will result in nitrate data biased high relative to the direct denuder/filter method.

    T Determination of nitrate by a sampling protocol that requires addition of nitrate collected on a Teflon filter that has been previously analyzed by vacuum XRF may be biased low by at least 40%, based on initial tests. Use of atmospheric pressure XRF may provide a suitable solution. Further tests are needed in this area.

Carbon

X Samplers should operate the OC channel at 16. 7 l/min or an equivalent face velocity of other flow rates or filter sizes are used to provide OC data that are consistent to the FRM, that is, to minimize bias between OC associated with FRM mass measured on a Teflon filter to that measured on a quartz-fiber filter. However, the FRM flow rate (face velocity) may not be the ideal face velocity for minimizing OC artifacts on quartz-fiber filters, it is only suggested here for obtaining equivalent OC concentrations (assuming face velocity is the major cause for differences observed). Use of organic denuders and reactive backup filters, similar to that used for nitrate, will be needed to obtain the least bias OC data, relative to OC concentrations observed in air, as long as filter based technology with retrospective chemical analysis is the method of choice. These implications are supported by the following results:

  T Positive artifact was observed for OC collected on quartz-fiber filters and accounted for up to 3.5 µg/m^3 of the observed OC concentrations.

  T OC concentrations measured on quartz-fiber filters were dependent on face velocity of the air stream through the filter, with lower face velocities reporting the highest OC concentrations.

X Additional understanding of the differences between the IMPROVE and NIOSH methods for OC and EC determination are required to allow comparable results to be obtained for EC and OC by the two, now commercially available methods. The Office of Research and Development is in the process of conducting tests to establish the equivalency of these two methods.

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Table II-1. Summary of Flow Audit Results Outside ± 10%*, Values in Percent (Indicated - Audit Flow); Data Shown are [Sampling Line] and Bias for Each Value Exceeding the Criteria. (I = Initial, M = Middle; F = Final Flow Audits).

		Rubidoux	**Phoenix**	**Philadelphia**	**RTP**
Andersen #1	I				
	M	[4] -43			
	F	[1] +17			
Andersen #2	I				
	M				
	F	[4] +167			
Met One #1	I				
	M				
	F				
URG #1	I				
	M				
	F				
URG #2	I				
	M				
	F				
IMPROVE #1	I				
	M				
	F				[3] -13
IMPROVE #2	I				
	M				
	F				
FRM #1	I				
	M				
	F				
FRM #2	I				
	M				
	F	[R] -13			
VAPS	I				
	M			[3] +11	
	F				
IMPROVE 25 mm	I				
	M				
	F		[E-B] +11; [W-B] +12	[3] +29	

* There were 9 values outside the range of < -10% and > +10% and; 19 values between the ranges of +5% to 10% and (-5%) to (-10%) of which 8 were associated with the IMPROVE sampler that used 25 mm filters, leaving 11 in this range over all other sampling lines. The total number of sampling lines where flow rates were audited across all sites and audits was about 315.

Table II-2a. Limits of Detection in ng/m^3.

Species	**Concentration (ng/m^3)**	**Method**
Mass[1]	2000*	Gravimetric Analysis
Sulfate[2]	19	Ion Chromatography
Nitrate[2]	14	Ion Chromatography
Ammonium[2]	14	Ion Chromatography
OC[3]	<300	Thermal Optical Reflectance
EC[3]	<500	Thermal Optical Reflectance
S[4]	12	EDXRF
Si[4]	30	EDXRF
K[4]	5.4	EDXRF
Ca[4]	7.8	EDXRF
Mn[4]	2.1	EDXRF
Fe[4]	5.4	EDXRF
Cu[4]	2.4	EDXRF
Zn[4]	2.1	EDXRF
Pb[4]	4.2	EDXRF
As[4]	2.4	EDXRF

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1. By Federal Reference Method: Using field blanks, mass detection limit of the FRM is defined as the absolute value of measured mean plus 10 times the standard deviation. From past studies, this resulted in approximately 46 micrograms. For a 16.7 Lpm sampler, this equates to a detection limit of approx. 2 micrograms per cubic meter.

2. LOD based on 3 times the baseline noise.

3. Detection limits calculated as 3 times the standard deviation of the field blanks, averaged across all field blanks collected during the study.

4. Detection limits calculated as 3 times the propagated uncertainty in the XRF method.

Table II-2b. Average Field Blank Data for All Species and Samplers Averaged Across All Sites In Atmospheric Concentrations (n=10).

Sampler	**FRM**	**AND**	**IMP**	**MET**	**URG**	**VAPS**	**Detection Limit***	**Detection Limit****
Species	***Average ± Standard Deviation in µg/m^3***							
PM2.5	0.2 ± 0.2	0.2 ± 0.1	0.1 ± 0.2	0.2 ± 0.5	0.1 ± 0.2	0.2 ± 0.2	2	5
$SO_4^=$-T		0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.1			0.01	0.03
$SO_4^=$-Q	0.05 ± 0.02				0.1 ± 0.0	0.0 ± 0.0	0.01	0.03
NO_3^--T		0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0			0.01	0.04
NO_3^-N		0.0 ± 0.0		0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.01	0.04
NO_3^--Q	0.02 ± 0.01				0.0 ± 0.0	0.0 ± 0.0	0.02	0.04
NH_4^+-T		0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0			0.01	0.03
NH_4^+-Q	0.02 ± 0.02					0.0 ± 0.0	0.01	0.03
OC	0.5 ± 0.2	1.5 ± 0.3	0.0 ± 0.2	0.7 ± 0.6	0.4 ± 0.01	0.4 ± 0.1	0.4	1
EC	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.09	0.2
	Average ± Standard Deviation in ng/m^3							
S	1.9 ± 3.1	3.2 ± 3.6	2.7 ± 3.0	18.8 ± 22.3	1.5 ± 3.3	4.4 ± 4.1	3.5	8.7
Si	10 ± 14	5.1 ± 8.4	9.3 ± 8.0	35 ± 38	6.4 ± 8.2	7.1 ± 8.2	8.5	21.2
K	0.6 ± 1.0	0.2 ± 0.6	0.0 ± 0.0	1.7 ± 4.1	0.0 ± 0.0	0.0 ± 0.0	1.5	3.7
Ca	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 1.4	16 ± 31	0.0 ± 0.0	0.0 ± 0.0	2.1	5.3
Mn	0.2 ± 0.3	0.2 ± 0.3	0.0 ± 0.0	0.3 ± 0.7	0.0 ± 0.0	0.3 ± 0.6	0.5	1.4
Fe	2.1 ± 3.0	0.7 ± 1.4	0.3 ± 0.88	5.5 ± 13.8	0.6 ± 1.7	0.3 ± 0.7	1.4	3.7
Cu	0.1 ± 0.3	0.1 ± 0.3	0.1 ± 0.3	0.8 ± 1.9	0.0 ± 0.0	0.2 ± 0.5	0.7	1.7
Zn	0.1 ± 0.2	0.3 ± 0.5	0.0 ± 0.0	2.4 ± 4.5	0.2 ± 0.5	0.2 ± 0.5	0.5	1.4

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* Based on 16.7 L/min

** Based on 6.7 L/min

Table II-2c. Precision (as % CV) Achieved by FRM and Speciation Samplers Based on the Results from the Collocated Samplers at Rubidoux.*

Sampler	**FRM**	**AND**	**IMP**	**MET**	**URG**
Species	*In Percent*				
PM2.5	5.8	3.2	5.4	4.7	7.6
$SO_4^=$	11.0	2.9	6.1	3.1	6.2
NO_3^--T	See Note 1	4.0	See Note 1	3.1	See Note 1
NO_3^--P	11.1	15.3	6.1	3.9	13.5
NH_4^+	12.8	2.4	7.8	3.3	6.4
OC	8.4	See Note 2	22.7	9.7	8.3
EC	12.7	See Note 2	38.4	7.0	7.6
S as $SO_4^=$	3.3	3.3	8.7	4.3	2.4
Si	23.1	24.4	17.9	19.5	19.9
K	6.7	4.4	10.5	11.3	5.6
Ca	15.1	12.4	11.3	18.3	10.2
Mn	16.6	37.8	17.9	46.1	17.1
Fe	8.7	8.9	9.3	11.9	8.2
Cu	54.9	30.6	38.0	39.3	29.7
Zn	10.4	6.8	16.0	10.6	10.7
Pb**	31	14	36	40	19
As**	140	120	120	130	140
PM10*					

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* Only a single VAPS sampler was located at Rubidoux.

** Values were at or near the limit of detection for that species and these species have been excluded in the remainder of the comparisons for that reason.

1. Nitrate was not measured on the Teflon filter for these samplers.

2. Precision for OC and EC could not be calculated for the Andersen Sampler because of an incorrect indicated flow rate on Channel 4 for the primary sampler at Rubidoux. Therefore, replicate data for these species were used for statistical analyses performed in this report.

Table II-3. Valid Data Capture in Percent by Sampler and Major Species.*

	Maximum Possible	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
		$PM_{2.5}$ Mass and Trace Elements					
Rubidoux	32	97%	94%	97%	91%	75%	75%
Phoenix	20	100%	95%	95%	90%	70%	65%
Philadelphia	20	100%	95%	90%	90%	100%	75%
RTP	20	100%	90%	95%	90%	95%	75%
		Sulfate, Nitrate, Ammonium Ions					
Rubidoux	32	94%	84%	100%	97%	100%	100%
Phoenix	20	100%	100%	85%	90%	100%	85%
Philadelphia	20	100%	100%	95%	90%	95%	95%
RTP	20	100%	100%	85%	90%	100%	85%
		Organic and Elemental Carbon					
Rubidoux	32	97%	88%	97%	97%	100%	94%
Phoenix	20	100%	100%	100%	95%	100%	85%
Philadelphia	20	100%	100%	95%	90%	95%	95%
RTP	20	100%	95%	95%	85%	100%	80%

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* Shaded values represent data capture less than 90%.

Table II-4. Summary of Problems Encountered In the Field During Operations Of Sampler Evaluated in this Study.

Sampler	**Category**	**Site**[1]	**Noted Problem or Deficiency**
Andersen RAAS	Sampler Installation	PA	Sampler weight noted to be heavier than average
	Initial Setup		
	Audits and Calibration	RU	Calibrations were lost on two different occasions
	Programming		
	Filter Holder Exchange	RU,PX,PA,RT	O-rings fell out during field filter exchange
	Data Retrieval		
	Sampler Maintenance		
	Operating Manual		
	Other operational problems	RU,PA,RT RU RU RU	Fluctuations in indicated flow rates Drifts in cabinet temperature noted Slight water intrusion in back panel Difficult to diagnose leaks in sampler manifold
MetOne SASS	Sampler Installation		
	Initial Setup		
	Audits and Calibration		
	Programming		
	Filter Holder Exchange	RTP lab	Laboratory disassembly of filter canister noted as difficult without damaging or contaminating collected filter sample
	Data Retrieval		
	Sampler Maintenance		

Table II-4. Summary of Problems Encountered In the Field During Operations Of Sampler Evaluated in this Study.

Sampler	Category	Site[1]	Noted Problem or Deficiency
MetOne SASS (cont.)	Operating Manual		
	Other operational problems	RU PX.RT PA RT RT RU PA PA	Sampler shut down after 10 hours on one occasion On one occasion, sampler indicated a 1sec run time On two occasions, sampler did not start as programmed. Initially, the sampler indicated incorrect flow rates due to use of improper flow transducers during the sampler's construction. Replacement of transducers corrected the problem. Pump failed and required replacement. Recommended changing the manner in which information is listed on the screen Sharp edges were encountered on inlet head assembly Screen not easily read in bright sunlight
URG MASS	Sampler Installation		
	Initial Setup		
	Audits and Calibration		
	Programming		
	Filter Holder Exchange		
	Data Retrieval		
	Sampler Maintenance		
	Operating Manual		
	Other operational problems	RU RU RU PX RU,PX, PA, RT PX,PA	Sampler could not provide sufficient flow rate. Higher capacity pumping system installed. Problems encountered with LED screens. Filter temperature flags frequently encountered. Filter temperature flags frequently encountered. Sampler could not provide sufficient flow rate. Higher capacity pumping system installed Filter holder subject to cross-threading

Table II-4. Summary of Problems Encountered In the Field During Operations Of Sampler Evaluated in this Study.

Sampler	Category	Site[1]	Noted Problem or Deficiency
IMPROVE	Sampler Installation	RU,PX,PA,RT	Setup of sampler noted to be cumbersome
	Initial Setup		
	Audits and Calibration		
	Programming		
	Filter Holder Exchange		
	Data Retrieval		
	Sampler Maintenance	RU RT	Faulty pumps, timers, and valves Transformer had to be replaced due to water intrusion into case
	Operating Manual	RT	A condensed operating manual was suggested to be of value
	Other operational problems	RU RU RU PX PX RT RT RT PX PA	Faulty pump timer and required replacement Pump failed and required replacement. Denuders difficult to change Problems encountered with magnahelics. On one occasion, timer did not display correct elapsed time. On two occasions, water was noted inside sampling case. On one occasion, solenoid valve did not function. On one occasion, elapsed timer failed. Filter holders difficult to change Connection from solenoid to filter holder was unreliable
VAPS	Sampler Installation		
	Initial Setup	RU	Problems encountered with flow calibration requiring tube replacement.
	Audits and Calibration		
	Programming	RT	Sampler did not start due to operator error
	Filter Holder Exchange	RU	Hoses connecting filter holders would frequently work loose

Table II-4. Summary of Problems Encountered In the Field During Operations Of Sampler Evaluated in this Study.

Sampler	Category	Site[1]	Noted Problem or Deficiency
VAPS (cont.)	Data Retrieval		
	Sampler Maintenance		
	Operating Manual		
	Other operational problems	PX PA RT RU,PX,PA RU PX RU,PX,PA,RT PA,RT PA	On one occasion, sampler did not automatically shut down as programmed. On one occasion, sampler did not automatically shut down as programmed. On two occasions, sampler did not automatically shut down as programmed. O-rings routinely fell out during filter exchange Sampler provided no information except total flow rate and elapsed time Problems encountered with timers Lower virtual impactor nozzle routinely fell out during filter exchange Simpler, more reliable form of timer was suggested Unit needs direct readout of sampling flow rate
FRM-BGI PQ 200	Sampler Installation		
	Initial Setup		
	Audits and Calibration		
	Programming		
	Filter Holder Exchange		
	Data Retrieval		
	Sampler Maintenance	RU RU RU	Sampling pump required replacement Entire sampler had to be replaced on one occasion Recommended sampler redesign to prevent impactor from falling out during sample exchange
	Operating Manual		

Table II-4. Summary of Problems Encountered In the Field During Operations Of Sampler Evaluated in this Study.

Sampler	Category	Site[1]	Noted Problem or Deficiency
FRM-BGI PQ 200 (cont.)	Other operational problems	RU	On one occasion, some water intrusion noted on impactor shelf and bottom of cabinet
			Sampler would not operate - firmware upgrades installed
		PA	On several occasions, some water intrusion noted within cabinet
		PA	Rotating handle mechanism needs to be redesigned
FRM - R&P	Sampler Installation		
	Initial Setup		
	Audits and Calibration		
	Programming		
	Filter Holder Exchange		
	Data Retrieval Sampler Maintenance		
	Operating Manual		
	Other operational problems	RT	Filter exchange mechanism did not operate properly on three occasions

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1. Ru = Rubidoux, PX = Phoenix, PA = Philadelphia, RT = Research Triangle Park

Table II-5. Species Concentration Data for the FRM at Each Location of the 4 City Study.

	Rubidoux					**Phoenix**					**Philadelphia**					**RTP**				
	AVG*	**Std Dev**	**Max**	**Min**	**Valid Data**	**AVG***	**Std Dev**	**Max**	**Min**	**Valid Data**	**AVG***	**Std Dev**	**Max**	**Min**	**Valid Data**	**AVG***	**Std Dev**	**Max**	**Min**	**Valid Data**
	Concentrations in (ug/m^3)																			
PM-2.5	26.7	20.2	74.3	2.2	14	14.9	6.8	25.3	3.9	17	17.4	9.0	37.6	5.0	17	11.0	5.4	23.8	4.4	16
SO4Q	1.7	1.6	6.0	0.3	13	0.9	0.4	1.8	0.2	18	4.1	2.1	8.4	1.5	18	3.3	1.6	6.2	0.7	18
NO3P	11.8	10.4	38.0	0.1	13	3.1	2.2	7.4	0.2	18	3.8	2.1	8.6	0.9	18	0.7	0.6	2.3	0.1	18
NH4	4.0	3.6	13.2	0.1	13	1.2	0.7	2.5	0.1	18	2.6	1.3	5.8	0.8	18	1.3	0.6	2.3	0.2	18
OC	5.7	2.1	10.0	2.1	13	7.6	2.5	12.5	4.0	18	4.3	2.0	9.6	2.3	18	3.4	1.9	8.5	1.5	17
EC	3.3	1.9	7.7	0.6	13	3.3	1.3	5.7	1.5	18	2.5	1.3	5.7	0.8	18	1.5	0.9	3.7	0.6	17
	Concentrations in(ng/m^3)																			
S	600	560	1930	110	12	300	150	640	71	17	1400	730	280	390	17	1100	560	210	260	16
Si	160	100	378	16	12	280	150	480	50	17	47	30	130	19	17	72	61	230	19	16
K	80	35	125	24	12	140	70	250	30	17	55	25	120	29	17	67	42	180	32	16
Ca	160	110	360	34	12	110	62	220	26	17	35	24	110	13	17	32	36	150	13	16
Fe	170	100	386	55	12	210	110	420	57	17	100	82	300	18	17	52	32	120	11	16
Cu	7	8	31	0	12	9	9	38	2	17	5	4	13	1	17	8	15	64	0	16
Zn	70	78	255	4	12	18	10	48	2	17	32	22	83	5	17	16	14	55	5	16
Pb	14	130	49	1.8	12	6.6	5.2	22	0.0	17	12	11	39	2.6	17	4.3	3.5	16	0.0	16
As	0.3	0.6	1.4	0.0	12	1.1	1.3	3.5	0.0	17	0.7	1.1	3.6	0.0	17	0.5	0.8	2.9	0.0	16

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* Sampling dates included in averages:

Rubidoux – 1/15/99 to 2/26/99
Phoenix – 1/14/99 to 2/21/99
Philadelphia – 1/21/00 to 2/26/99
RTP – 1/19/99 to 2/24/99

Table II-6. Estimated $PM_{2.5}$ Mass Balance of Species versus Measured $PM_{2.5}$ Mass (ug/m^3) for the FRM at Each Site.

Species+	RUB	PHO	PHI	RTP
SO4Q	1.7	0.9	4.1	3.3
NO3P	11.8	3.1	3.8	0.7
NH4	4.0	1.2	2.6	1.3
Organic Material	8.0	10.7	6.0	4.8
EC	3.3	3.3	2.5	1.5
Crustal Material	0.8	1.1	0.3	0.3
Sum of Components	29.6	20.1	19.2	11.9
Measured Mass	26.7	14.9	17.4	11.0
Percent Measured Mass	111	135	110	108
Coarse PM**	21.6	17.2	4.2	4.0
%NO3*	44.2	20.5	21.6	6.7
%SO4*	6.4	5.8	23.3	30.1
%Organics*	30.1	71.5	34.2	43.8
% Crustal*	3.0	7.0	1.7	2.5
Fine/PM10 in %	55	46	81	73

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* Relative to the measured mass.

****** Rubidoux coarse mass estimated from difference between VAPS $PM_{2.5}$ mass minus $PM_{2.5}$ mass measured on the Andersen, assumes VAPS sample is PM_{10}.

\+ **Species**

SO4Q is sulfate measured on the quartz-fiber filter by IC

NO3P is nitrate measured on the quartz-fiber filter by IC and represents the best measurement of nitrate by that sampler and is referred to in this report as particle nitrate

Organic Material = OC *1.4

Crustal Material Estimate (µg/m^3) = (2.14*Si + 1.43*Fe+1.4*Ca)/1000

Table II-7. Average Volatilized Nitrate (NO3V) in µg/m^3 Observed for Each Sampler at Each City.

	Rubidoux	Phoenix	Philadelphia	RTP	Flow Rate	
					T or Q	**Denuder**
	(µg/m^3)				**(Lpm)**	
Volatilized Nitrate						
Andersen	-0.36	1.46	0.22	0.48	16.7	7.3
MetOne	1.01	1.14	0.41	0.48	6.7	6.7
URG	0.99	1.57	0.37	0.56	16.7	16.7
VAPS	0.64	1.41	0.78	0.58	16.7	16.7
IMP-FRM	0.12	0.87	0.26	0.47	16.7	22.7
Average NO3P[2] All Samplers	11.5	3.3	3.7	1.0		
Average PM2.5 Mass, All Samplers[2]	32.4	17.1	18.4	11.8		
n	65	77	83	82		
NO3V/Avg NO3P (Average ± ó) (%)	12 ± 19	37 ± 20	13 ± 16	51 ± 26		
NO$_3$V / PM2.5 Mass (Average ± ó) (%)	1.5 ± 1.8	7.6 ± 1.7	2.2 ± 1.2	4.4 ± 0.4		
	Temp. (^{O}F) During Study Days					
Average	57	56	41	47		
Avg. Max.	70	70	50	60		
Avg. Min.	45	44	33	34		

[1] Nitrate measured on the nylon filter on the IMPROVE sampler minus nitrate measured on the Teflon filter of the Andersen sampler.

[2] Averaged over all samplers except the FRM at a given site; these PM2.5 mass and nitrate values are given to allow for general comparisons amongst sites of the amount of nitrate volatilized from the Teflon filter under the conditions of this experiment.

Table II-8a. Mean Analyte Concentrations for Each Sampler at All Sites.[1]

			Mean Concentrations					
Analyte	**Site**	**N**	**FRM**	**AND**	**IMP**	**MET**	**URG**	**VAPS**
			($\mu g/m^3$)					
$PM_{2.5}$	Rubidoux	9	17.9	17.7	17.4	**23.5**	**24.1**	**38.4**
	Phoenix	7	15.1	15.4	13.3	**27.8**	14.7	16.1
	Philadelphia	13	18.9	19.0	18.8	19.7	19.2	22.7
	RTP	10	11.4	11.3	10.9	12.1	11.7	13.2
Sulfate	Rubidoux	13	1.7	1.7	1.6	1.8	1.8	1.9
	Phoenix	13	0.8	0.7	0.7	0.9	0.8	0.8
	Philadelphia	16	4.0	3.8	3.8	3.9	3.9	3.5
	RTP	13	3.4	3.3	3.3	3.3	3.4	3.3
Sulfur as Sulfate	Rubidoux	4	1.6	1.7	1.6	1.9	1.8	1.9
	Phoenix	7	0.9	0.9	1.0	1.1	0.9	0.9
	Philadelphia	11	4.1	4.2	3.7	4.5	4.4	4.3
	RTP	10	3.1	3.1	2.9	3.2	3.3	3.0
Particulate Nitrate	Rubidoux	8	14.7	13.8	14.4	16.0	16.8	17.0
	Phoenix	9	2.7	2.7	2.2	2.9	4.0	4.0
	Philadelphia	15	3.7	3.5	3.5	3.7	4.0	3.9
	RTP	10	1.0	1.1	1.1	1.1	**1.7**	**1.7**
Ammonium	Rubidoux	13	4.0	3.7	3.2	4.0	4.4	3.8
	Phoenix	13	1.2	**0.6**	**0.6**	0.8	1.0	1.1
	Philadelphia	16	2.6	2.4	2.2	2.6	2.6	2.2
	RTP	13	1.3	1.3	1.2	1.2	1.5	1.5
Organic Carbon	Rubidoux	12	5.6	6.9	4.1	6.2	5.3	6.4
	Phoenix	14	7.6	9.1	6.5	8.1	6.5	**4.7**
	Philadelphia	16	4.4	**5.6**	4.0	4.0	3.8	**2.8**
	RTP	12	3.6	4.1	3.0	4.1	2.9	3.1
Elemental Carbon	Rubidoux	12	3.2	2.8	1.8	3.0	3.1	3.0
	Phoenix	14	3.3	2.8	2.7	3.0	3.2	2.8
	Philadelphia	16	2.6	2.4	2.3	2.2	2.4	2.2
	RTP	12	1.5	1.4	1.2	1.4	1.5	1.5
			(ng/m^3)					
Silicon	Rubidoux	4	103	159	134	**553**	106	**821**
	Phoenix	7	293	356	364	**1502**	232	**383**
	Philadelphia	11	54	59	64	**119**	57	61
	RTP	10	89	82	80	**105**	79	**166**
Potassium	Rubidoux	4	61	70	66	**140**	63	**188**
	Phoenix	7	141	144	148	**328**	134	150
	Philadelphia	11	61	62	61	73	64	64
	RTP	10	75	73	69	82	77	82
Calcium	Rubidoux	4	79	126	118	**478**	81	**577**
	Phoenix	7	119	152	157	**671**	98	**166**
	Philadelphia	11	38	44	42	**84**	35	39
	RTP	10	41	40	38	51	35	56
Iron	Rubidoux	4	111	153	141	**339**	117	**503**
	Phoenix	7	223	262	264	**669**	193	**276**
	Philadelphia	11	122	135	128	**177**	122	126
	RTP	10	54	52	49	70	49	70
Zinc	Rubidoux	4	12.3	13.4	12.0	**25.4**	12.9	**18.5**
	Phoenix	7	18.1	18.4	18.8	**29.6**	17.6	17.3
	Philadelphia	11	36.2	38.2	34.6	38.5	38.9	38.7
	RTP	10	19.3	14.9	14.5	14.4	15.6	14.8

1. Shaded data indicate values inconsistent with other samplers. Reasons for differences are explained in the text for most data points. Questionable data, with no direct explanation, remain in the data base and are included in the statistical analyses presented in this report.

Table II-8b. Ratio of Speciation Sampler to FRM for Chemical Components by Site[5,2].

	Site	Andersen	IMPROVE	URG	MetOne	Average	StdDev
$PM_{2.5}$	Rubidoux	0.99	0.97	**1.35**	**1.31**	**1.16**	**0.20**
	Phoenix	1.02	0.88	0.97	**1.84**	**1.18**	**0.45**
	Philadelphia	1.01	0.99	1.02	1.04	1.01	0.02
	RTP	0.99	0.96	1.03	1.06	1.01	0.05
Sulfate	Rubidoux	1.00	**0.94**	**1.06**	**1.06**	1.01	**0.06**
	Phoenix	**0.88**	**0.88**	1.00	**1.13**	0.97	**0.12**
	Philadelphia	0.95	0.95	0.98	0.98	0.96	0.01
	RTP	0.97	0.97	1.00	0.97	0.98	0.01
P-nitrate	Rubidoux	0.94	0.98	**1.14**	1.09	1.04	0.09
	Phoenix	1.00	**0.81**	**1.48**	1.07	1.09	**0.28**
	Philadelphia	0.95	0.95	1.08	1.00	0.99	0.06
	RTP	1.10	1.10	**1.70**	1.10	**1.25**	**0.30**
Ammonium	Rubidoux	0.93	**0.80**	1.10	1.00	0.96	**0.13**
	Phoenix	**0.50**	**0.50**	**0.83**	**0.67**	**0.63**	**0.16**
	Philadelphia	0.92	**0.85**	1.00	1.00	0.94	0.07
	RTP	1.00	0.92	**1.15**	0.92	1.00	**0.11**
Organic Carbon[6]	Rubidoux	1.08	0.64	0.83	0.97	0.88	0.19
	Phoenix	1.94	1.38	1.38	1.72	1.61	0.27
	Philadelphia	2.00	1.43	1.36	1.43	1.55	0.30
	RTP	1.32	0.97	0.94	1.32	1.14	0.21
Elemental Carbon	Rubidoux	0.88	0.56	0.97	0.94	0.84	0.19
	Phoenix	0.85	0.82	0.97	0.91	0.89	0.07
	Philadelphia	0.92	0.88	0.92	0.85	0.89	0.04
	RTP	0.93	0.80	1.00	0.93	0.92	0.08
Sulfur	Rubidoux	1.05	1.00	1.10	1.13	1.07	0.06
	Phoenix	0.98	1.03	0.99	1.17	1.04	0.09
	Philadelphia	1.02	0.90	1.06	1.08	1.02	0.08
	RTP	1.00	0.94	1.08	1.04	1.01	0.06
Silicon	Rubidoux	1.54	1.30	1.03	5.35	2.31	2.04
	Phoenix	1.21	1.24	0.79	5.13	2.09	2.03
	Philadelphia	1.09	1.17	1.04	2.19	1.37	0.54
	RTP	0.91	0.89	0.88	1.18	0.97	0.14
Potassium	Rubidoux	1.15	1.08	1.03	2.29	1.39	0.60
	Phoenix	1.02	1.05	0.95	2.33	1.34	0.66
	Philadelphia	1.02	1.01	1.06	1.20	1.07	0.09
	RTP	0.98	0.93	1.04	1.10	1.01	0.07
Calcium	Rubidoux	1.59	1.49	1.02	6.04	2.53	2.35
	Phoenix	1.27	1.31	0.82	5.62	2.26	2.25
	Philadelphia	1.15	1.10	0.92	2.20	1.34	0.58
	RTP	0.98	0.93	0.86	1.25	1.00	0.17
Iron	Rubidoux	1.39	1.28	1.06	3.06	1.70	0.92
	Phoenix	1.17	1.19	0.86	3.00	1.56	0.97
	Philadelphia	1.10	1.05	1.00	1.45	1.15	0.20
	RTP	0.96	0.90	0.90	1.28	1.01	0.18
Zinc	Rubidoux	1.09	0.98	1.05	2.07	1.29	0.52
	Phoenix	1.02	1.04	0.97	1.64	1.17	0.31
	Philadelphia	1.06	0.96	1.07	1.06	1.04	0.05
	RTP	0.77	0.75	0.81	0.75	0.77	0.03

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[5] Shaded cells represent values exceeding the PM Expert Panel's performance criteria: Slope = 1 ± 0.1 for mass, nitrate, and ammonium, and 1 ± 0.05 for sulfate

[6] Organic carbon is relative to OC measured on the quartz-fiber filter behind the XAD denuder located in the VAPS sampler.

Table II-9. Regression Statistics of FRM (x-axis) versus Speciation Samplers (y-axis) for All Sites, Samplers, and Major Species.

	PM2.5 Mass*						Sulfate*					
Site	**Sampler**	**Slope**	**Std Err. Slope**	**Intercept**	**Std. Err. Intercept**	**R^2**	**Sampler**	**Slope**	**Std Err. Slope**	**Intercept**	**Std. Err. Intercept**	**R^2**
Rubidoux	Andersen	1.10	0.05	-2.94	1.55	0.979	Andersen	1.03	0.04	-0.06	0.10	0.982
	IMPROVE	1.11	0.07	-3.61	2.30	0.955	IMPROVE	0.93	0.04	0.00	0.09	0.982
	MetOne	1.15	0.14	4.16	4.61	0.851	MetOne	0.97	0.04	0.12	0.10	0.977
	URG	**1.43**	0.04	-2.18	1.35	0.992	URG	1.10	0.03	-0.09	0.08	0.990
	VAPS	**1.90**	0.23	1.88	5.11	0.883	VAPS	1.08	0.05	0.05	0.11	0.979
Phoenix	Andersen	0.98	0.02	0.29	0.26	0.996	Andersen	0.89	0.04	-0.02	0.04	0.971
	IMPROVE	0.76	0.05	1.56	0.81	0.940	IMPROVE	0.89	0.04	-0.01	0.04	0.969
	MetOne	**1.67**	0.21	1.52	3.44	0.826	MetOne	0.96	0.04	0.13	0.04	0.971
	URG	0.94	0.04	0.32	0.68	0.979	URG	0.95	0.05	0.03	0.05	0.957
	VAPS	1.19	0.10	-1.26	1.65	0.936	VAPS	0.87	0.06	0.03	0.06	0.947
Philadelphia	Andersen	1.01	0.01	-0.11	0.19	0.999	Andersen	1.04	0.04	-0.40	0.16	0.981
	IMPROVE	1.00	0.02	0.00	0.38	0.995	IMPROVE	0.99	0.03	-0.14	0.13	0.988
	MetOne	1.08	0.05	-0.59	1.02	0.970	MetOne	1.02	0.03	-0.17	0.12	0.990
	URG	1.02	0.03	0.01	0.54	0.989	URG	1.01	0.02	-0.16	0.10	0.992
	VAPS	1.33	0.06	-2.45	1.31	0.976	VAPS	0.90	0.02	-0.15	0.09	0.993
RTP	Andersen	0.97	0.03	0.09	0.42	0.983	Andersen	1.04	0.02	-0.18	0.07	0.995
	IMPROVE	0.99	0.03	-0.20	0.35	0.988	IMPROVE	1.04	0.02	-0.22	0.09	0.993
	MetOne	1.09	0.04	-0.28	0.46	0.985	MetOne	1.05	0.03	-0.21	0.12	0.986
	URG	1.05	0.02	-0.02	0.30	0.993	URG	1.02	0.03	-0.03	0.10	0.988
	VAPS	1.12	0.05	0.57	0.67	0.981	VAPS	1.04	0.04	-0.17	0.14	0.982

	Nitrate*						Ammonium*					
Rubidoux	Andersen	0.92	0.03	-0.13	0.49	0.987	Andersen	1.01	0.02	-0.32	0.09	0.997
	IMPROVE	0.93	0.04	0.23	0.56	0.984	IMPROVE	0.83	0.03	-0.12	0.16	0.986
	MetOne	1.06	0.03	0.06	0.51	0.989	MetOne	1.03	0.02	-0.16	0.09	0.997
	URG	1.05	0.06	1.15	1.13	0.975	URG	1.06	0.03	0.14	0.14	0.993
	VAPS	1.09	0.07	0.55	1.09	0.967	VAPS	0.99	0.05	-0.22	0.26	0.975
Phoenix	Andersen	0.95	0.04	0.14	0.14	0.977	Andersen	**0.57**	0.06	0.00	0.08	0.872
	IMPROVE	**0.73**	0.04	0.20	0.16	0.951	IMPROVE	**0.49**	0.05	-0.01	0.07	0.861
	MetOne	1.00	0.06	0.23	0.21	0.959	MetOne	**0.73**	0.06	-0.01	0.09	0.902
	URG	**1.41**	0.07	0.26	0.24	0.970	URG	0.89	0.07	0.00	0.10	0.911
	VAPS	**1.21**	0.08	0.46	0.30	0.951	VAPS	0.89	0.08	0.05	0.10	0.915
Philadelphia	Andersen	0.88	0.08	0.21	0.34	0.884	Andersen	1.03	0.03	-0.25	0.09	0.985
	IMPROVE	0.96	0.04	-0.05	0.18	0.972	IMPROVE	0.92	0.04	-0.22	0.13	0.966
	MetOne	1.02	0.05	-0.21	0.24	0.959	MetOne	1.04	0.05	-0.10	0.13	0.972
	URG	1.09	0.06	-0.14	0.27	0.949	URG	1.09	0.04	-0.27	0.11	0.979
	VAPS	1.03	0.09	0.04	0.39	0.905	VAPS	0.93	0.03	-0.25	0.08	0.985
RTP	Andersen	0.96	0.06	0.15	0.06	0.937	Andersen	0.97	0.05	0.03	0.07	0.958
	IMPROVE	0.92	0.08	0.16	0.08	0.903	IMPROVE	0.92	0.07	-0.04	0.10	0.931
	MetOne	0.85	0.19	0.27	0.18	**0.570**	MetOne	1.00	0.07	-0.05	0.10	0.933
	URG	**1.54**	0.11	0.11	0.11	0.926	URG	1.07	0.05	0.07	0.06	0.971
	VAPS	**1.39**	0.22	0.28	0.23	**0.792**	VAPS	1.17	0.07	-0.05	0.10	0.952

[1] Highlighted values are slopes out side the range from 0.8 to 1.2 or R^2 less than 0.8

Units for Intercept and Standard Error of the Intercept are * = ug/m^3; and ** = ng/m^3.

Table II-9. Regression Statistics of FRM (x-axis) versus Speciation Samplers (y-axis) for All Sites, Samplers, and Major Species (cont.)

	Organic Carbon*						**Elemental Carbon***					
Site	**Sampler**	**Slope**	**Std Err. Slope**	**Intercept**	**Std. Err. Intercept**	**R^2**	**Sampler**	**Slope**	**Std Err. Slope**	**Intercept**	**Std. Err. Intercept**	**R^2**
Rubidoux	Andersen	**1.39**	0.15	-1.05	0.92	0.886	Andersen	**0.78**	0.08	0.30	0.30	0.895
	IMPROVE	**0.39**	0.19	1.76	1.13	0.289	IMPROVE	**0.23**	0.16	1.00	0.59	**0.168**
	MetOne	1.08	0.12	0.12	0.73	0.882	MetOne	0.85	0.08	0.23	0.29	0.919
	URG	1.06	0.12	-0.72	0.71	0.884	URG	0.82	0.07	0.46	0.28	0.917
	VAPS	**1.76**	0.30	-3.40	1.77	**0.776**	VAPS	**0.78**	0.07	0.47	0.27	0.918
Phoenix	Andersen	1.13	0.05	0.61	0.39	0.972	Andersen	0.94	0.10	-0.23	0.35	0.852
	IMPROVE	0.82	0.06	0.10	0.50	0.916	IMPROVE	0.82	0.06	0.02	0.20	0.927
	MetOne	1.03	0.29	-0.17	2.38	0.453	MetOne	**0.74**	0.24	0.31	0.85	**0.399**
	URG	**0.79**	0.10	0.31	0.82	**0.789**	URG	0.91	0.03	0.11	0.12	0.977
	VAPS	**0.77**	0.09	-1.16	0.68	0.852	VAPS	0.89	0.04	-0.16	0.12	0.979
Philadelphia	Andersen	0.99	0.11	1.22	0.52	0.833	Andersen	**0.29**	0.23	1.59	0.63	**0.096**
	IMPROVE	0.85	0.06	0.26	0.26	0.936	IMPROVE	**0.77**	0.05	0.26	0.14	0.934
	MetOne	0.99	0.13	-0.35	0.60	0.802	MetOne	1.01	0.12	-0.43	0.34	0.827
	URG	0.89	0.05	-0.13	0.23	0.954	URG	0.94	0.05	-0.02	0.13	0.963
	VAPS	**0.66**	0.06	-0.09	0.27	0.902	VAPS	0.95	0.05	-0.31	0.14	0.960
RTP	Andersen	1.11	0.07	-0.02	0.27	0.944	Andersen	0.80	0.05	0.12	0.10	0.934
	IMPROVE	0.88	0.04	-0.28	0.15	0.975	IMPROVE	**0.64**	0.05	0.20	0.09	0.916
	MetOne	1.10	0.06	0.06	0.25	0.960	MetOne	0.87	0.04	0.05	0.06	0.979
	URG	0.95	0.06	-0.41	0.25	0.936	URG	0.90	0.06	0.10	0.10	0.941
	VAPS	0.92	0.13	-0.23	0.53	0.821	VAPS	1.13	0.16	-0.22	0.29	0.819

	Sulfur**						**Silicon****					
Rubidoux	Andersen	1.14	0.04	-47.3	30.7	0.991	Andersen	1.03	0.14	33.3	23.7	0.866
	IMPROVE	1.08	0.04	-52.6	29.1	0.989	IMPROVE	**1.46**	0.14	-35.9	26.5	0.913
	MetOne	1.11	0.04	26.3	34.6	0.985	MetOne	**5.61**	0.95	-111	177	**0.776**
	URG	1.17	0.06	-44.0	62.0	0.986	URG	0.82	0.15	15.6	30.6	0.854
	VAPS	1.12	0.08	-2.2	40.0	0.962	VAPS	**7.50**	0.81	15.9	111	0.924
Phoenix	Andersen	0.97	0.02	3.6	7.0	0.993	Andersen	1.08	0.06	27.5	19.6	0.953
	IMPROVE	1.17	0.11	-56.0	35.3	0.888	IMPROVE	1.03	0.12	50.8	38.4	0.827
	MetOne	1.09	0.07	19.2	23.0	0.949	MetOne	**4.51**	0.77	77.5	252	**0.708**
	URG	1.01	0.02	-10.3	7.5	0.995	URG	**0.76**	0.05	5.9	17.3	0.952
	VAPS	0.85	0.06	28.4	18.7	0.962	VAPS	**0.76**	2.59	473	707	**0.009**
Philadelphia	Andersen	1.03	0.03	-20.4	41.1	0.990	Andersen	**0.79**	0.13	18.3	7.3	**0.707**
	IMPROVE	0.92	0.08	-19.6	125	0.913	IMPROVE	0.85	0.16	17.4	9.6	**0.675**
	MetOne	1.08	0.03	2.0	55.3	0.986	MetOne	**2.08**	0.48	22.2	26.4	**0.576**
	URG	1.08	0.03	-29.9	52.3	0.986	URG	0.90	0.15	6.8	8.5	**0.699**
	VAPS	1.07	0.05	-63.8	70.5	0.982	VAPS	1.14	0.15	-1.8	9.1	0.854
RTP	Andersen	1.00	0.02	-8.9	27.7	0.993	Andersen	0.80	0.08	10.9	7.1	0.887
	IMPROVE	1.01	0.04	-57.9	46.0	0.981	IMPROVE	0.81	0.10	4.7	9.2	0.846
	MetOne	1.03	0.02	4.2	25.8	0.995	MetOne	1.16	0.18	7.4	17.3	**0.757**
	URG	1.06	0.01	6.6	17.6	0.997	URG	**0.69**	0.08	17.7	7.8	0.846
	VAPS	1.06	0.15	-96.5	185	0.853	VAPS	**0.43**	0.46	120	48.9	**0.091**

[1] Highlighted values are slopes out side the range from 0.8 to 1.2 or R^2 less than 0.8

Units for Intercept and Standard Error of the Intercept are * = ug/m^3; and ** = ng/m^3.

Table II-9. Regression Statistics of FRM (x-axis) versus Speciation Samplers (y-axis) for All Sites, Samplers, and Major Species (cont.).

Calcium**

Site	Sampler	Slope	Std Err. Slope	Intercept	Std. Err. Intercept	R^2
Rubidoux	Andersen	0.97	0.15	39.0	26.8	0.831
	IMPROVE	1.16	0.17	9.5	32.5	0.821
	MetOne	**5.40**	1.21	-26.4	229.3	**0.667**
	URG	**0.60**	0.16	34.1	33.2	**0.729**
	VAPS	**6.93**	0.51	1.6	69.9	0.964
Phoenix	Andersen	1.10	0.05	15.3	6.7	0.966
	IMPROVE	1.03	0.12	27.1	15.0	0.834
	MetOne	**4.82**	0.86	43.4	111.6	**0.691**
	URG	**0.76**	0.04	6.3	5.2	0.973
	VAPS	0.96	2.83	189	312	**0.013**
Philadelphia	Andersen	1.09	0.09	0.6	3.8	0.905
	IMPROVE	1.08	0.09	0.9	3.5	0.925
	MetOne	**2.49**	0.37	-12.7	16.0	**0.761**
	URG	0.88	0.07	0.5	3.2	0.902
	VAPS	1.18	0.06	-5.9	2.6	0.977
RTP	Andersen	1.03	0.04	-1.6	2.0	0.978
	IMPROVE	1.12	0.07	-6.2	3.3	0.953
	MetOne	1.17	0.07	4.0	3.4	0.955
	URG	0.92	0.03	-1.8	1.6	0.983
	VAPS	1.10	0.26	10.1	14.4	**0.666**

Iron**

Site	Sampler	Slope	Std Err. Slope	Intercept	Std. Err. Intercept	R^2
Rubidoux	Andersen	**1.22**	0.09	2.9	17.5	0.948
	IMPROVE	1.18	0.13	-5.0	24.3	0.898
	MetOne	**3.16**	0.50	-72.3	96.9	0.800
	URG	0.92	0.06	13.8	13.2	0.977
	VAPS	**3.62**	0.43	65.1	63.9	0.911
Phoenix	Andersen	1.04	0.04	24.9	8.7	0.982
	IMPROVE	1.00	0.11	34.0	26.7	0.836
	MetOne	**2.73**	0.40	12.1	96.7	**0.768**
	URG	0.83	0.03	4.1	8.5	0.981
	VAPS	0.95	1.42	185	303	**0.047**
Philadelphia	Andersen	1.02	0.05	8.5	6.6	0.964
	IMPROVE	1.01	0.05	3.2	7.0	0.966
	MetOne	**1.48**	0.10	-3.6	13.5	0.938
	URG	0.98	0.04	2.1	4.8	0.979
	VAPS	1.05	0.08	-1.7	11.8	0.943
RTP	Andersen	0.93	0.07	1.0	4.2	0.927
	IMPROVE	0.96	0.06	-2.9	3.6	0.954
	MetOne	**1.28**	0.08	-1.4	4.7	0.956
	URG	0.90	0.05	-1.9	3.1	0.963
	VAPS	0.98	0.20	15.4	12.3	**0.719**

Zinc**

Site	Sampler	Slope	Std Err. Slope	Intercept	Std. Err. Intercept	R^2
Rubidoux	Andersen	1.01	0.10	6.2	9.4	0.922
	IMPROVE	0.92	0.11	4.5	11.2	0.878
	MetOne	1.02	0.10	14.4	9.8	0.919
	URG	1.10	0.16	10.0	16.2	0.908
	VAPS	**0.59**	0.14	14.2	10.5	**0.719**
Phoenix	Andersen	**0.69**	0.08	5.2	1.7	0.820
	IMPROVE	**0.65**	0.13	5.1	2.8	**0.612**
	MetOne	0.99	0.23	8.9	4.8	**0.576**
	URG	**0.69**	0.10	4.1	2.1	0.825
	VAPS	0.85	0.29	4.3	4.8	**0.495**
Philadelphia	Andersen	1.10	0.07	-2.4	2.7	0.942
	IMPROVE	1.08	0.08	-3.9	3.2	0.932
	MetOne	1.12	0.06	-2.9	2.3	0.961
	URG	1.13	0.07	-2.4	2.6	0.949
	VAPS	1.19	0.08	-4.1	3.5	0.952
RTP	Andersen	**0.46**	0.15	6.3	3.2	**0.390**
	IMPROVE	**0.19**	0.20	10.0	4.1	**0.070**
	MetOne	**0.43**	0.15	6.1	3.2	**0.391**
	URG	**0.39**	0.15	8.5	3.1	**0.352**
	VAPS	**0.33**	0.23	7.9	5.4	**0.195**

Potassium**

Site	Sampler	Slope	Std Err. Slope	Intercept	Std. Err. Intercept	R^2
Rubidoux	Andersen	1.06	0.13	5.4	11.1	0.884
	IMPROVE	0.96	0.19	6.3	16.5	**0.718**
	MetOne	**2.07**	0.82	22.8	70.8	**0.391**
	URG	1.20	0.15	-9.2	14.3	0.924
	VAPS	**1.51**	0.87	91.0	63.5	**0.299**
Phoenix	Andersen	0.97	0.02	6.8	3.3	0.993
	IMPROVE	0.95	0.11	8.9	17.0	0.827
	MetOne	**2.14**	0.30	10.9	46.7	**0.784**
	URG	0.94	0.02	0.2	2.5	0.997
	VAPS	**0.66**	0.71	94.7	97.7	**0.088**
Philadelphia	Andersen	1.02	0.04	0.8	2.1	0.982
	IMPROVE	0.89	0.08	6.7	4.7	0.912
	MetOne	1.16	0.10	3.8	6.2	0.902
	URG	1.05	0.05	0.4	3.2	0.962
	VAPS	1.17	0.06	-7.4	4.1	0.972
RTP	Andersen	0.98	0.03	-0.2	2.3	0.987
	IMPROVE	0.96	0.05	-1.4	4.0	0.964
	MetOne	1.04	0.05	4.8	3.7	0.975
	URG	1.05	0.02	-1.2	1.9	0.993
	VAPS	1.10	0.06	-0.2	4.8	0.978

[1] Highlighted values are slopes out side the range from 0.8 to 1.2 or R^2 less than 0.8

Units for Intercept and Standard Error of the Intercept are * = ug/m^3; and ** = ng/m^3.

Table II-10a Results from the Paired T-Tests Between the Andersen and the FRM Samplers for Each Analyte/Site.

SITE	**$PM_{2.5}$**	**$SO_4^=$**	**S**	**$P\text{-}NO_3$**	**NH4**	**OC**	**EC**	**Si**	**K**	**Ca**	**Fe**	**Zn**
P-values from the Paired T-tests (Values less than 0.05 Mean That the Andersen and FRM Samplers Are Statistically Different)												
Rubidoux	0.8046	0.9811	0.1878	0.0147	0.0003	0.0003	0.0200	0.0119	0.0443	0.0517	0.0060	0.3403
Phoenix	0.8567	0.0001	0.0992	0.8751	0.0001	0.0001	0.0042	0.0001	0.0521	0.0001	0.0001	0.6960
Philadelphia	0.2428	0.0028	0.2042	0.1933	0.0004	0.0001	0.5427	0.0594	0.0509	0.1044	0.0160	0.6290
RTP	0.3181	0.3618	0.2995	0.0043	0.7789	0.0083	0.0070	0.5253	0.2029	0.6908	0.2760	0.3710
Statistical Decision Based on P-values ("Y" Means That the Andersen and FRM Are Statistically the Same and "N" Means They Are Statistically Different)												
Rubidoux	Y	Y	Y	N	N	N	N	N	N	Y	N	Y
Phoenix	Y	N	Y	Y	N	N	N	N	Y	N	N	Y
Philadelphia	Y	N	Y	Y	N	N	Y	Y	Y	Y	N	Y
RTP	Y	Y	Y	N	Y	N	N	Y	Y	Y	Y	Y
Number of the Differences (FRM - Andersen) That Were Positive/total Number of Differences Used in T-test[1]												
Rubidoux	9/12	7/13	5/13	11/13	13/13	1/13	2/13	2/11	1/11	1/11	1/11	6/11
Phoenix	8/17	18/18	12/17	16/18	18/18	0/18	14/18	14/18	7/17	0/17	0/17	7/17
Philadelphia	8/17	15/18	8/17	16/18	16/18	1/18	12/18	12/18	5/17	3/17	3/17	9/17
RTP	12/16	11/18	8/16	4/18	6/18	4/17	12/17	12/17	11/16	10/16	9/16	8/16

[1] Individual data are presented in Appendices G-1 and G-2 as absolute differences and percent differences.

Table II-10b. Results from the Paired T-Tests Between the MetOne and the FRM Samplers for Each Analyte/Site.

SITE	**$PM_{2.5}$**	**$SO_4^=$**	**S**	**$P\text{-}NO_3$**	**NH4**	**OC**	**EC**	**Si**	**K**	**Ca**	**Fe**	**Zn**
P-values from the Paired T-tests (Values less than 0.05 Mean That the Met One and FRM Samplers Are Statistically Different)												
Rubidoux	0.0121	0.3549	0.0076	0.0572	0.4718	0.0367	0.1350	0.0036	0.0030	0.0059	0.0035	0.0413
Phoenix	0.0001	0.0001	0.5387	0.0521	0.0002	0.8109	0.0772	0.0001	0.0001	0.0001	0.0001	0.0008
Philadelphia	0.1022	0.0592	0.0007	0.3036	0.9839	0.8820	0.3125	0.0005	0.0002	0.0067	0.0067	0.5579
RTP	0.0085	0.5417	0.0031	0.1805	0.2622	0.0038	0.0049	0.1007	0.0013	0.0048	0.0048	0.2977
Statistical Decision Based on P-values (“Y” Means That the Met One and FRM Are Statistically the Same and “N’ Means They Are Statistically Different)												
Rubidoux	N	Y	N	Y	Y	N	Y	N	N	N	N	N
Phoenix	N	N	Y	Y	N	Y	Y	N	N	N	N	N
Philadelphia	Y	Y	N	Y	Y	Y	Y	N	N	N	N	Y
RTP	N	Y	N	Y	Y	N	N	Y	N	N	N	Y
Number of Differences (FRM - Met One) that Were Positive/total Number of Differences Used in T-test[1]												
Rubidoux	2/12	5/13	0/12	1/13	10/13	4/13	8/13	0/12	1/12	0/12	1/12	1/12
Phoenix	0/16	1/16	2/16	4/16	16/16	5/17	11/17	0/16	0/16	0/16	0/17	2/17
Philadelphia	8/16	14/17	0/16	10/17	11/17	12/17	13/17	1/16	1/16	2/16	1/16	8/16
RTP	2/15	10/17	3/15	2/17	10/17	3/14	12/15	2/15	1/15	1/15	1/15	9/15

[1] Individual data are presented in Appendices G-1 and G-2 as absolute differences and percent differences.

Table II-10c. Results from the Paired T-Tests Between the IMPROVE and the FRM Samplers for Each Analyte/Site.

SITE	**$PM_{2.5}$**	**$SO_4^=$**	**S**	**$P-NO_3$**	**NH4**	**OC**	**EC**	**Si**	**K**	**Ca**	**Fe**	**Zn**
P-values from the Paired T-tests (Values less than 0.05 Mean That the IMPROVE and FRM Samplers Are Statistically Different)												
Rubidoux	0.8006	0.0850	0.3672	0.1839	0.0016	0.0034	0.0074	0.0714	0.3461	0.0743	0.2084	0.4717
Phoenix	0.0011	0.0855	0.6851	0.0017	0.0001	0.0001	0.0001	0.0041	0.7233	0.0004	0.0104	0.4664
Philadelphia	0.7233	0.0300	0.0567	0.0378	0.0001	0.0015	0.0034	0.0655	0.0655	0.0997	0.2654	0.5416
RTP	0.0326	0.0440	0.8762	0.0957	0.0041	0.0001	0.0025	0.1696	0.1696	0.3837	0.0135	0.4598
Statistical Decision Based on P-values (“Y” Means That the IMPROVE and FRM Are Statistically the Same and “N” Means That They Are Statistically Different)												
Rubidoux	Y	Y	Y	Y	N	N	N	Y	Y	Y	Y	Y
Phoenix	N	Y	Y	N	N	N	N	N	Y	N	N	Y
Philadelphia	Y	N	Y	N	N	N	N	Y	Y	Y	Y	Y
RTP	N	N	Y	Y	N	N	N	Y	Y	Y	N	Y
Number of Differences (FRM - IMPROVE) that Were Positive/total Number of Differences Used in T-test[1]												
Rubidoux	8/12	11/13	10/12	10/13	12/13	11/13	13/13	2/12	4/12	1/12	1/12	8/12
Phoenix	15/17	11/15	12/17	17/18	18/18	17/18	18/18	3/17	7/17	2/17	2/17	10/17
Philadelphia	7/16	14/18	15/15	13/18	18/18	14/18	15/18	5/15	7/15	7/15	7/15	9/14
RTP	11/15	12/15	11/15	4/15	13/15	15/16	14/16	9/15	12/15	12/15	11/15	9/15

[1] Individual data are presented in Appendices G-1 and G-2 as absolute differences and percent differences.

Table II-10d. Results from the Paired T-Tests Between the URG and the FRM Samplers for Each Analyte/Site.

SITE	**$PM_{2.5}$**	**$SO_4^=$**	**S**	**$P\text{-}NO_3$**	**NH4**	**OC**	**EC**	**Si**	**K**	**Ca**	**Fe**	**Zn**
P-values from the Paired T-tests (Values less than 0.05 Mean That the URG and FRM Samplers Are Statistically Different)												
Rubidoux	0.0126	0.2518	0.1252	0.0285	0.0039	0.1228	0.3385	0.3121	0.2054	0.2852	0.9188	0.2359
Phoenix	0.1028	0.4804	0.0312	0.0001	0.0194	0.0001	0.0023	0.0004	0.0003	0.0007	0.0005	0.1797
Philadelphia	0.0849	0.0306	0.0058	0.1530	0.7010	0.0001	0.0097	0.6142	0.0235	0.0541	0.9746	0.3195
RTP	0.0035	0.4797	0.0001	0.0001	0.0001	0.0001	0.2117	0.4226	0.1004	0.0059	0.0007	0.5242
Statistical Decision Based on P-values (“Y” Means That the URG and FRM Are Statistically the Same and “N” Means They Are Statistically Different)												
Rubidoux	N	Y	Y	N	N	Y	Y	Y	Y	Y	Y	Y
Phoenix	Y	Y	N	N	N	N	N	N	N	N	N	Y
Philadelphia	Y	N	N	Y	Y	N	N	Y	N	Y	Y	Y
RTP	N	Y	N	N	N	N	Y	Y	Y	N	N	Y
Number of Differences (FRM - URG) that Were Positive/total Number of Differences Used in T-test[1]												
Rubidoux	0/7	3/13	0/7	1/9	1/13	9/13	9/13	3/7	1/7	5/7	6/7	2/7
Phoenix	9/13	11/18	10/13	0/15	13/18	15/18	14/18	13/13	12/13	13/13	12/13	8/13
Philadelphia	7/16	12/18	2/17	7/17	11/18	18/18	12/18	7/17	4/17	13/17	9/17	6/17
RTP	3/15	7/18	0/14	0/17	1/18	15/17	10/17	6/15	4/15	12/15	13/15	3/15

[1] Individual data are presented in Appendices G-1 and G-2 as absolute differences and percent differences.

Table II-10e. Results from the Paired T-Tests Between the VAPS and the FRM Samplers for Each Analyte/Site.

SITE	$PM_{2.5}$	$SO_4^{=}$	S	P-NO_3	NH4	OC	EC	Si	K	Ca	Fe	Zn
P-values from the Paired T-tests (Values less than 0.05 Mean That the VAPS and FRM Samplers Are Statistically Different)												
Rubidoux	0.0017	0.0317	0.0646	0.0558	0.1426	0.3898	0.1948	0.0022	0.0009	0.2852	0.0005	0.5488
Phoenix	0.1079	0.0283	0.3578	0.0004	0.2232	0.0001	0.0001	0.1281	0.1685	0.1297	0.1180	0.2688
Philadelphia	0.0029	0.0001	0.2833	0.3888	0.0001	0.0001	0.0001	0.2766	0.1892	0.7160	0.5425	0.3816
RTP	0.0003	0.4910	0.7570	0.0021	0.0063	0.0330	0.7603	0.0438	0.0291	0.1869	0.0526	0.4045
Statistical Decision Based on P-values ("Y" Means That the VAPS and FRM Are Statistically the Same and "N' Means That They Are Statistically Different)												
Rubidoux	N	N	Y	Y	Y	Y	Y	N	N	N	N	Y
Phoenix	Y	N	Y	N	Y	N	N	Y	Y	Y	Y	Y
Philadelphia	N	N	Y	Y	N	N	N	Y	Y	Y	Y	Y
RTP	N	Y	Y	N	N	N	Y	N	N	Y	Y	Y
Number of Differences (VAPS and FRM) that Were Positive/total Number of Differences Used in T-test[1]												
Rubidoux	0/9	1/13	1/9	1/11	10/13	5/12	7/12	0/9	0/9	0/9	0/9	2/8
Phoenix	3/11	15/15	7/11	1/12	11/15	15/15	15/15	0/11	0/11	0/11	0/11	6/13
Philadelphia	1/13	17/17	7/12	6/16	17/17	16/17	16/17	5/12	5/12	6/12	4/12	8/12
RTP	0/11	8/15	3/10	0/13	2/15	9/13	9/13	1/11	1/11	4/11	3/11	6/11

[1] Individual data are presented in Appendices G-1 and G-2 as absolute differences and percent differences.

Table II-11. Results from the ANOVA for Examining Equivalency Among the Samplers for Particle Nitrate.

SITE	Sampler Means (µg/m^3) and Number of Values (X) Used to Compile Each Mean				Statistically Equivalent Samplers
	Andersen	IMPROVE	MetOne	URG	
Rubidoux	10.0 (14)	10.5 (14)	11.7 (14)	16 (9)	(Andersen, IMPROVE)
Phoenix	3.1 (18)	2.5 (18)	3.4 (16)	4.3 (15)	Andersen, IMPROVE); (Andersen, Met One)
Philadelphia	3.5 (18)	3.6 (18)	3.6 (17)	4.0 (18)	(Andersen, IMPROVE, Met One); (IMPROVE, Met One, URG)
RTP	0.86 (18)	0.88 (15)	0.96 (17)	1.3 (17)	(Andersen, IMPROVE, Met One); (Met One, URG)

Table II-12a. Nitrate Concentrations (μg/m^3) Measured on Teflon (T) or Quartz-Fiber (Q) Filters by Sampler Type Averaged Over the Study Period .

Site	AND-T	MetOne-T	FRM-Q	URG-Q	VAPS-Q
Rubidoux	10.4	10.7	11.8	11.4	11.7
Phoenix	1.6	2.4	3.1	2.8	2.5
Philadelphia	3.3	3.2	3.8	3.6	3.1
RTP	0.4	0.4	0.7	0.7	0.8

Table II-12b. Total Particle Nitrate Concentrations (μg/m^3) Measured by Each Sampler Averaged Over the Study Period.

Site	AND	MetOne	URG	VAPS	IMP	FRM
Sampling Configuration*	(MgO/N) (direct)	(MgO/N) (direct)	(Q+ Na_2CO_3/N) (indirect)	(Q+ Na_2CO_3/N) (indirect)	(Na_2CO_3/N)(direct)	(Q)
Rubidoux	10.0	11.7	12.7	12.8	10.5	11.8
Phoenix	3.0	3.4	4.3	3.9	2.5	3.1
Philadelphia	3.5	3.6	4.0	3.9	3.6	3.8
RTP	0.86	0.89	1.3	1.4	0.9	0.7

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* MgO/N = The direct method for particle nitrate -- MgO coated denuder followed by a nylon filter, total nitrate is measured on the nylon filter; the indirect method for particle nitrate -- Na/Q/N = Na_2CO_3 coated denuder with total particulate nitrate equal to the sum of nitrate measured on the Quartz-fiber filter, also used for OC/EC analysis, plus nitrate measured on the nylon filter behind the Na_2CO_3 coated denuder; Na/Q/N / MgO/N = ratio of two methods. Also see Figures I-1 to I-5.

Table II-12c. Volatilized Nitrate Concentrations (µg/m^3) Measured by Each Sampler Averaged Over the Study Period.

Site	**AND**	**MetOne**	**URG**	**VAPS**	**IMP**
Sampling Configuration	(MgO/N) (indirect)	(MgO/N) (indirect)	(Q+ Na_2CO_3/N) (direct)	(Q+ Na_2CO_3/N) (direct)	(Na_2CO_3/N) (indirect)
Rubidoux	-0.36	1.01	0.99	0.64	0.12
Phoenix	1.46	1.14	1.57	1.41	0.87
Philadelphia	0.22	0.41	0.37	0.78	0.26
RTP	0.48	0.48	0.56	0.58	0.47

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* MgO/N = The indirect method to measure volatilized nitrate -- MgO coated denuder followed by a nylon filter, volatilized nitrate is the difference between the nitrate on the nylon filter minus that on the Teflon filter collected in parallel; The direct method to measure volatilized nitrate -- Na/Q/N = Na_2CO_3 coated denuder with particulate nitrate equal to the sum of nitrate measured on the Quartz-fiber filter, also used for OC/EC analysis, plus nitrate measured on the nylon filter behind the Na_2CO_3 coated denuder and volatilized nitrate is measured directly on the nylon back-up filter; Na/Q/N / MgO/N = ratio of two methods. Also see Figures I-1 to I-5.

Table II-12d. Sulfate Concentrations (µg/m^3) Measured on Teflon (T) and Quartz-Fiber (Q) Filters Averaged Over the Study Period.

Site	**AND-T**	**MET-T**	**FRM-Q**	**URG-Q**	**VAPS-Q**	**FRM-Q**
Rubidoux	1.6	1.7	1.7	1.7	1.8	1.5
Phoenix	0.8	1.0	0.9	0.8	0.8	0.8
Philadelphia	3.8	4.1	4.1	4.0	3.4	3.8
RTP	3.3	3.3	3.3	3.3	3.2	3.2

Table II-13a. Nitrate Concentrations (µg/m^3) Measured on Teflon or Quartz-Fiber Filters Averaged Over the Study Period*.

Site	Teflon	Quartz	(Q - T)	Q ' T**
Rubidoux	10.5	11.4	0.9	1.3 ± 0.7
Phoenix	1.9	2.9	1.0	1.7 ± 0.8
Philadelphia	3.2	3.4	0.2	1.2 ± 0.3
RTP	0.4	0.7	0.3	1.8 ± 0.6

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* In Tables II-13a through II-14d, Rubidoux has 14 data points in the averages, while the other three sites have 18.

** Average and standard deviation.

Figure II-13b. Total Particle Nitrate Concentrations (µg/m^3) Measured by Different Denuder-Filter Pack Methods Averaged Over the Study Period.

	Denuder-Filter Pack Configuration*			
Site	**MgO/N (direct)**	**Na/Q/N (indirect)**	**(Na/Q/N) - (MgO/N)**	**(Na/Q/N) ' (MgO/N)****
Rubidoux	10.9	12.5	1.6	1.1 ± 0.4
Phoenix	3.2	4.4	1.2	1.3 ± 0.2
Philadelphia	3.6	4.0	0.4	1.1 ± 0.1
RTP	0.9	1.3	0.4	1.5 ± 0.5

* MgO/N = The direct method for particle nitrate -- MgO coated denuder followed by a nylon filter, total nitrate is measured on the nylon filter; the indirect method for particle nitrate -- Na/Q/N = Na_2CO_3 coated denuder with total particulate nitrate equal to the sum of nitrate measured on the Quartz-fiber filter, also used for OC/EC analysis, plus nitrate measured on the nylon filter behind the Na_2CO_3 coated denuder; Na/Q/N / MgO/N = ratio of two methods. Also see Figures I-1 to I-5.

** Average and standard deviation.

Table II-13c. Volatilized Nitrate Concentrations (μg/m^3) Measured by Different Denuder-Filter Pack Methods Averaged Over the Study Period.

Site	**Direct***	**Indirect****	**(Direct - Indirect)**	**(Direct ÷ Indirect)**
Rubidoux	0.51	0.32	0.19	1.9 ± 2.7***
Phoenix	1.35	1.28	0.07	1.0 ± 0.3
Philadelphia	0.45	0.30	0.15	1.91 ± 2.3
RTP	0.52	0.48	0.04	1.1 ± 0.7

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* Direct is volatilized nitrate measured directly on a Nylon Filter behind a denuder and a Teflon Filter (URG, VAPS). Also see Figures I-1 to I-5.

** Indirect is nitrate measured by difference (Nylon - Teflon) (Andersen and MetOne). Also see Figures I-1 to I-5.

*** Average and standard deviation.

Table II-13d. Sulfate Concentrations (μg/m^3) Measured on Teflon and Quartz Filters Averaged Over the Study Period.

Site	**Teflon**	**Quartz**	**(Q - T)**	**Q ÷ T**
Rubidoux	1.6	1.7	0.1	1.1
Phoenix	0.8	0.8	0.00	1.0
Philadelphia	3.9	3.9	0.00	1.0
RTP	3.3	3.3	0.00	1.0

Table II-14. Loss of Nitrate Resulting from Analysis of Teflon Filter by Vacuum XRF.

	Nitrate Lost from Filter		**Sulfate Lost from Filter**	
	Loss NO_3^- (ug)	**NO_3^- (%)**	**SO_4^{2-}**	**SO_4^{2-} (%)**
Average	73.7	38.8	0.4	-1.4
Standard Deviation	47.7	15.7	2.6	6.1
n	26.0	26.0	26.0	26.0
Standard Error	9.3	3.1	0.5	1.2

Table II-15. Summary of Site Operators Surveys Regarding Speciation Sampler Setup and Operation.

Evaluation Criteria	**Andersen RAAS**	**Met One SASS**	**URG MASS**	**IMPROVE**	**VAPS**	**FRM**
Sampler Installation						
Was more than one person required for field installation?	Yes	No	Yes	Yes	Yes	Yes
Were the operating manual and schematics of value during assembly?	Partially	Yes	Yes	Yes	Yes	Yes
Number of sampler components involved during installation	Moderate	Moderate	Moderate	Too many	Moderate	Moderate
Were sampler components easily accessible during installation?	Yes	Yes	Yes	Yes	Yes	Yes
Relative sampler installation time	Long	Quick	Moderate to Quick	Long	Moderate	Moderate to Quick
Ease of adjusting sampler's initial date, time, flow rate, etc.	Good	Good	Good	Fair	Average	Good
Overall rating pertaining to ease of sampler field installation	Good	Good to Excellent	Good	Fair to Average	Average	Good
Sampler Audits and Calibrations						
Ease of temperature and pressure audit procedures	Good to Excellent	Good	Good	Good	-	Good
Ease of leak check procedure	Good to Excellent	Good to Excellent	Good	Good	Average	Good
Ease of flow audit procedure	Good	Good	Good	Average	Average	Good
Were specialized tools or adaptors required for flow audit procedure?	Yes	Yes	No	No	Yes	No
Can the sampler be temperature calibrated in the field?	Yes	No	Yes	No	No	Yes
Can the sampler be pressure audited in the field?	Yes	No	Yes	No	No	Yes

Table II-15. Summary of Site Operators Surveys Regarding Speciation Sampler Setup and Operation.

Evaluation Criteria	**Andersen RAAS**	**Met One SASS**	**URG MASS**	**IMPROVE**	**VAPS**	**FRM**
Can the sampler be flow calibrated in the field?	Yes	No	Yes	Yes	Yes	Yes
Ease of temperature calibration procedure	Average to Good	-	Average	-	-	Average to Good
Ease of pressure calibration procedures	Average to Good	-	Average	-	-	Average to Good
Ease of flow calibration procedure	Average	-	Average to Good	Average to Good	Fair to Average	Good
Sampler Programming						
Ease of programming sampler start and stop times	Good to Excellent	Excellent	Good to Excellent	Average	Fair to Average	Good to Excellent
Reliability of the programming	Good	Excellent	Good to Excellent	Average	Average	Good to Excellent
Filter Holder Exchange Between Sampling EventS						
Would parts such as o-rings, fractionator components, etc. fall during filter exchange?	Always	No	No	No	Yes	No
Ease of assembling and disassembling filter holders and denuders in the laboratory	Good to Excellent	Fair to Average	Good	Good	Fair to Average	Good
Overall rating pertaining to ease of filter holders and denuders in the field	Fair to Average	Good to Excellent	Good	Average to Good	Fair to Average	Good
Time required to change filter holders and denuders in the field	Moderate	Quick	Quick	Moderate to Long	Moderate to Long	Quick to Moderate

Table II-15. Summary of Site Operators Surveys Regarding Speciation Sampler Setup and Operation.

Evaluation Criteria	Andersen RAAS	Met One SASS	URG MASS	IMPROVE	VAPS	FRM
Data Retrieval						
Did the sampler provide the necessary post-sampling information?	Yes	Yes	Yes	No	Yes	Yes
Was the data easily retrievable from the sampler?	Yes	Yes	Yes	Yes	Yes	Yes
Overall rating pertaining to the ease of data retrieval in the field	Good	Good to Excellent	Good	Average	Fair to Average	Good
Operating Manuals						
Were the contents of the operating manual clear?	Yes	Yes	Yes	Yes	Yes	Yes
Were the contents of the field SOP clear?	Yes	Yes	Yes	Yes	Yes	Yes

Table II-16. Recommended Spare Parts and Supplies for Use of Chemical Speciation Samplers and FRM Used in the Chemical Speciation Evaluation Study

Sampler	Item Description	Part #	Quantity	Price/item[1]
FRM	Filter Cassettes	RAAS-CASS	4	35.00
	WINS Oil	RAAS-Oil	Two 0.5 ounce bottles	10.00
Andersen RAAS	Filter Cassettes	RAAS-CASS	16	35.00
	O-ring kit	RAAS-OR1	2	5.00
	Denuder - for MgO coating	RAAS-S-DN	2	700.00
URG MASS 400, 450	Two stage filter holder - male threads (top), & quick connect (bottom)	URG-2000-30F	4	334.15
	Single stage filter holder - male threads(top), & female threads (bottom)	URG-2000-30FB	4	333.13
	76 mm flow straightners - male threads	URG-2000-30WN	2	102.20
	WINS oil	URG-2000-30PB	Two 1 ounce bottles	15.30
	Denuder (down tube) - for Na2CO3 coating	URG-M130-80DD	2	321.28
MetOne SASS	MetOne filter holders	8370	10	190.00
	Filter Cassettes	460128	20	28.00
	Carbon denuders	8375	4	100.00
	MgO denuder	8374	4	100.00
	Sharp cut cyclone	8670	5	250.00
VAPS	Two stage filter holder - male threads (top), and quick connect (bottom)	URG-2000-30F	4	334.15
	Single stage filter holder - male threads (top), & quick connect (bottom)	URG-2000-30F	8	281.11
	Couplers	URG-2000-30BC2	2	46.82
	#30 Teflon Seal Ring	URG-2000-30x24x3T	6	16.93
	Glass denuder - for XAD coating	URG-2000-30CF	4	527.75
	Denuder - for Na2CO3 coating	URG-2000-30x242-3CSS	4	311.92
Improve	Improve filter cassettes	-	12	5.00
	Denuder - for Na2CO3 coating	-	4	75.00

1. Price estimate based on current manufacturers prices at the time of this study and not estimates for current day purchases.

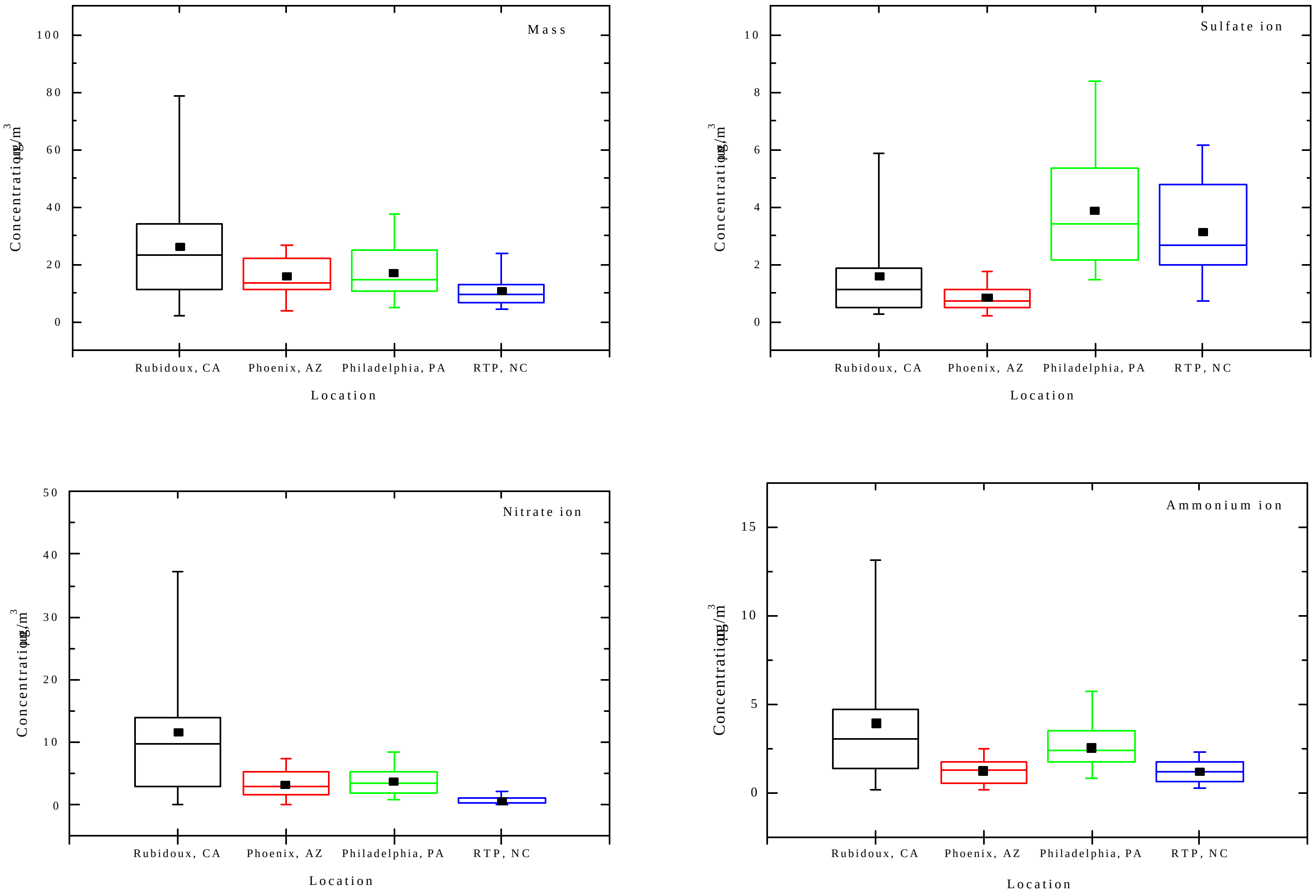


Figure II-1a. Frequency Distributions, Given as Box and Whisker Plots, of PM2.5 FRM Mass and Sulfate, Nitrate, and Ammonium ions at Each of the Four Cites Studied.

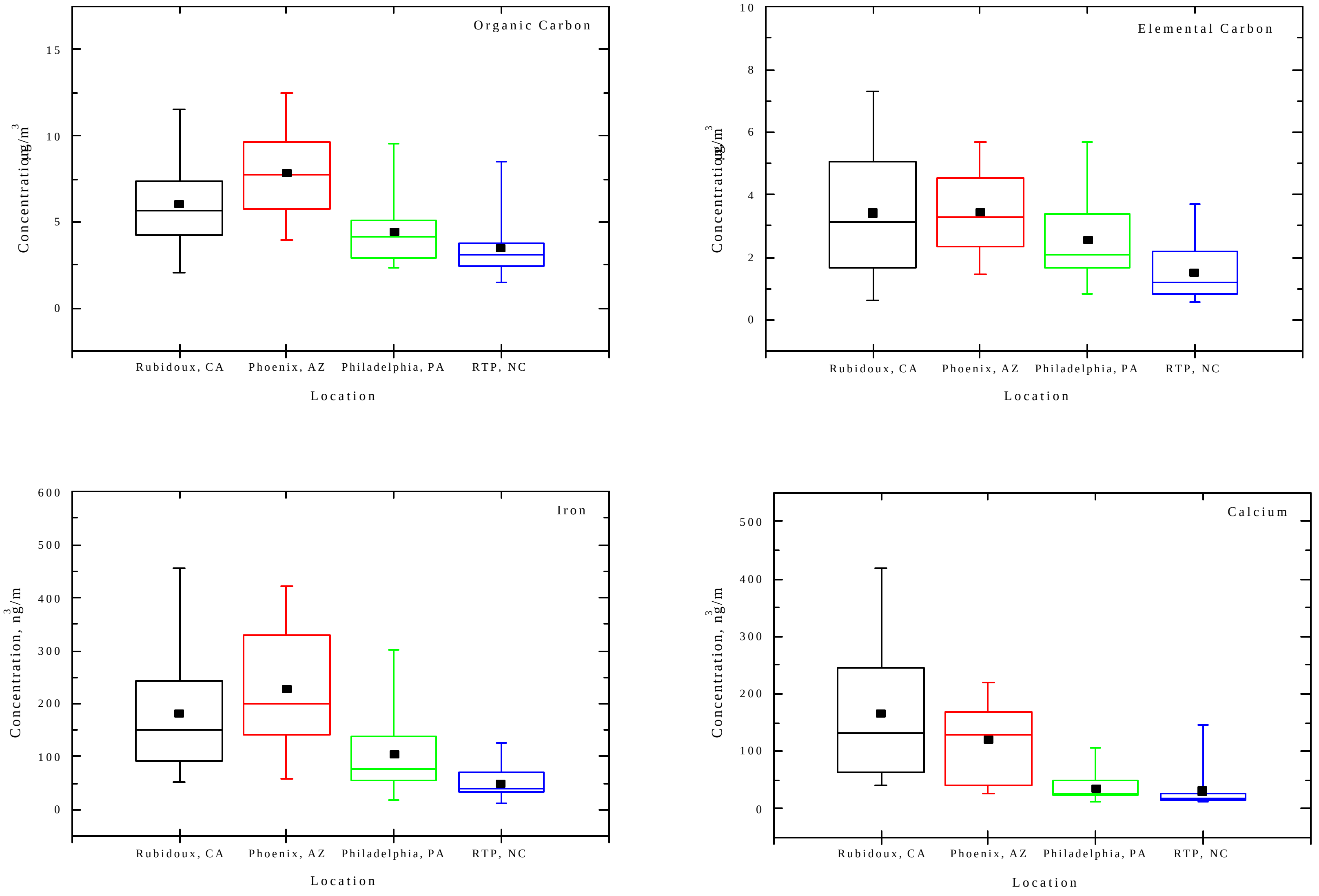


Figure II-1b. Frequency Distributions, Given as Box and Whisker Plots, of FRM PM2.5 OC, EC, Iron, and Calcium at Each of the Four Cites Studied.

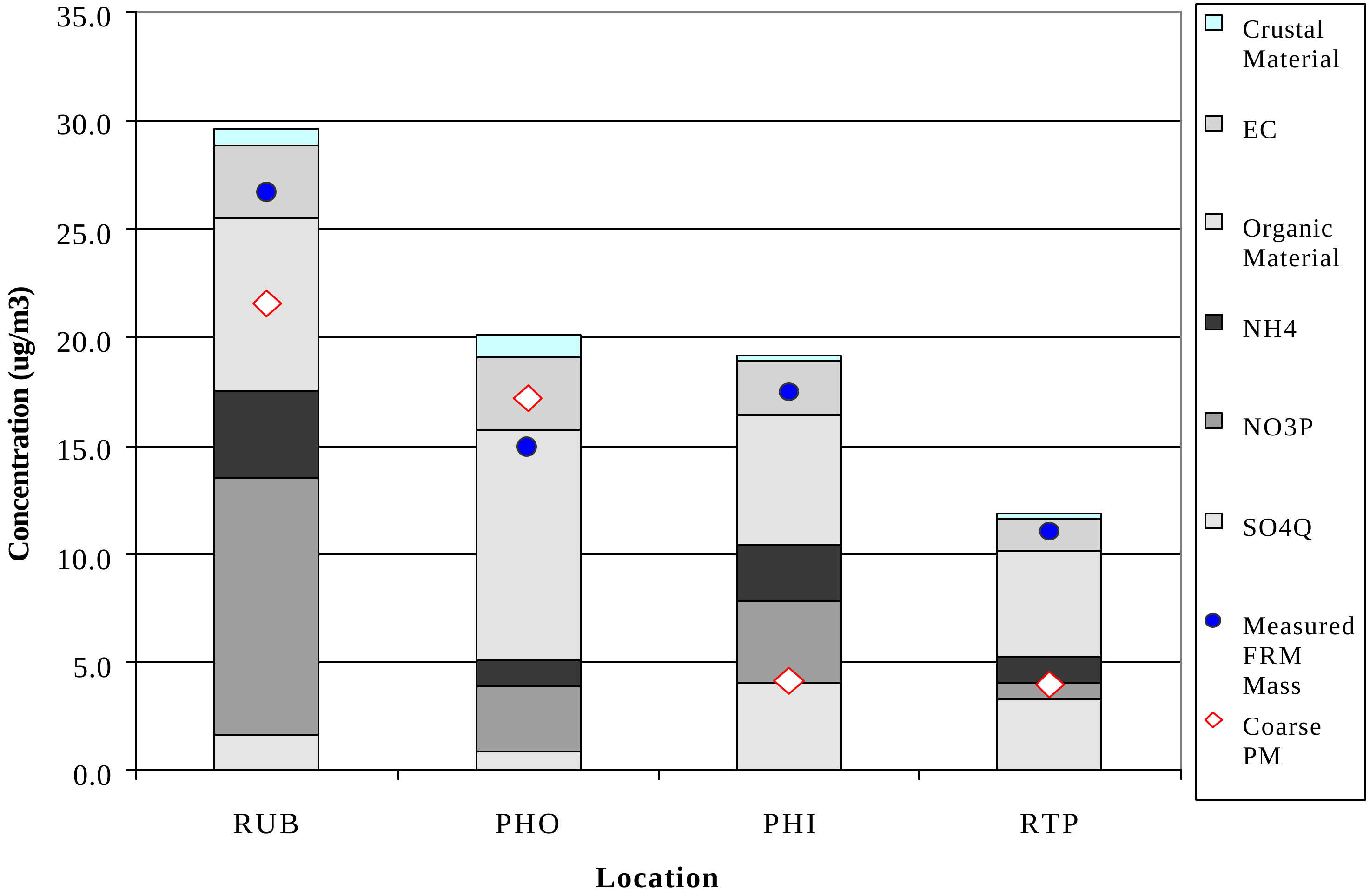


Figure II-2. Chemical Mass Balance of $PM_{2.5}$ at Each City. Mass Balance is Relative to the Measured Mass by the FRM (Coarse Mass as Measured by the VAPS). (See Table II-6 for Concentration Data and Percentages.)

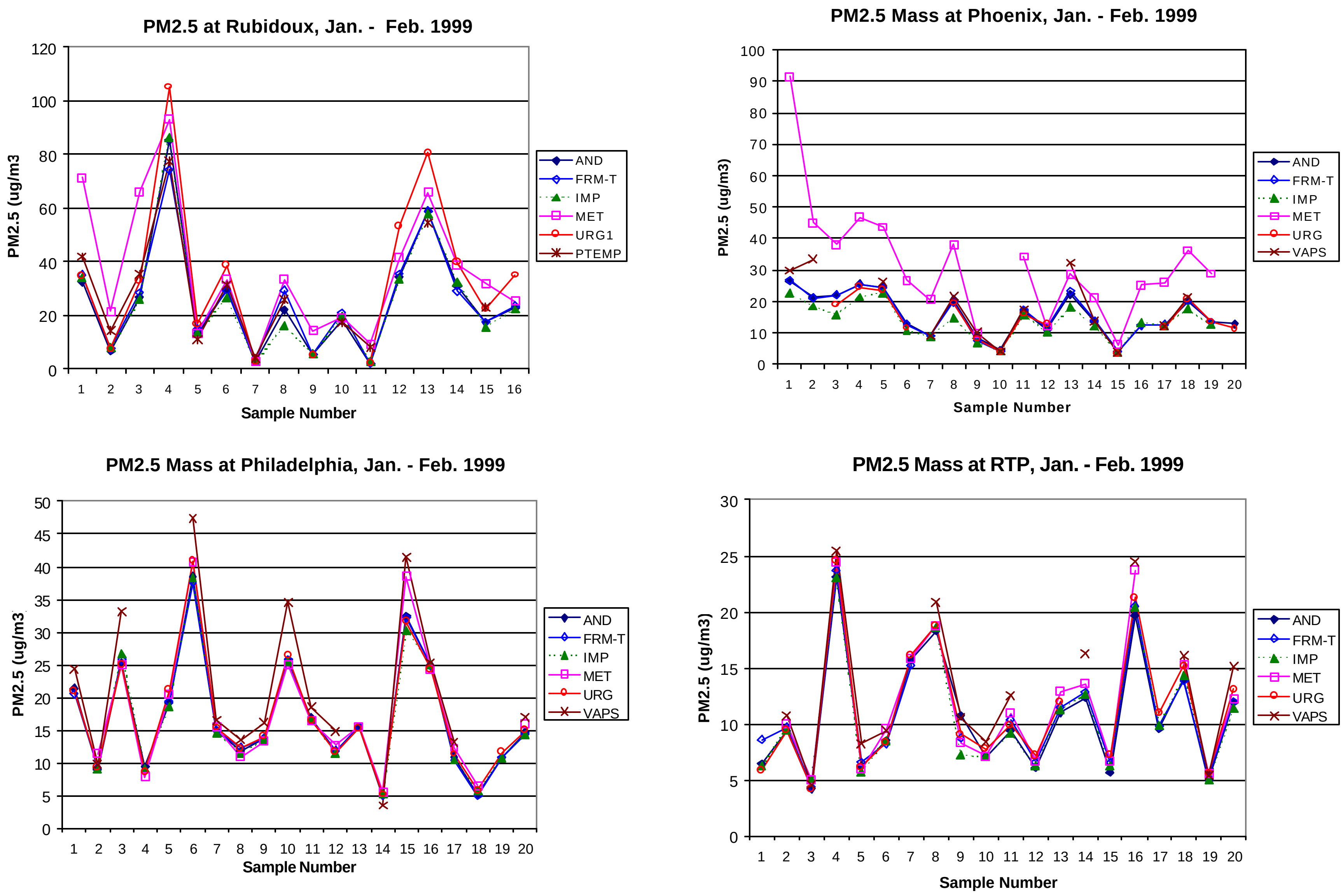


Figure II-3a. Time Series for Mass.

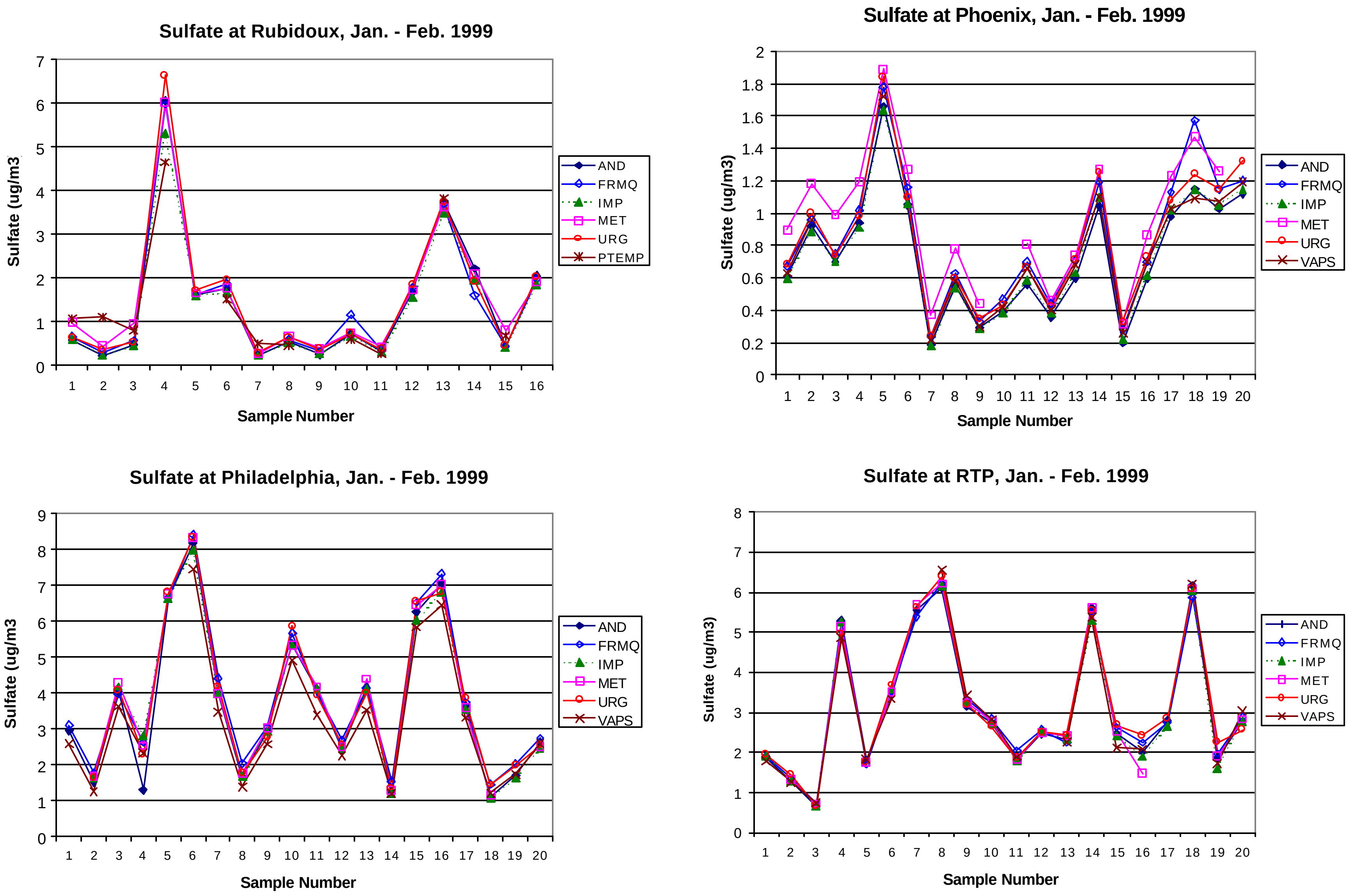


Figure II-3b. Time Series for Sulfate.

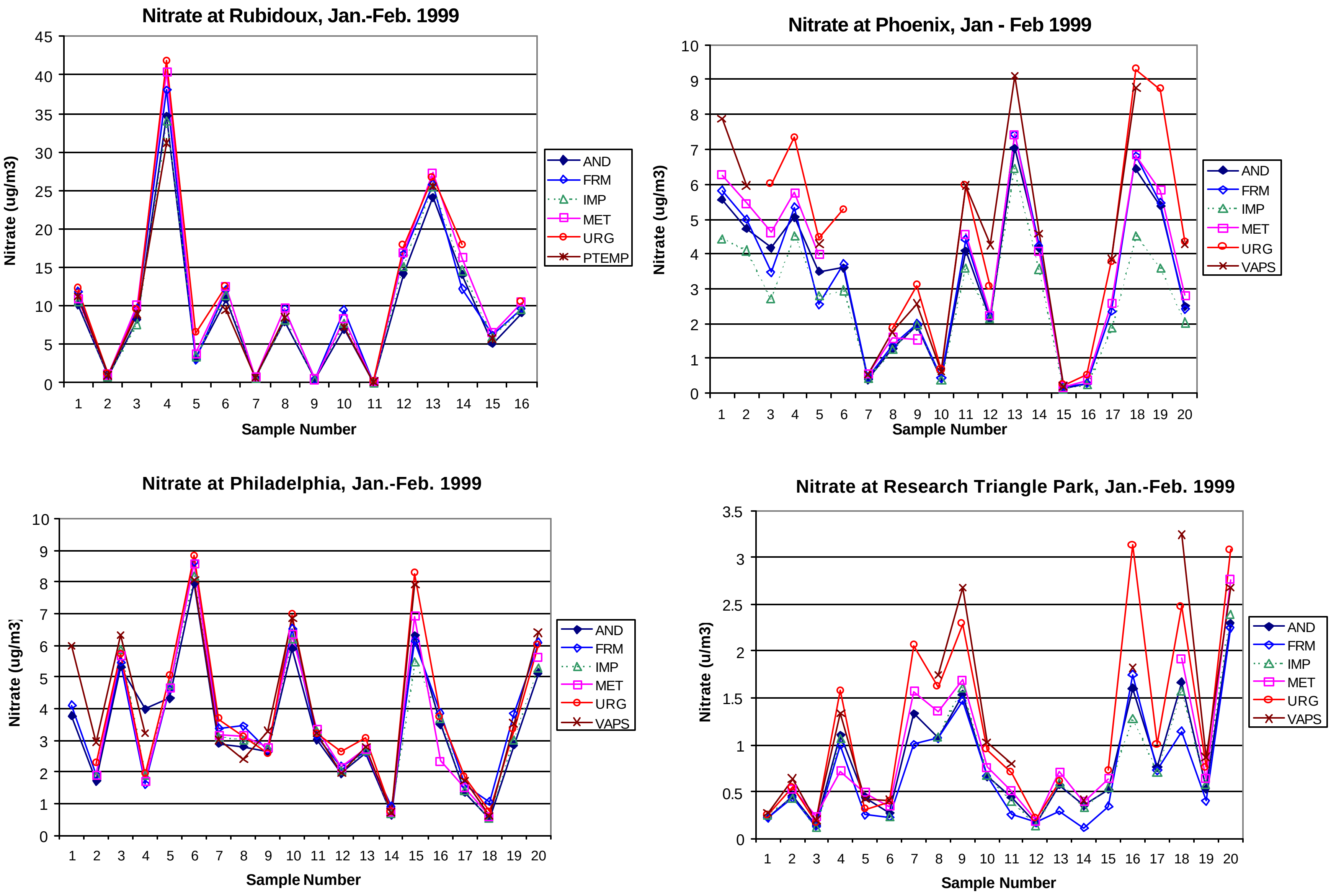


Figure II-3c. Time Series for Nitrate.

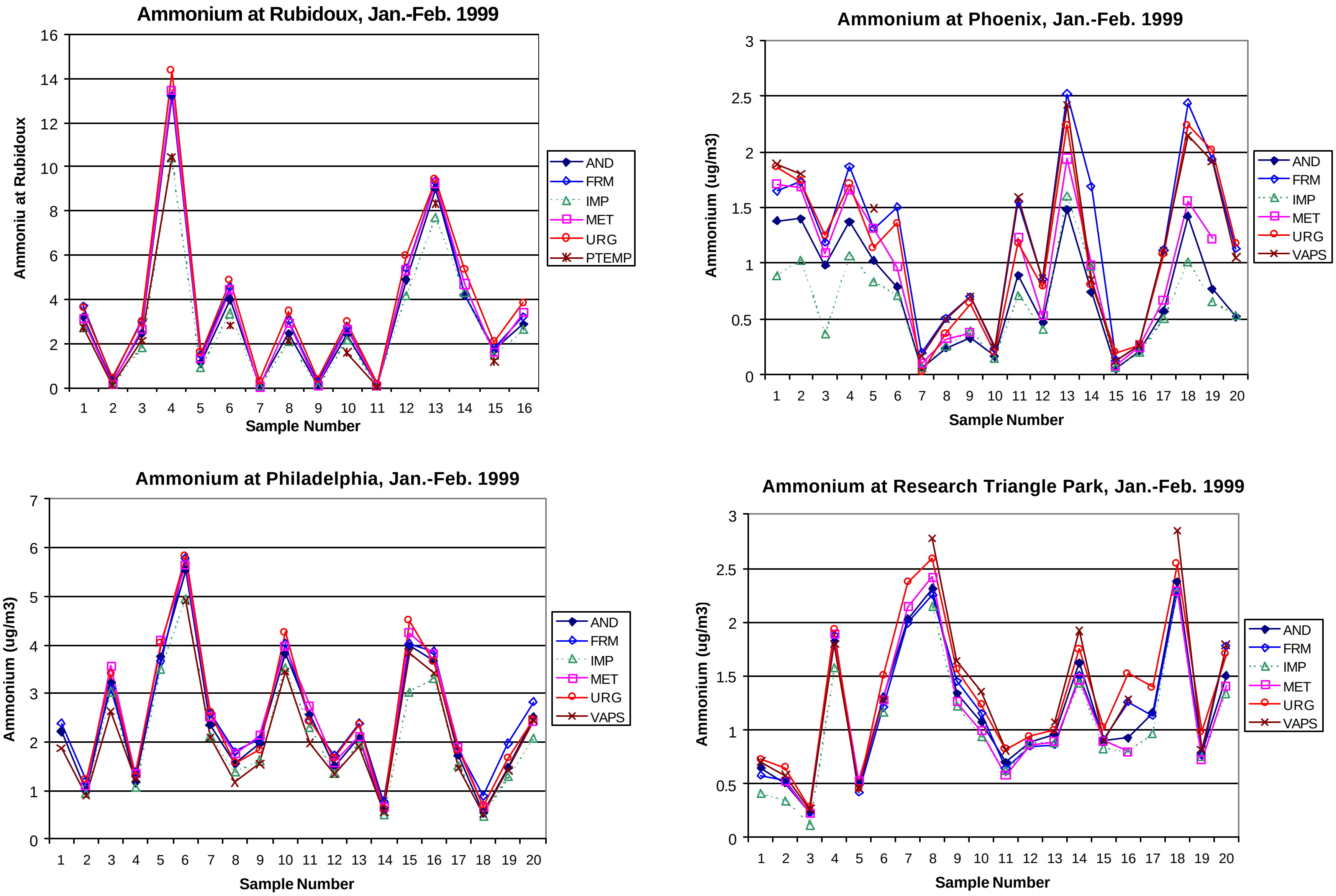


Figure II-3d. Time Series for Ammonium.

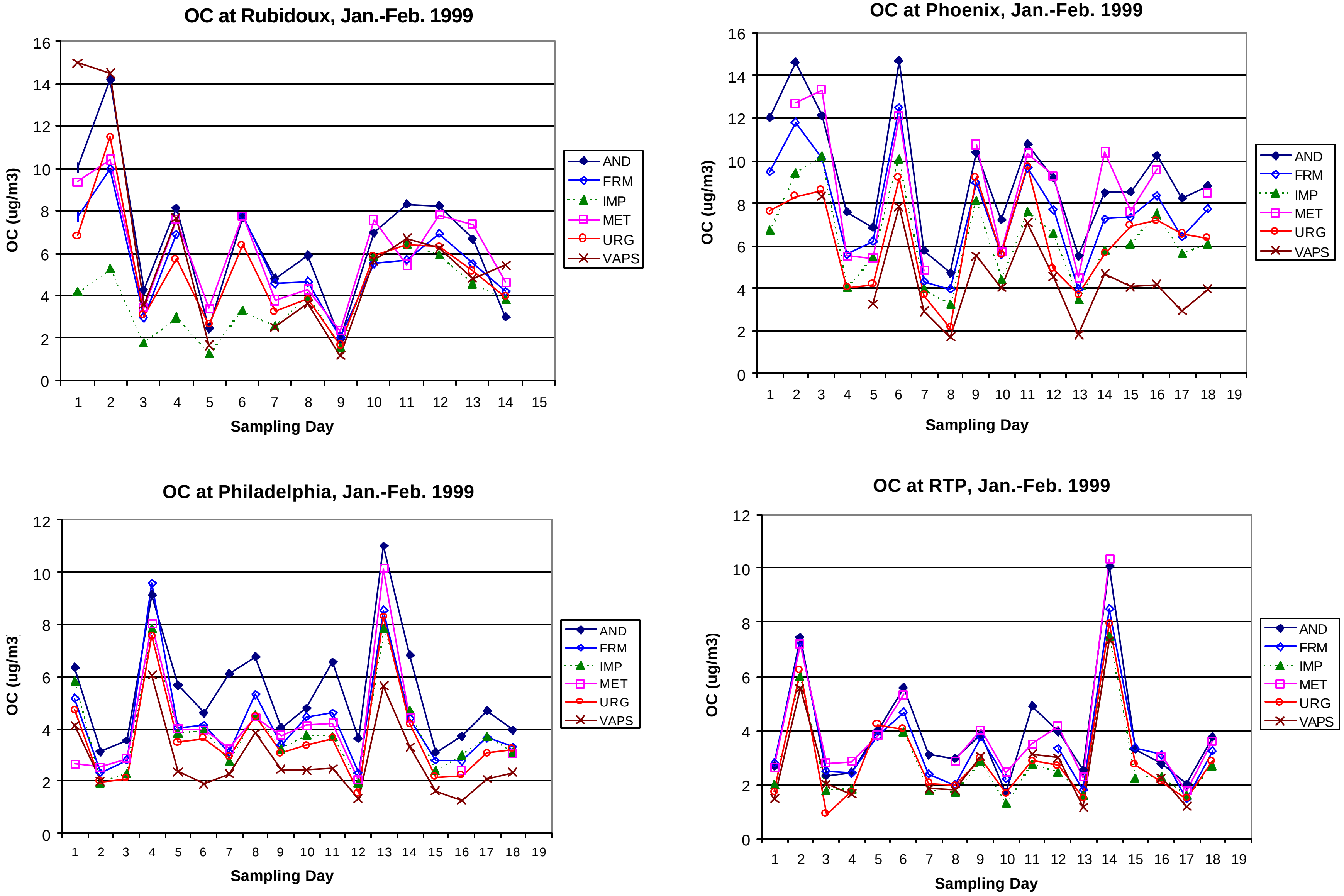


Figure II-3e. Time Series for OC.

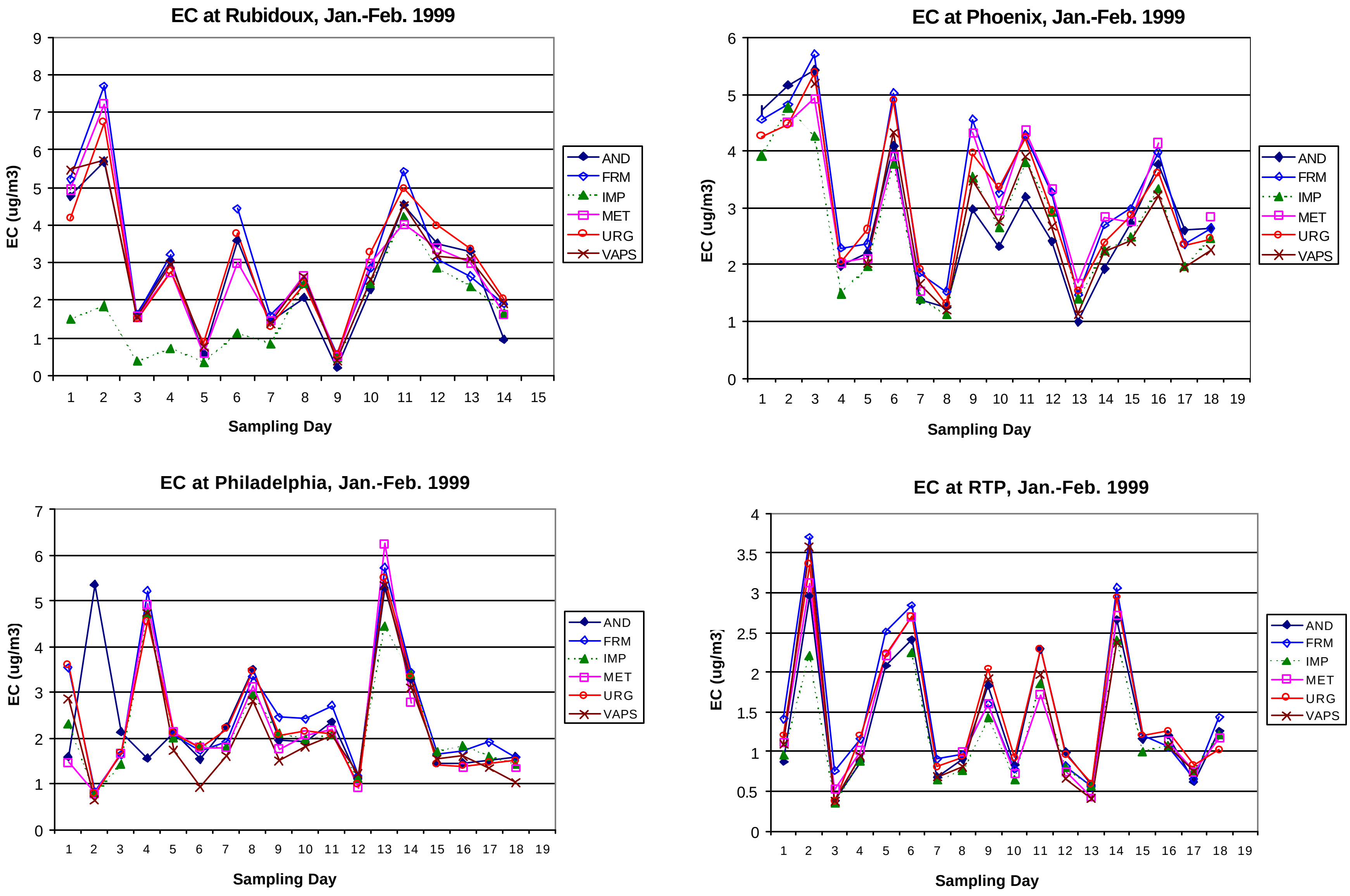


Figure II-3f. Time Series for EC.

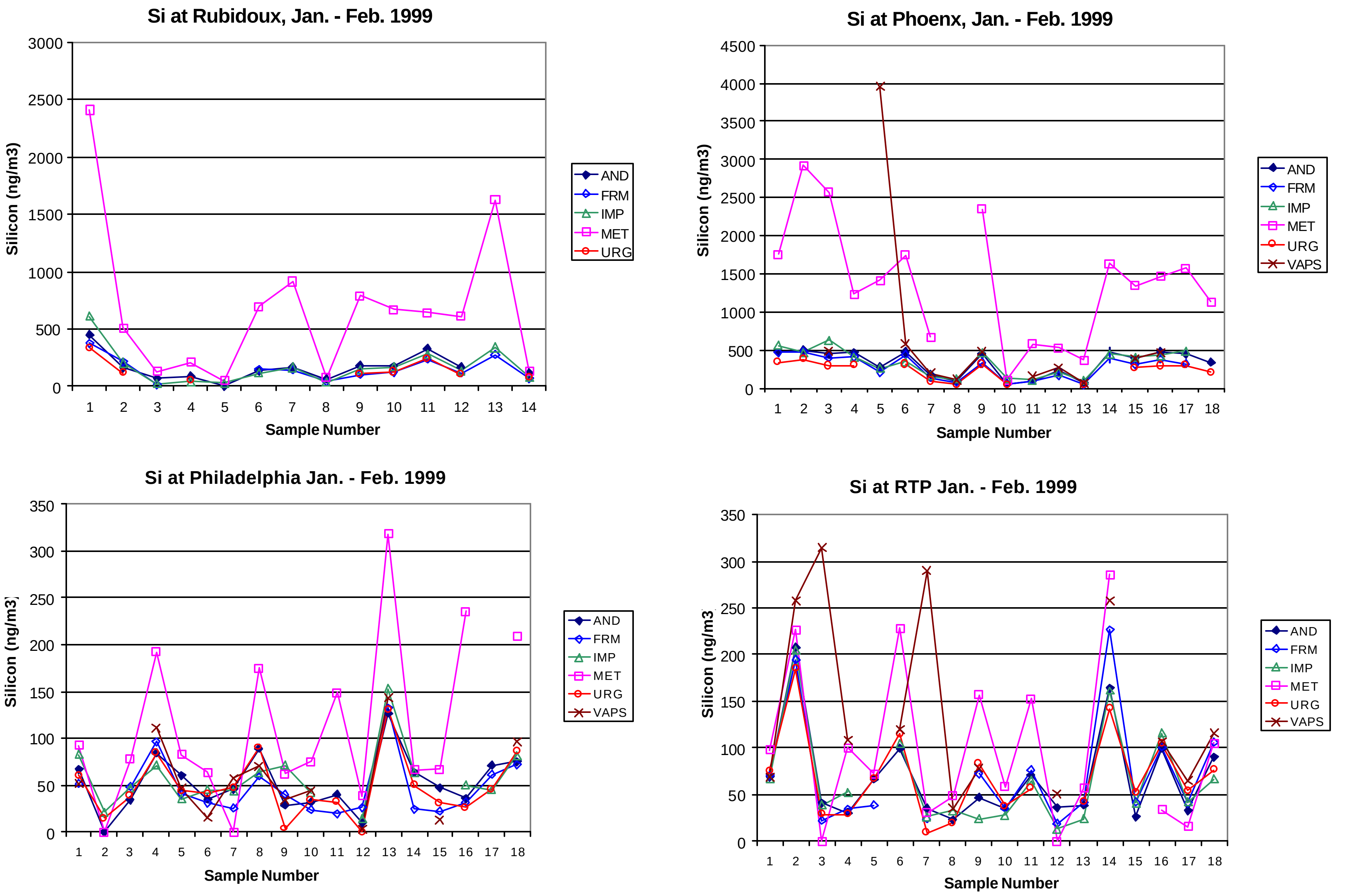


Figure II-3g. Time Series for Silicon.

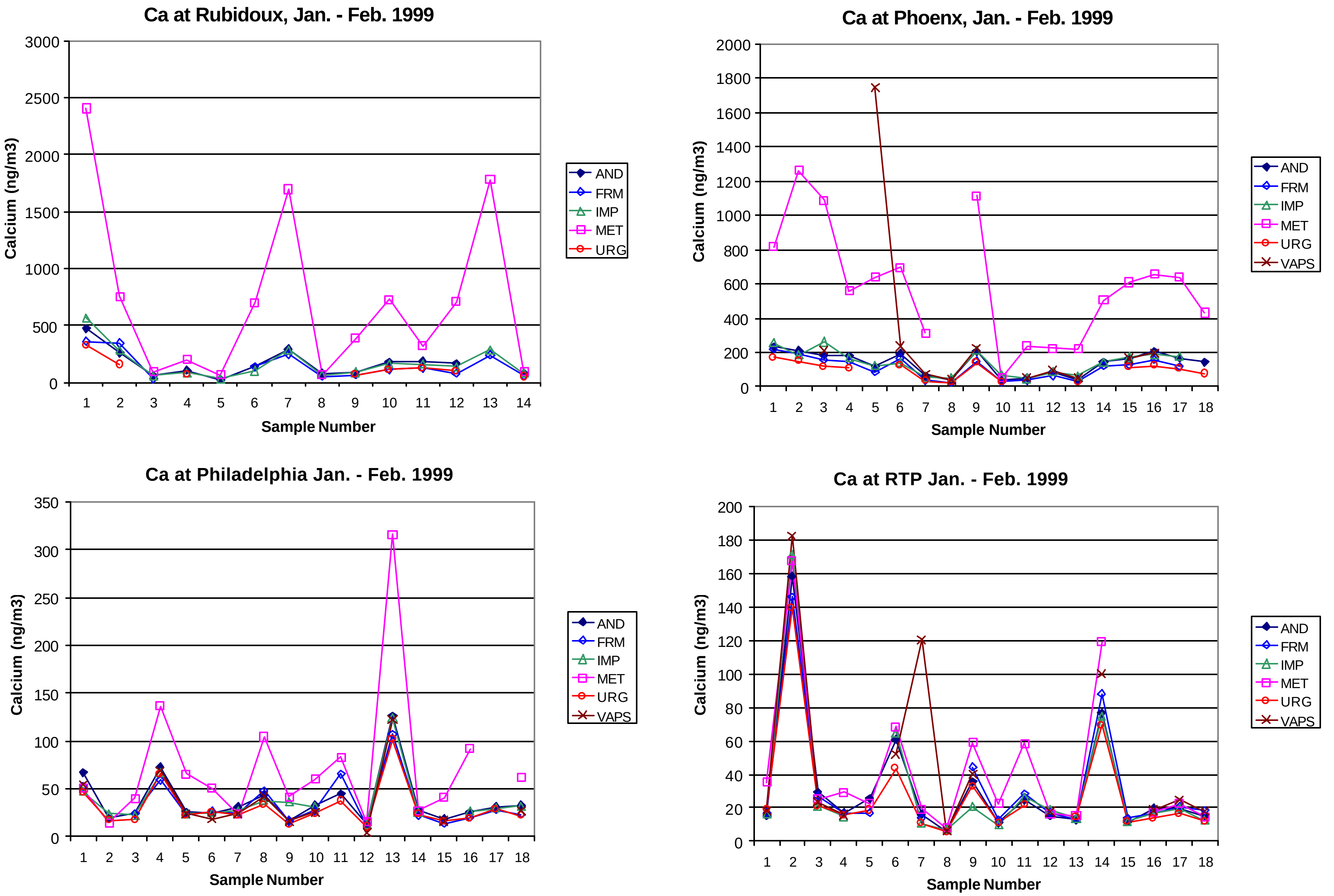


Figure II-3h. Time Series for Calcium.

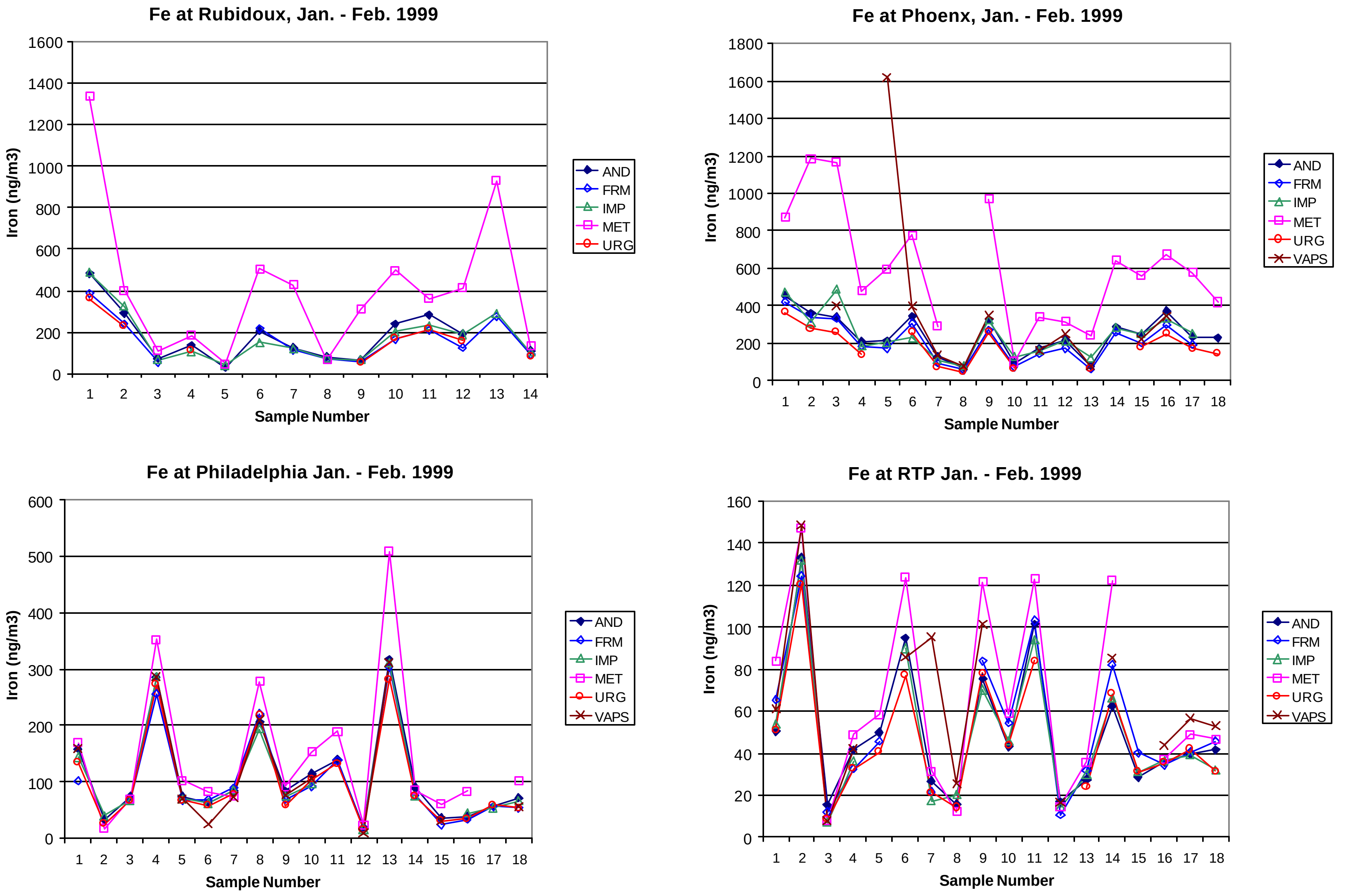


Figure II-3i. Time Series for Iron.

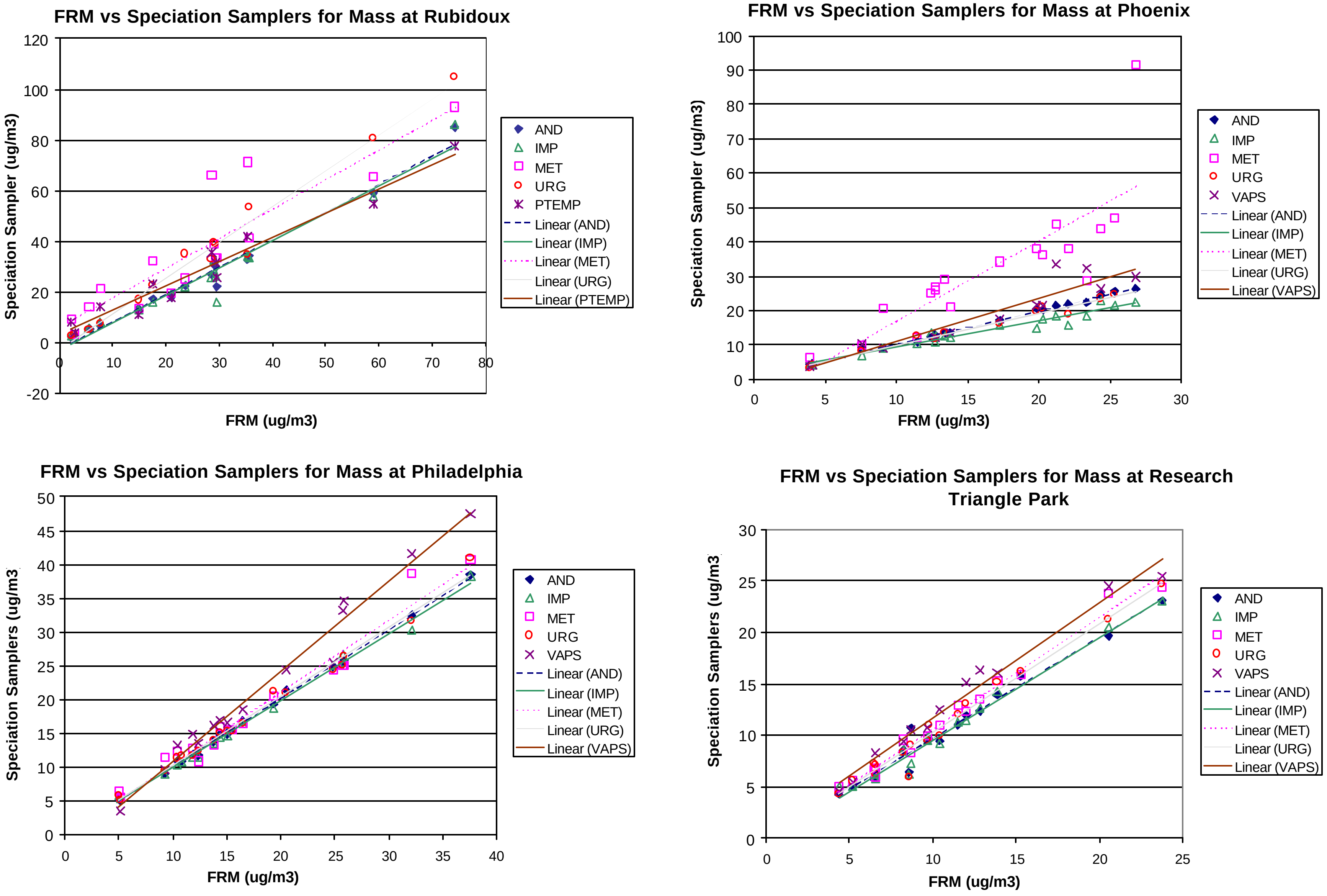
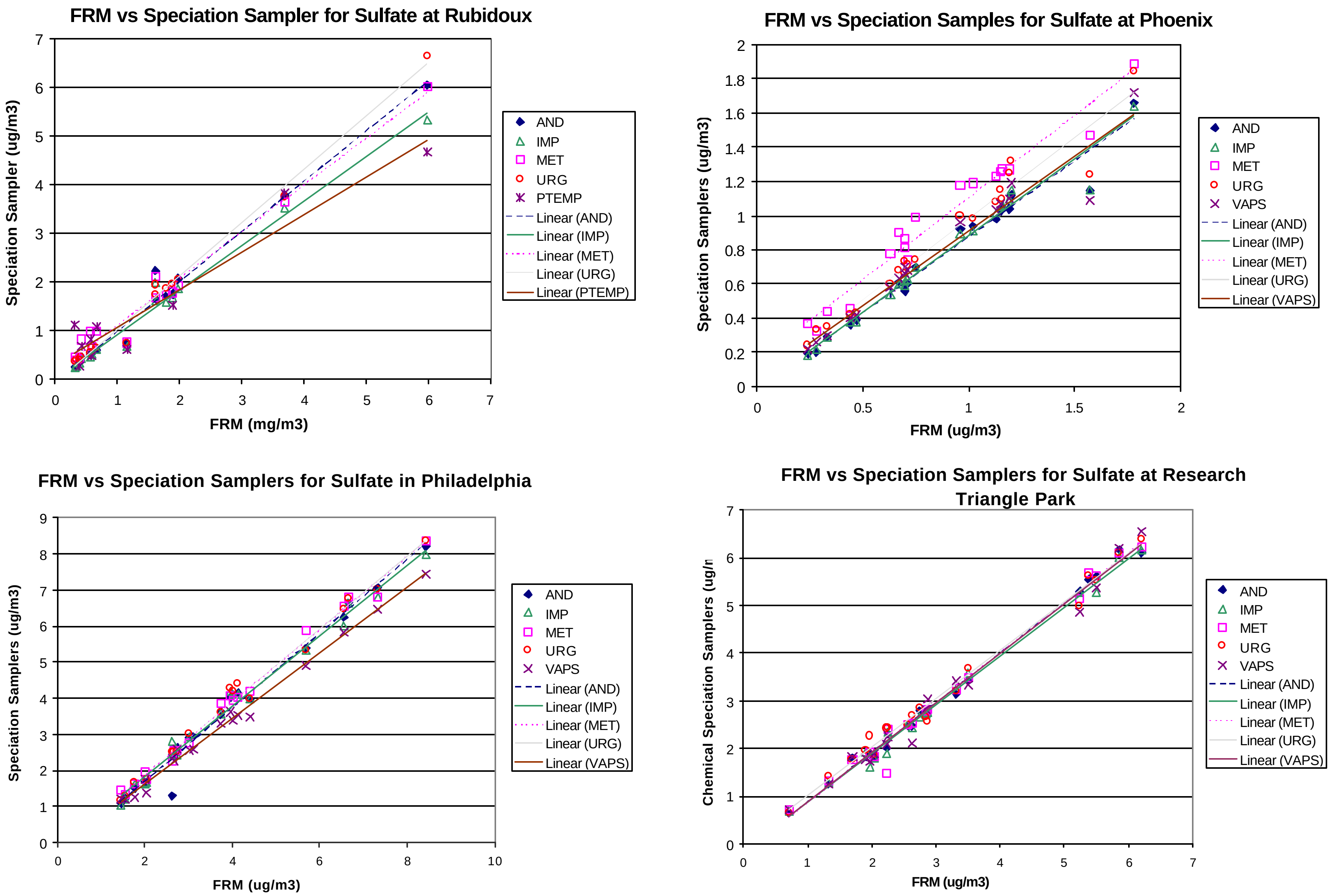


Figure II-4a. Regression Analysis for Mass.


FRM vs Speciation Sampler for Sulfate at Rubidoux

FRM vs Speciation Samples for Sulfate at Phoenix

FRM vs Speciation Samplers for Sulfate in Philadelphia

FRM vs Speciation Samplers for Sulfate at Research Triangle Park

Figure II-4b. Regression Analysis for Sulfate.

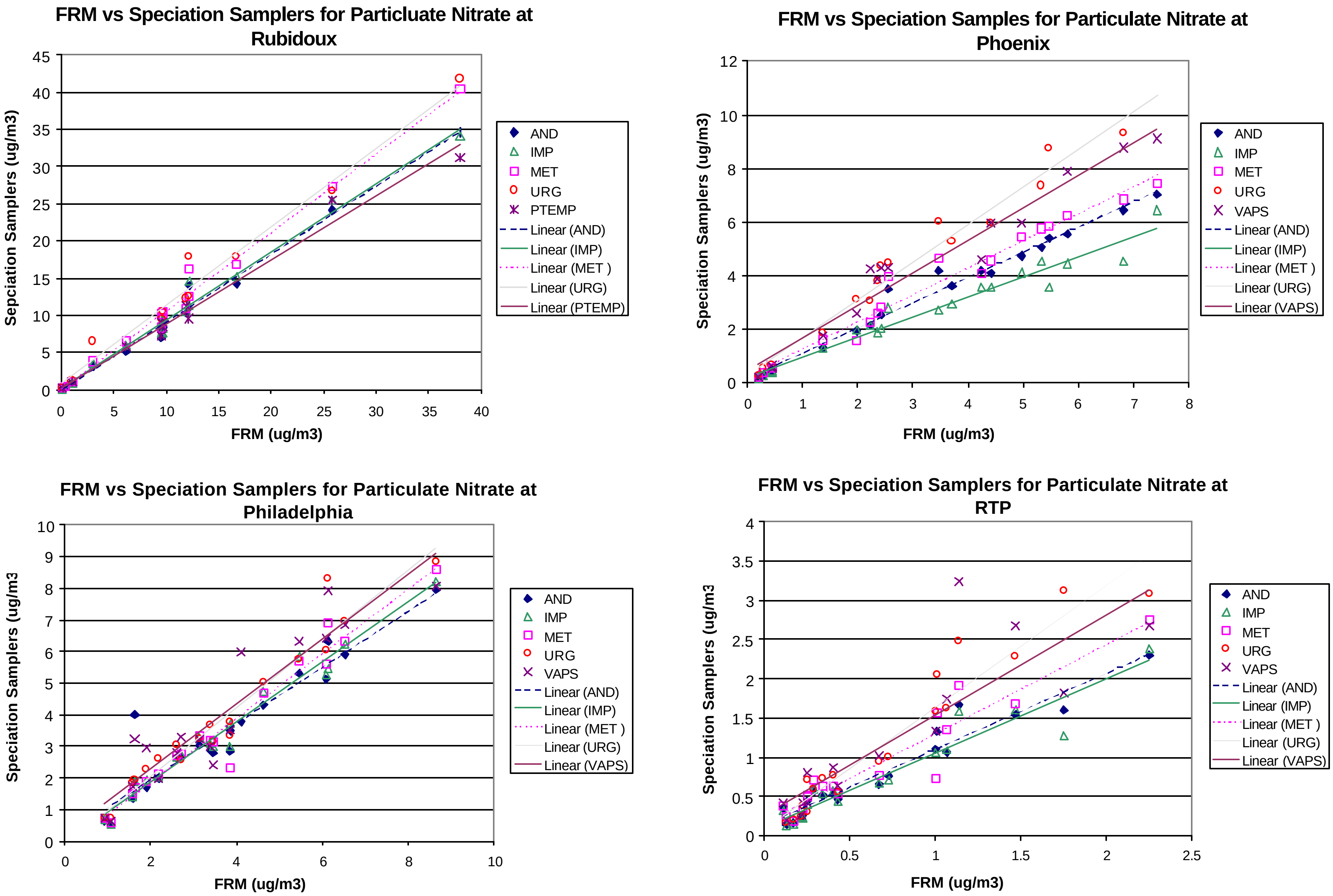


Figure II-4c. Regression Analysis for Nitrate.

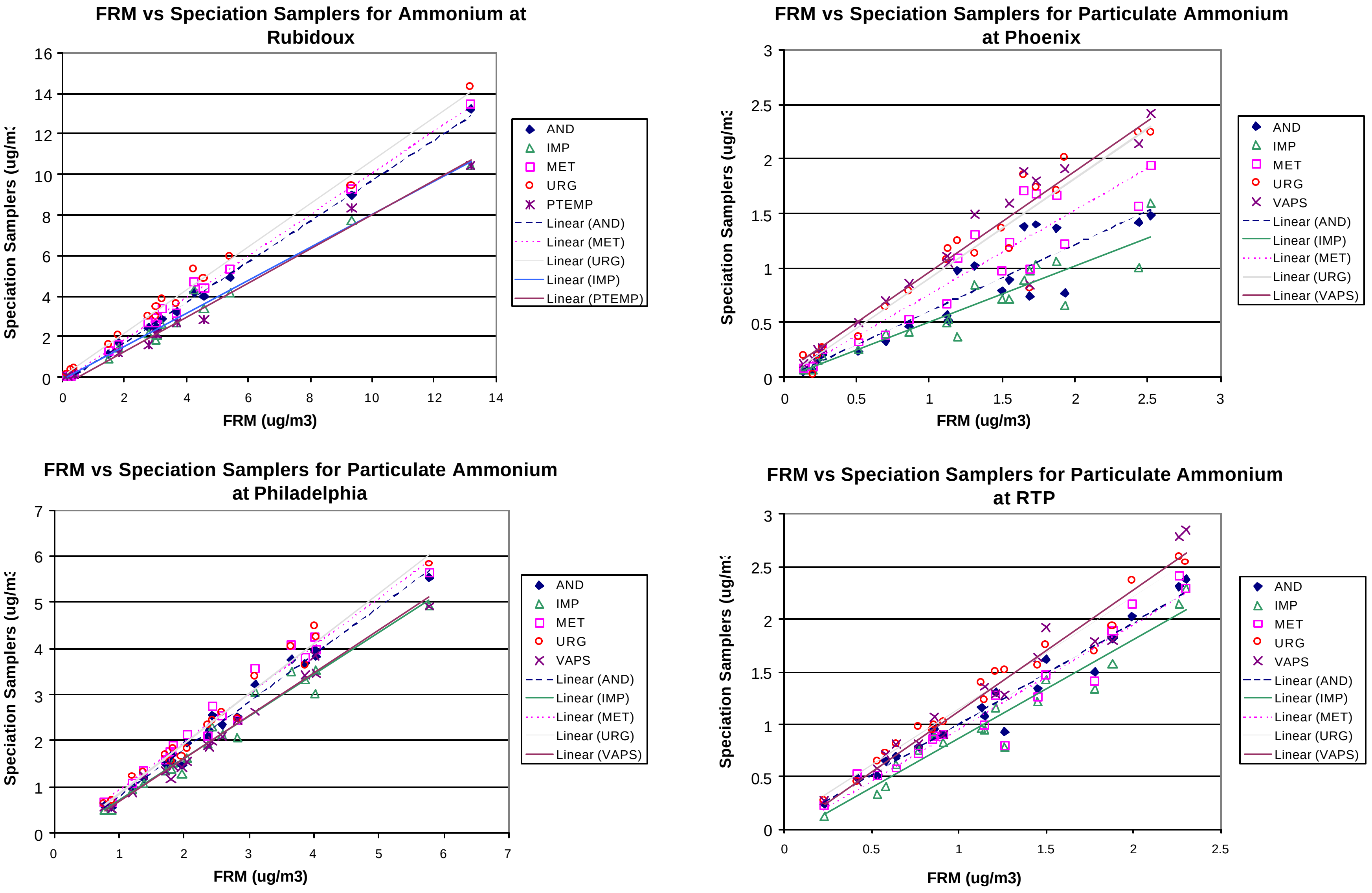


Figure II-4d. Regression Analysis for Ammonium.

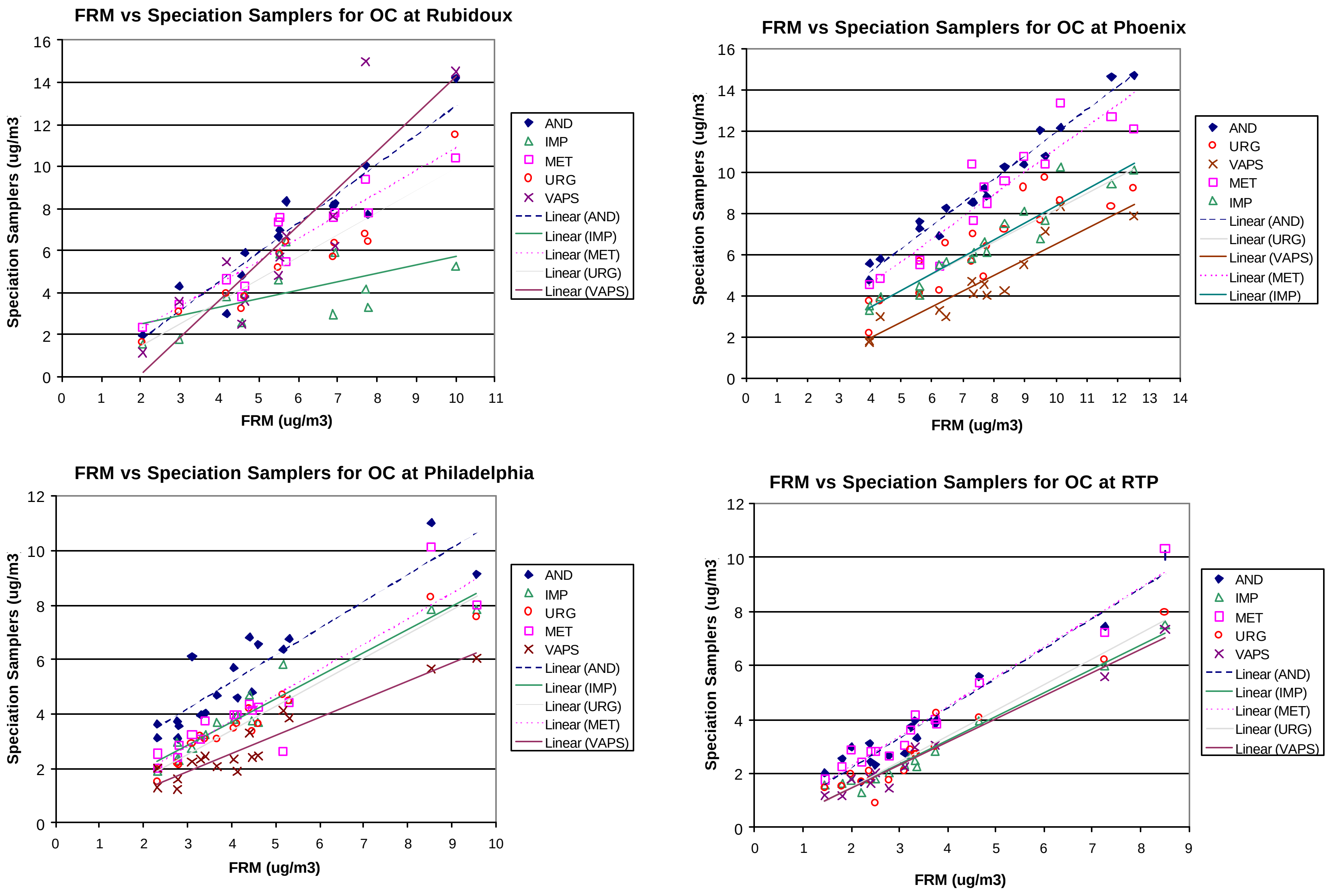


Figure II-4e. Regression Analysis for OC.

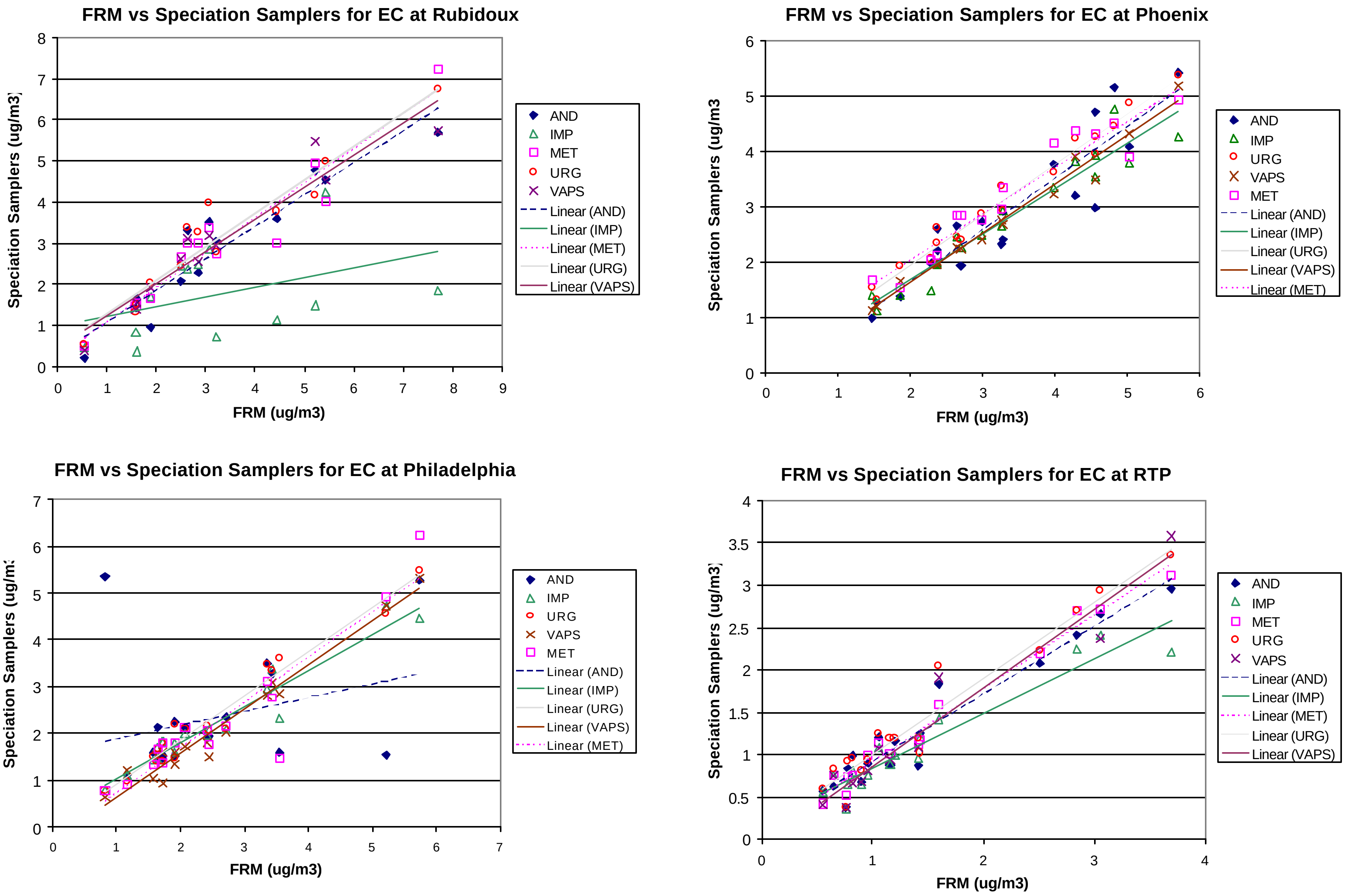


Figure II-4f. Regression Analysis for EC.

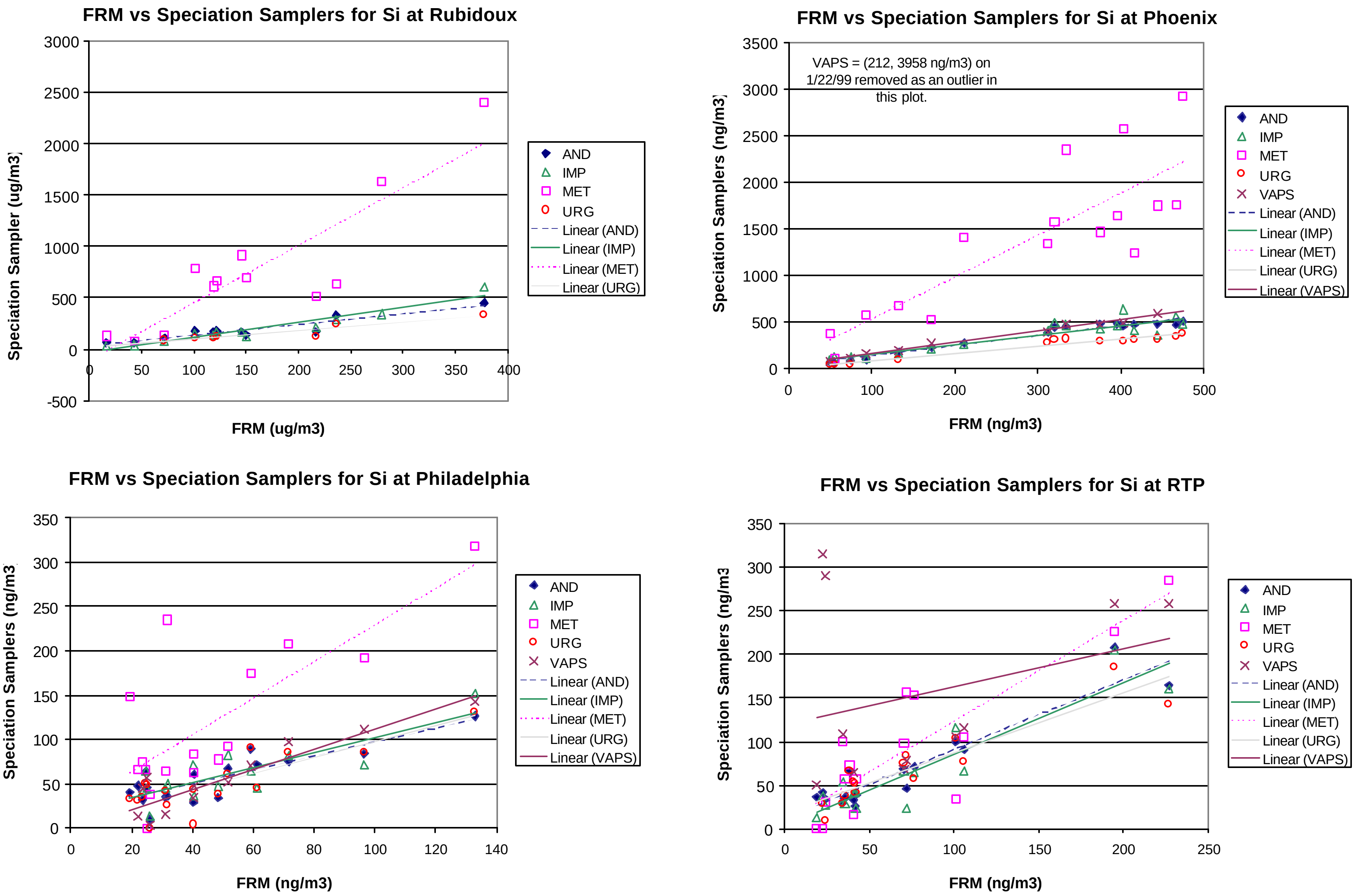


Figure II-4g. Regression Analysis for Si.

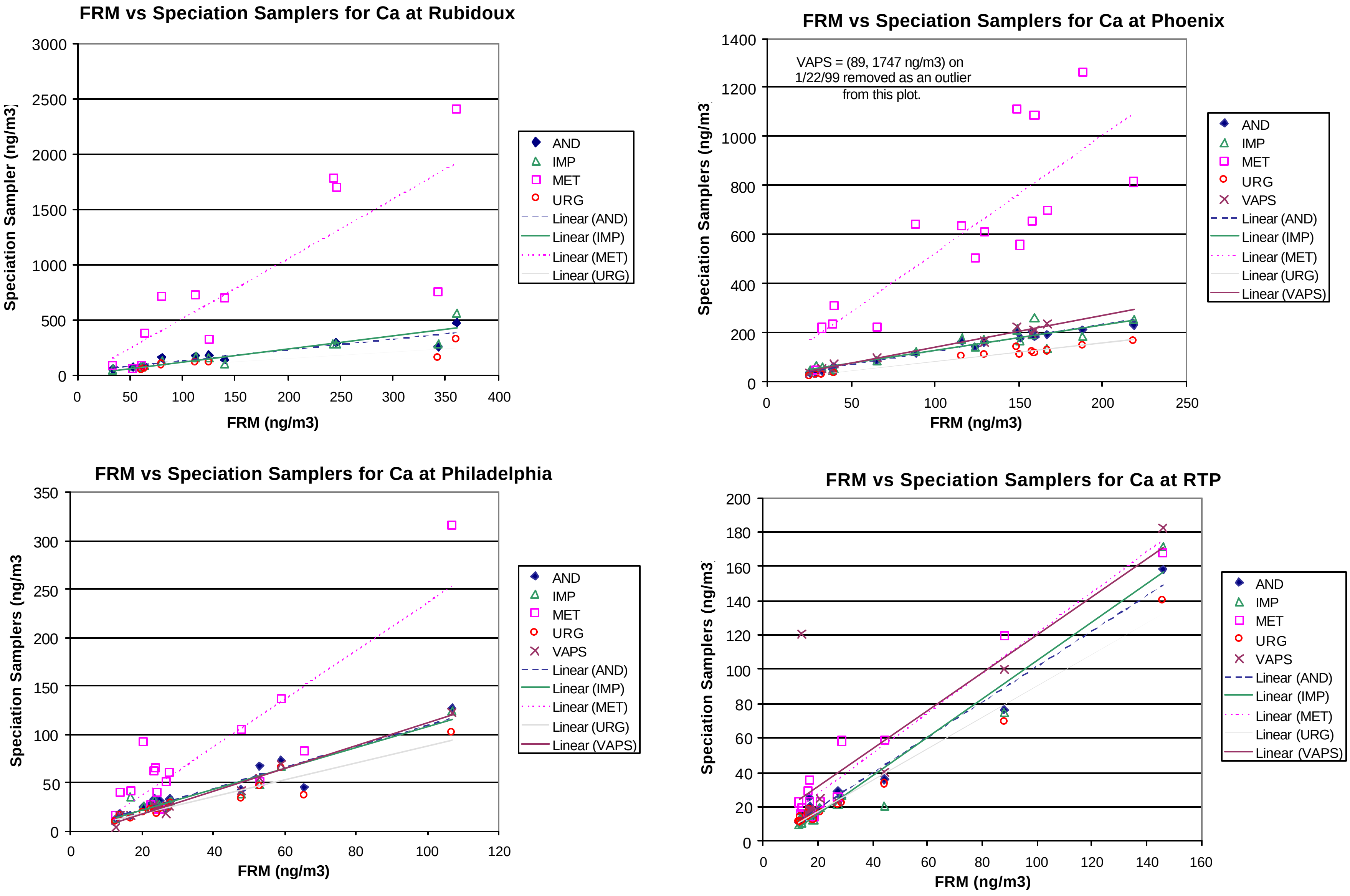
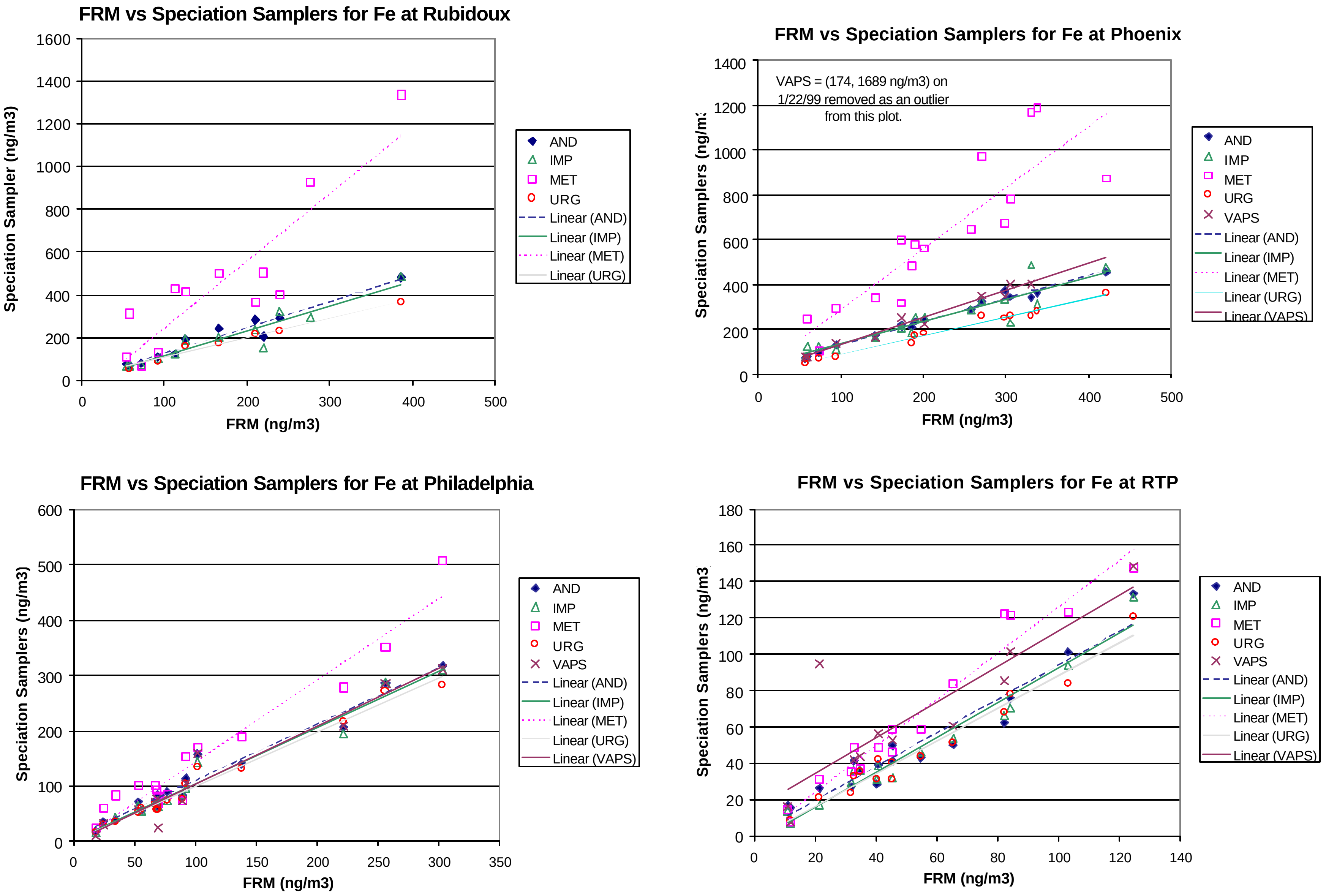


Figure II-4h. Regression Analysis for Calcium.


FRM vs Speciation Samplers for Fe at Rubidoux

FRM vs Speciation Samplers for Fe at Phoenix

FRM vs Speciation Samplers for Fe at Philadelphia

FRM vs Speciation Samplers for Fe at RTP

Figure II-4i. Regression Analysis for Iron.

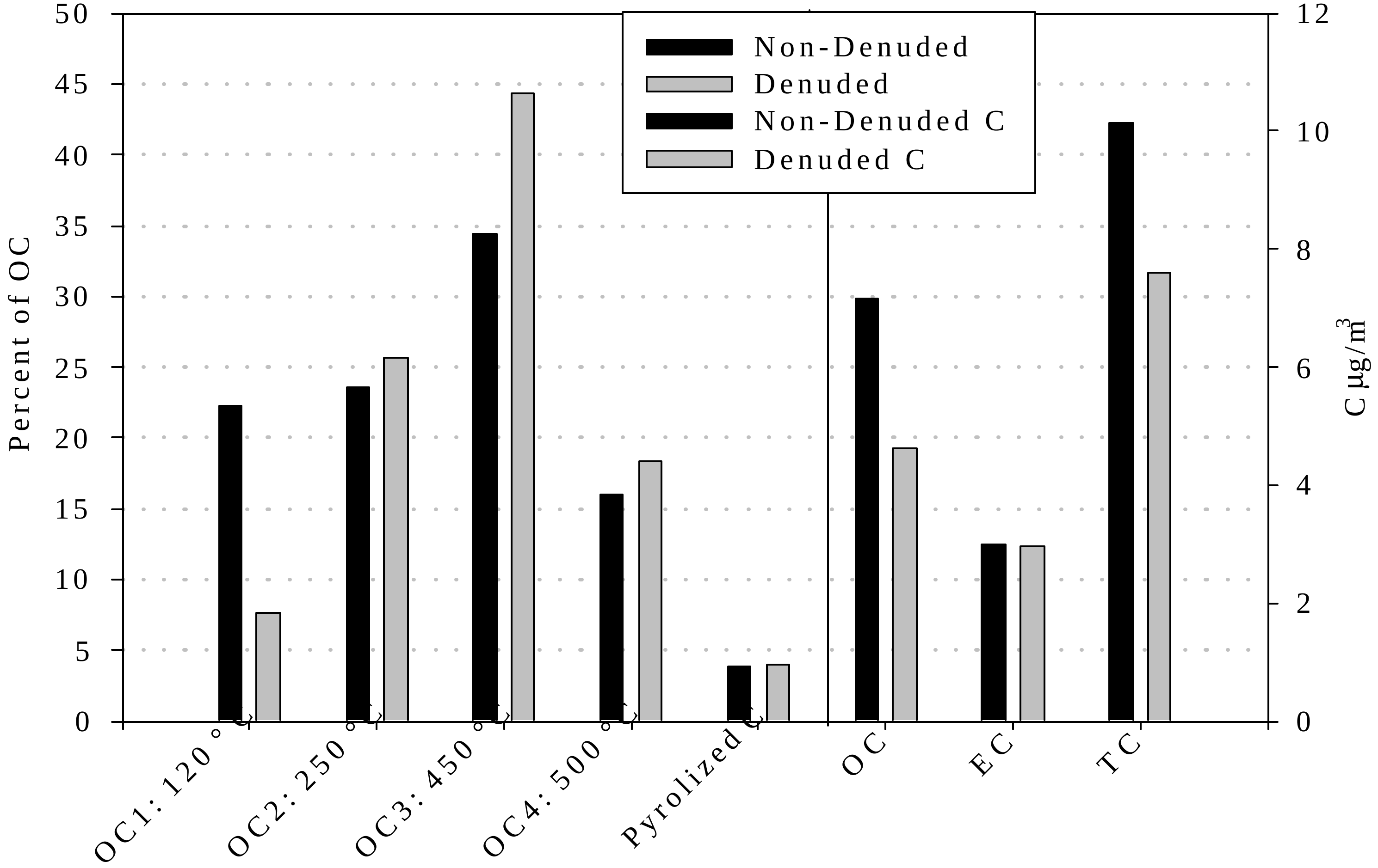


Figure II-5a. Average of Denuded (5 samplers) and Non-denuded (1 sampler) OC Samples as a Function of the TOR Carbon Fractions.

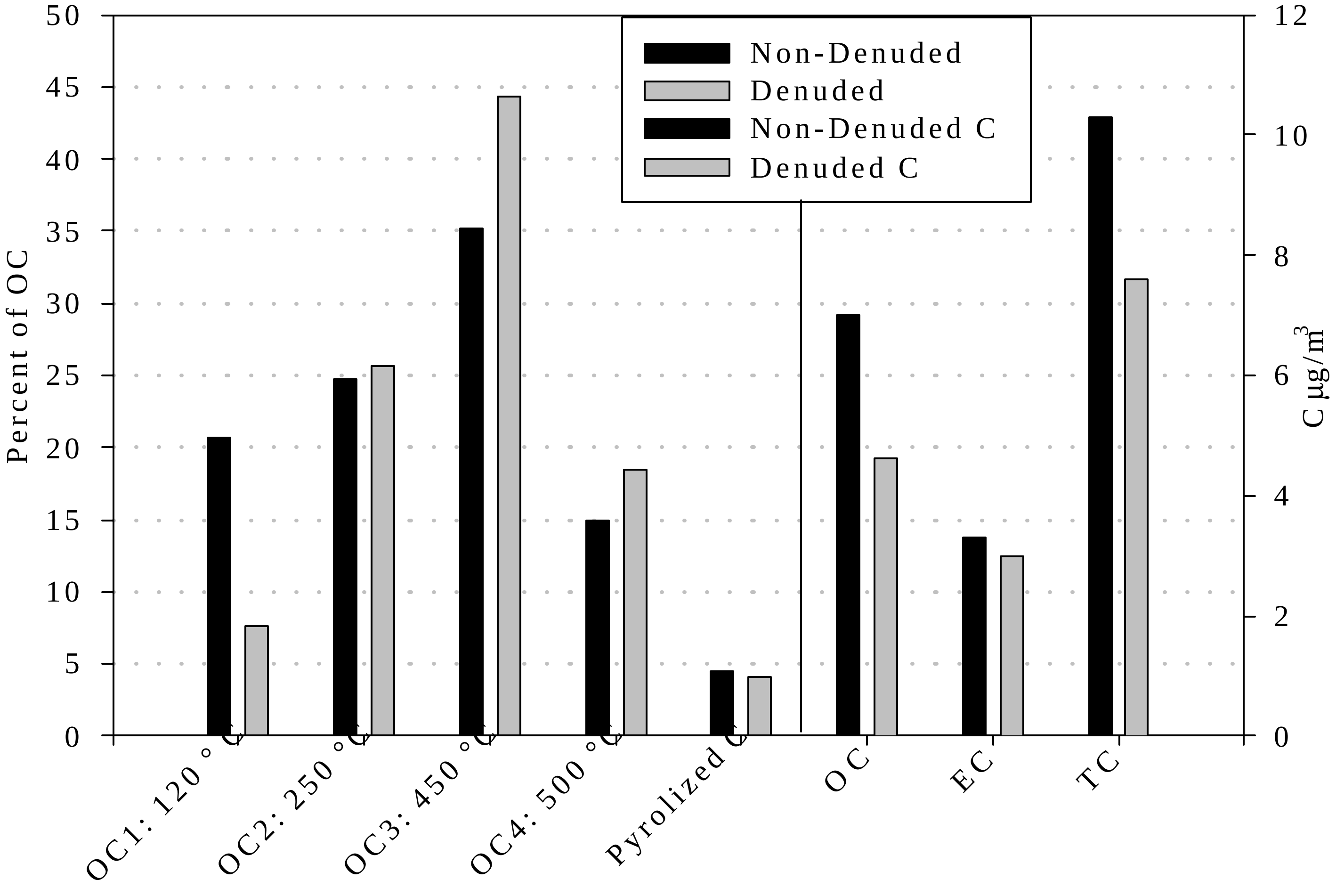


Figure II-5b. Denuded (15 LPM, 1 sampler) and Non-denuded OC (16.7 LPM, 2 samplers) Samples as a Function of the TOR Carbon Fractions.

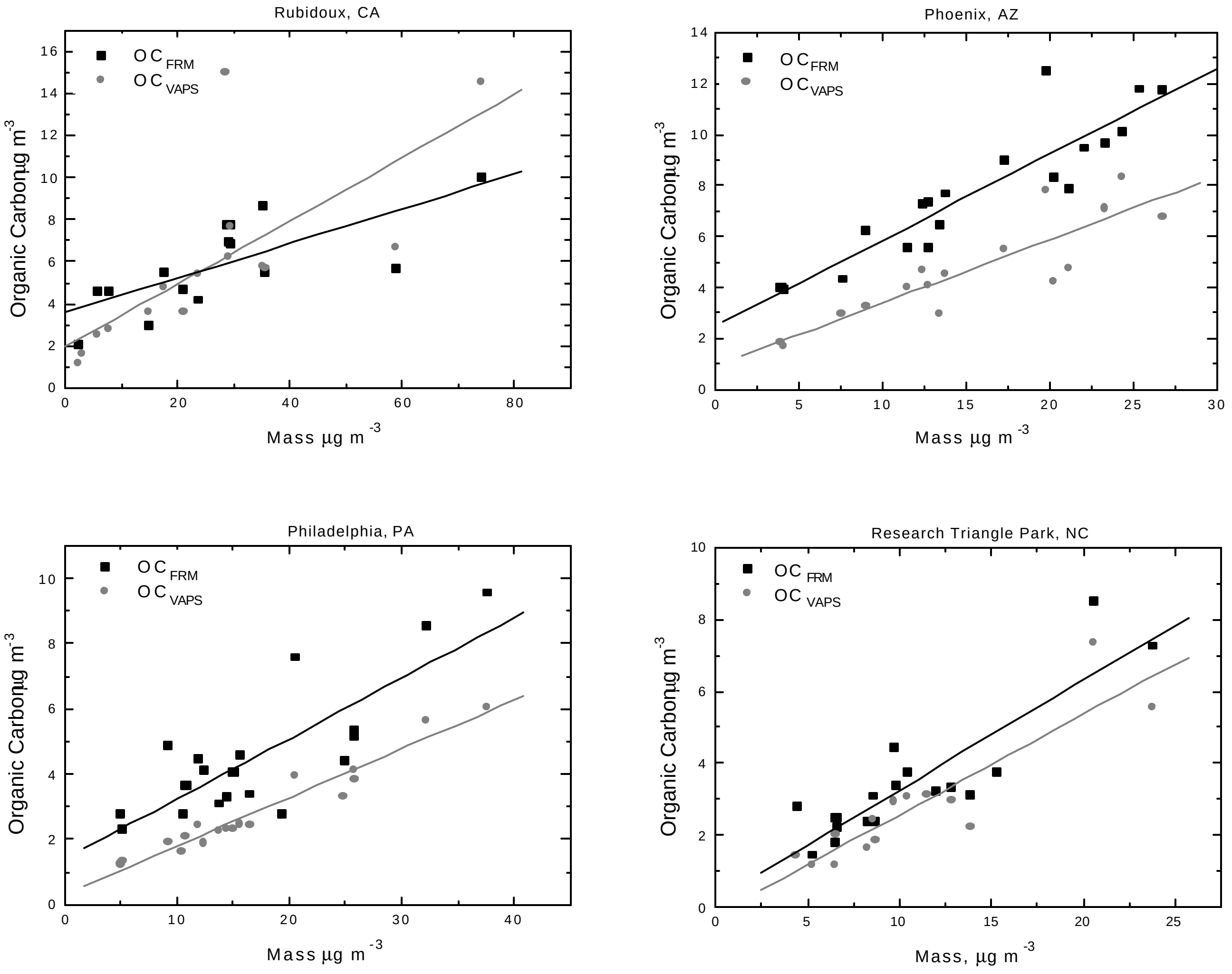


Figure II-6. Organic Carbon (OC) Concentrations Obtained from Both the FRM and the VAPS (Using an XAD Denuder in Front of the Quartz-fiber Filter to Remove SVOC) Compared to Total $PM_{2.5}$ Mass a Measured by the FRM. Regression Statistics as (Slope, Intercept, r): Rubidoux – FRM (0.082, 3.6, 0.728), VAPS (0.15, 2.0, 0.738); Phoenix – FRM (0.33, 2.5, 0.908), VAPS (0.25, 0.9, 0.875); Philadelphia – FRM (0.18, 1.4, 0.810), VAPS (0.15, 0.3, 0.971); RTP – FRM (0.30, 0.22, 0.878), VAPS (0.28, -0.21, 0.899).

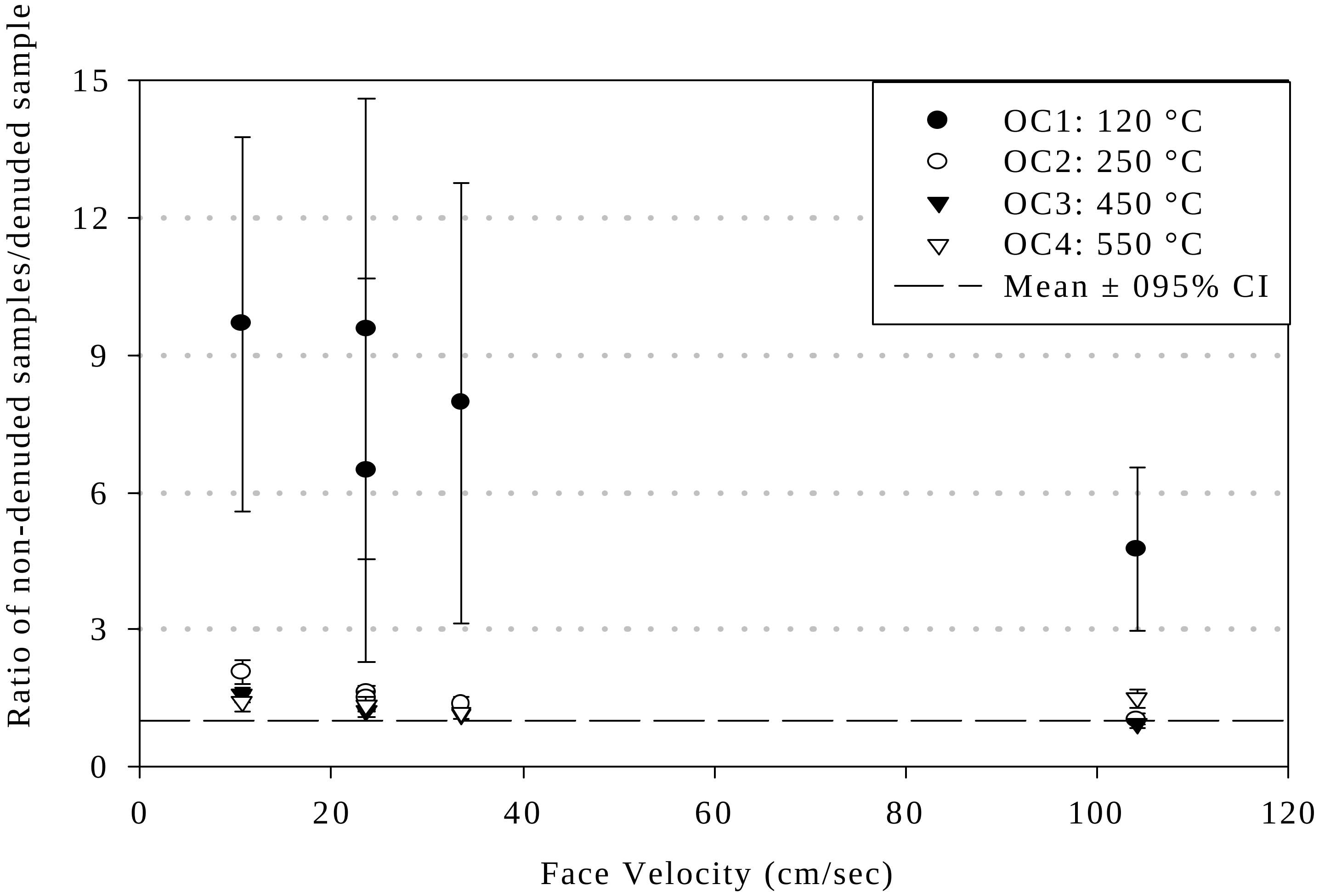


Figure II-7a. Organic Carbon as a Function of Face Velocity.

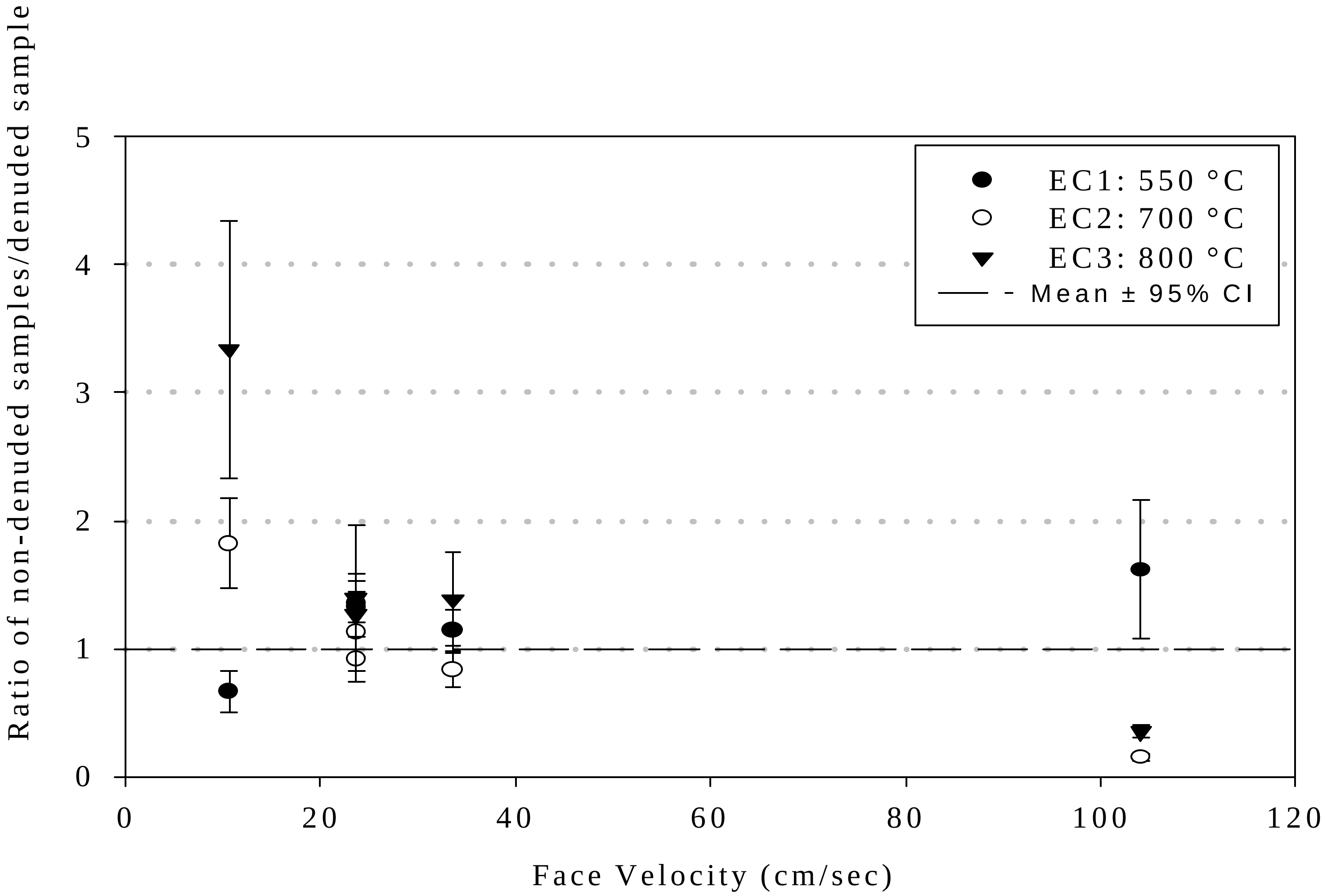


Figure II-7b. Elemental Carbon as a Function of Face Velocity.

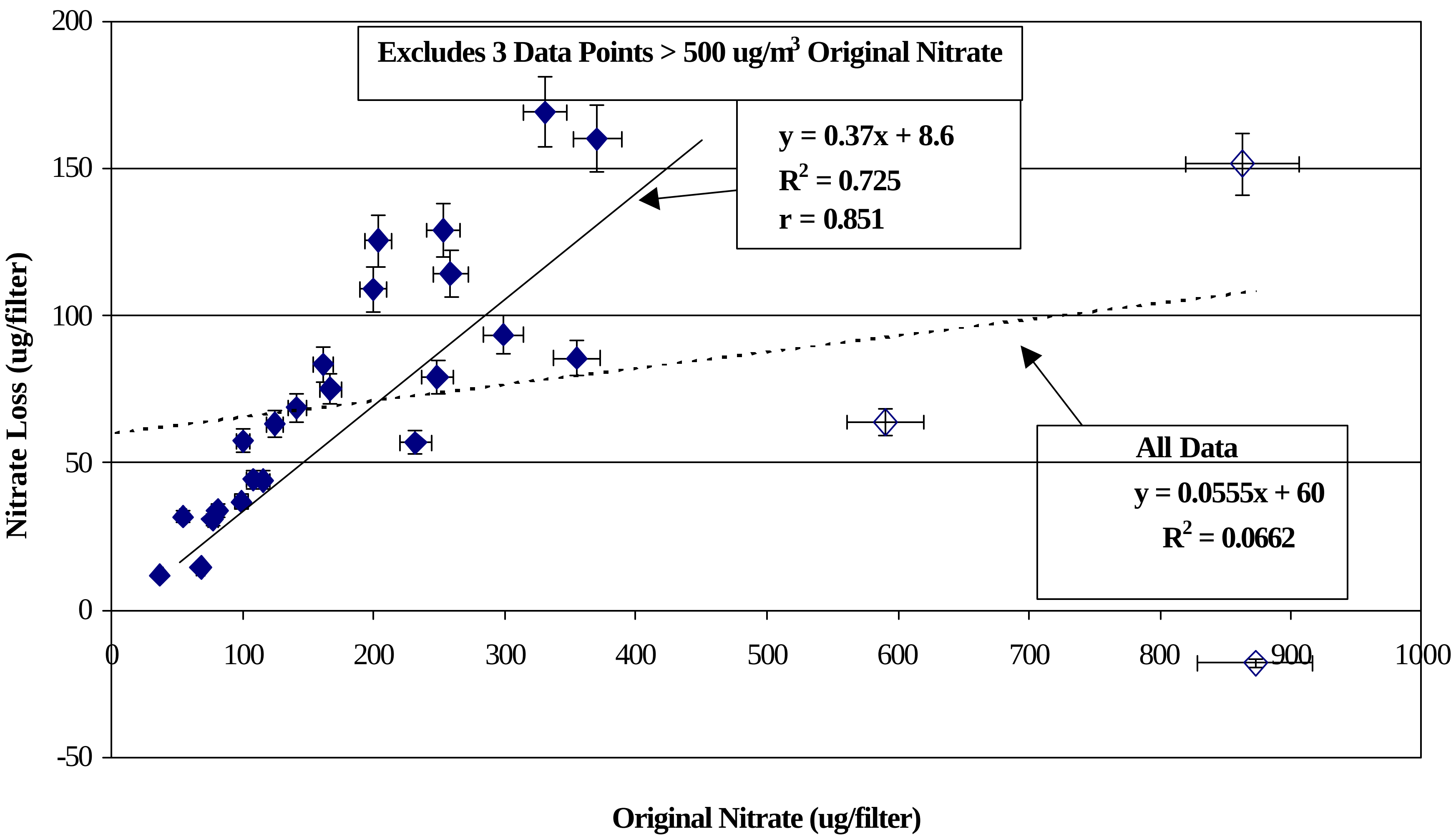


Figure II-8. Loss of Aerosol Nitrate from Teflon Filters Due to Vacuum XRF Analysis. Loss Is Difference Between Nitrate Concentrations on Collocated Teflon Filters Before and After XRF Analysis. Error Bars are 5% of the X- Value and 7% of the Y-Value Plotted.

Evaluation of $PM_{2.5}$ Chemical Speciation Samplers for Use in the EPA National $PM_{2.5}$ Chemical Speciation Network

Volume II – Appendices

Final Report

15 July 2000

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List of Appendices

Appendix A

Sample Analysis Methods for Chemical Speciation

from

PARTICULATE MATTER ($PM_{2.5}$)
SPECIATION GUIDANCE
DOCUMENT

DRAFT

13 July 1998

US Environmental Protection Agency
Monitoring and Quality Assurance Group
Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
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7.0 SAMPLE ANALYSIS METHODS

With the goal of ensuring data quality for several thousand filter analyses per year which may utilize a range of analytical methods, it is critical to establish an analytical laboratory framework which is consistent to support these needs. One key aspect of the framework is the establishment of a standardized of SOPs for speciation analyses. The SOPs must be based on analytical methods with proven application to the analysis of ambient particulate matter filter samples. In addition to guidance on sampling and handling, the EPA will also develop guidance and documentation for SOPs on the laboratory analysis of the target analytes given in Table 3-1 of the Guidance Document (EPA, 1999). The guidance will include laboratory quality assurance guidelines specific to the methods of analysis and guidelines on standardized data reduction, validation, sample handling, chain-of-custody, and reporting formats. The EPA plans for the speciation data to be submitted to the Aerometric Information Retrieval System (AIRS) data base. The U.S. EPA is developing laboratory SOPs for the NAMS that are complementary to the techniques used by various agencies and research groups operating ambient air particulate matter speciation programs.

The operational schedule for providing the speciation laboratory support services begins with development of a program team of EPA Office of Air Quality Planning and Standards (OAQPS) and Regional Office personnel. The OAQPS will lead the development of the required guidance information and the SOPs with input from the Office of Research and Development (ORD), EPA Regional Offices, and the $PM_{2.5}$ monitoring technical community. Initial deployment of approximately 50 of the speciation monitors is projected for the second quarter of calendar year 1999. Allowing for time by site operators to be trained in the use of the monitors, we project that the laboratory services support portion of the National $PM_{2.5}$ Speciation Program will be in place by May of 1999. The speciation analytical guidelines developed by EPA can also be used by State laboratories with appropriate facilities to provide local support, if appropriate, for an individual State-level monitoring network. In addition EPA is studying the process of evaluating alternative test methodology which may be proposed by States. In such a process, an equivalency methodology guideline would have to be developed that can be used by States to prove that their proposed method performs well as defined by the guidelines.

The methods used for analyses of the filter media include gravimetry (electro-microbalance) for mass and various instrumental methods for determining the chemical composition of the particles. In addition to chemical analyses, special measurement needs may include determining particle size and morphology through optical and/or electron microscopy.

A national laboratory services support program consisting of contracted services with up to three qualified laboratories capable of providing consistent laboratory service support for all of the target analytes will be developed. The extent of the services will depend upon capacity needed, as well as the level of participation by State and local government laboratories for providing analytical services. Analytical support from the contract laboratories will be accessed through three EPA Regional Project Officers or Delivery Order Project Officers (DOPOs) who will be located at Regional Offices in the eastern (Region 1), Midwestern (Region 5), and western (Region 8) parts of the country. The Project Officers will coordinate site needs for those States located in the three geographic areas. Selected EPA Regional laboratories will operate in a quality assurance role for the contractor laboratories involved in the speciation program. A flow diagram of the sample analysis delivery order process is given in Figure A-1.

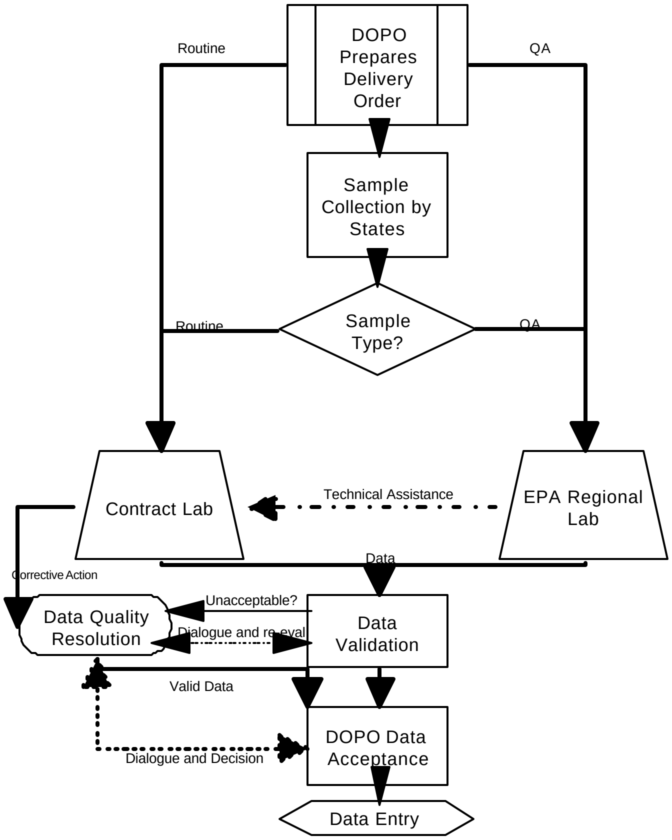


Figure A-1. Flow Diagram of the Sample Analysis Delivery Order Process

The most commonly applied aerosol analyses methods can be divided into the following categories: mass, elements, ions, and carbon. It is possible to obtain several different analyses from the same substrate, but not possible to obtain all desired chemical species from a single substrate; therefore, the appropriate filter media, sampling hardware, and analysis methods must be combined. Depending on the study objectives and sources in an area, different chemical species may need to be added or omitted. A flow diagram of filter processing and analysis activities for the NAMS is shown in Figure A-2.

The following sections outline the filter analysis methods for the target chemical species categories of elements, ions, and organic carbon.

7.1 Elemental Analysis

Energy dispersive X-ray fluorescence (EDXRF) is the analytical method of choice to characterize the elemental composition of the aerosol deposits on PTFE filters for the $PM_{2.5}$ NAMS chemical speciation program. Interest in elemental composition is commonly derived from concerns about health effects and the utility of these elements to trace the sources of suspended particles or source characterization. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which causes volatile compounds (nitrates and organic compounds) to evaporate. Volatilization will not be an issue for the NAMS since PTFE filters will not be subsequently analyzed for volatile species.

In XRF the filter deposit is irradiated by high energy X-rays which causes the ejection of inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are determined by comparing photon counts for a sample with those obtained from thin-film standards of known concentration. XRF methods can be broadly divided into two categories: wavelength dispersive XRF (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive x-ray fluorescence (EDXRF), which uses a silicon semiconductor detector.

The WDXRF method is characterized by high spectral resolution which minimizes peak overlaps. WDXRF requires high power excitation to overcome low sensitivity which results in excessive sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

The type of filter is important and thin membrane filters (PTFE) are required so that the background is low and penetration of particles into the matrix of the filter is small. The XRF provides rapid, simultaneous, and nondestructive detection of the target elements from Na to Pb. Advantages of using XRF are the quantitative analysis of bulk elemental composition, the ability to perform trace level particulate analysis with sensitivity to ppm levels, and the availability of instrumentation. The XRF method of analysis employs an energy dispersive spectrometer. Analysis atmospheres are selectable with choices of helium or air; helium is used for all target elements except Gd where air is employed because it gives a lower background. Vacuum is not used, therefore, avoiding the loss of volatile compounds.

Calibration is by far the most complicated task in the operation of the XRF. Re-calibration is only performed when a change in fluorescors or x-ray tubes is made or a serious instrument malfunction occurs. Three types of XRF standards are available for calibration: vacuum deposited thin film elements; polymer films; and NIST thin-glass films. The vacuum deposited thin film standards are available for almost all elements analyzed and are used to establish calibration curves. Some standards have high inherent volatility and do not serve well as calibration standards. These are selenium (Se), bromine (Br), mercury (Hg), and elemental arsenic (As). The same set of standards is used every time the spectrometer is calibrated. These standards are sufficiently durable to last many years. Polymer films contain two elements in the form of organo-metallic compounds dissolved in the polymer as described in Dzubay et al., 1988. These standards are available for elements with atomic numbers above 21 (titanium or heavier). The polymer films and NIST standards are typically used for quality control measures. NIST produces reference materials for iron, lead, potassium, silicon, titanium, and zinc (SRM 1833).

The sensitivity of this method is on the order of few ng/m$_3$ for 24-hour samples (flow rates of 10-20 liters per minute). Nonetheless, quite often environmental samples have elemental measurements below the detection limit of this method. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. It should be mentioned that, during the analysis using XRF, the sample is introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. This volatilization is important if the Teflon7 filter is to be subjected to subsequent analyses.

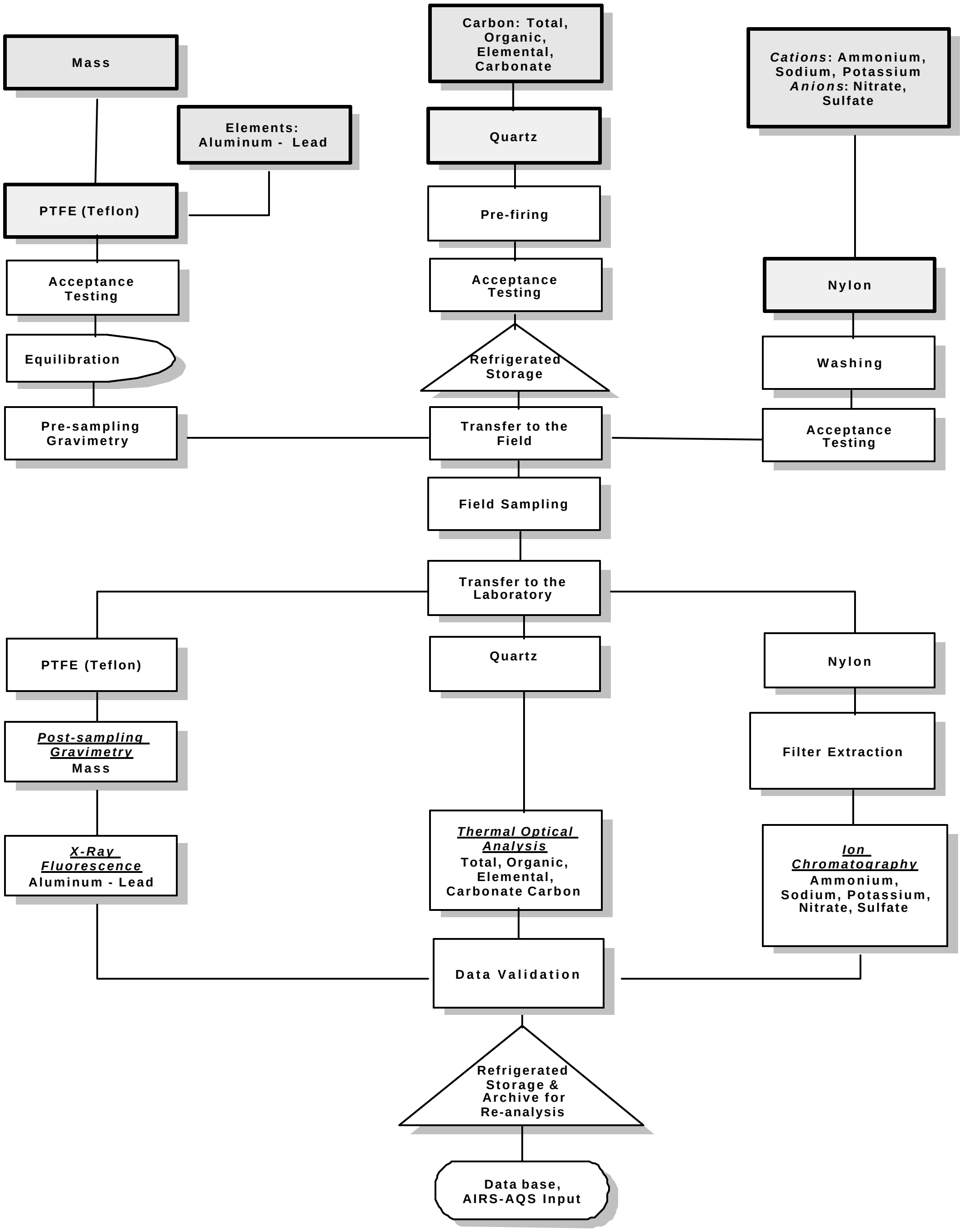


Figure A-2. Flow Diagram of Filter Processing and Analysis Activities for the NAMS

7.2 Ion Analysis

Aerosol ions refer to chemical compounds which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and non-soluble fractions as in the case of soluble potassium. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Polyatomic ions such as sulfate, nitrate, ammonium, and phosphate are quantified by methods such as ion chromatography (IC). Simple ions, such as chloride, and fluoride may also be measured by IC along with the Polyatomic ions. When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by micro titration. It is important to keep the filter away from ammonia sources, such as human breath, to minimize neutralization of the acidic compounds.

Applied to aerosol samples, the anions and cations are most commonly analyzed by IC. IC can be used for anions (fluoride, phosphate, chloride, nitrate, sulfate) and cations (potassium, ammonium, sodium) by employing separate columns. All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water and then filtered to remove insoluble residues prior to analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient $PM_{2.5}$ samples. IC is the method of choice for the $PM_{2.5}$ NAMS speciation program for the analysis of the target cations (ammonium, sodium, and potassium) and anions (nitrate and sulfate).

A major sampling requirement for analysis of water-soluble species is that the filter material be hydrophilic, allowing the water to penetrate the filter and fully extract the desired chemical components. A nylon filter is used for volatilized and particulate nitrate and sulfate anions and a pre-fired quartz fiber filter is used for the ammonium, sodium, and potassium cations. The anions are extracted with a sodium carbonate/sodium bicarbonate solution, and the cations are extracted with a dilute hydrochloric acid/distilled water solution.

In IC, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electro-conductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites.

The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column where the cations are exchanged for H^+ ions. Species are then detected as their acids by a conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract with low detection limits.

The cations are analyzed in the same manner except the sample extract passes through a surface-sulfonated ion exchange resin where separation occurs. After separation and prior to detection, the cations enter a suppressor column where all the anions are exchanged for OH^- ions. The species are then detected as their bases (hydroxides) by a conductivity meter. Concentrations of ions and cations are proportional to the conductivity changes.

7.3 Particulate Organic Speciation

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. $PM_{2.5}$ samples were collected at four urban locations in southern California in 1982 to quantify several individual organic compounds. This study identified and quantified over 80 individual organic compounds in the $PM_{2.5}$ fraction, including n-alkanes, n-alkanoic acid, one n-alkenoic acid, one n-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons, polycyclic aromatic ketones, polycyclic aromatic quinones, diterpenoid acids, and some nitrogen-containing compounds. In general, the same type of organic compounds, although in different proportions, are found in direct emissions from various sources such as diesel and gasoline powered vehicle exhaust, charbroilers and meat cooking operations, cigarette smoke, biogenic sources, etc. Thus, organic compounds are potentially valuable tracers for characterizing different emission sources as well as for atmospheric transformation processes.

7.3.1 Carbon Analysis

Three classes of carbon are typically measured in ambient aerosol samples collected on pre-fired quartz-fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate-source carbon [i.e., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] is determined from a separate filter section after acidification. Without acidification, the determination of carbonate carbon is not specific and is detected as either organic or elemental carbon.

Two thermal-optical methods currently are in use for the analysis of carbonaceous aerosols. The measurement principle is fundamentally the same, but the methods differ with respect to calibration, analysis time, temperature ramping and settings, types of carbon speciated, and pyrolysis correction technique. The method=s pyrolysis correction feature allows correction for the char that forms on the filter during analysis of some materials (e.g., cigarette smoke). Correction for pyrolysis is made by continuously monitoring the filter transmittance (NIOSH Method 5040) or reflectance (TOR) throughout the analysis.

For the NAMS chemical speciation program, total, organic, elemental, and carbonate carbon will be determined by thermal/optical instrumentation specified in NIOSH Method 5040 (NIOSH,

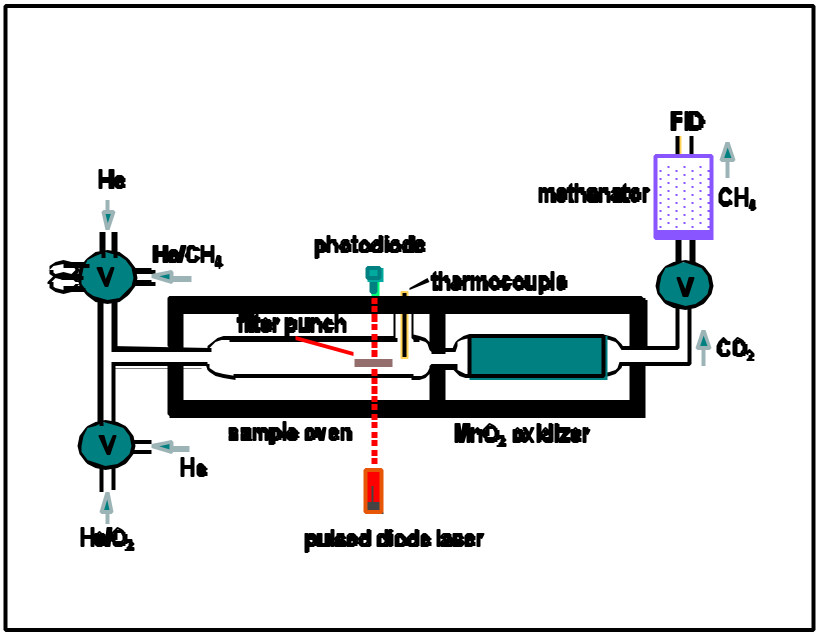


Figure A-3. Schematic of the Thermal-optical Analyzer Evaluated by NIOSH

1996, 1998) and described in the literature (Birch and Cary, 1996). Method 5040 was developed for occupational monitoring of diesel particulate, but its evaluation also included a round-robin study involving a variety of carbonaceous aerosols (Birch, 1998). The thermal-optical method is applicable to nonvolatile, carbon-containing species only. Thermal-optical analyzers are practical, economical, and are routinely used for environmental and occupational monitoring of carbonaceous aerosols. Although the number of commercial laboratories currently is limited, an adequate number (3 in the U.S.) are available to cover the analytical demands of this program.

Thermal-optical analyzers operate by liberating carbon compounds under different temperature and oxidation environments. A small portion (or punch) is taken from a quartz-fiber filter sample and placed in the sample oven. The oven is purged with helium and the temperature is then stepped to a preset value. Volatilized compounds are converted to carbon dioxide (CO_2) in an oxidizer oven (MnO_2 at 870C or higher), the CO_2 is subsequently reduced to methane (CH_4) in a methanator (nickel-impregnated firebrick heated to ~550C in a stream of hydrogen), and CH_4 is quantified by a flame ionization detector (FID). In the second part of the analysis, an oxygen-helium mix is introduced and the remaining carbon is removed through combustion and quantified in the same manner. A schematic of the thermal-optical analyzer evaluated by NIOSH researchers is shown in Figure A-3; an example of the instrument=s output, called a “thermogram,” is given in Figure A-4.

In NIOSH Method 5040, the sample oven is purged with helium and the temperature is stepped (to 250, 500, 650 and 850C) to volatilize the organic and carbonate-source carbon. It is critical to ensure that trace oxygen is not present during the first part of the analysis. Potential sources of oxygen include leaks and inadequate helium gas purification. If present, trace oxygen will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. In the second part of the analysis, the temperature is lowered, a 2% oxygen/98% helium mix is introduced, and the temperature is then stepped to a maximum of 940C. At the end of the analysis, a calibration gas standard (CH_4) is injected. Correction for pyrolysis is made by continuously monitoring the filter transmittance throughout the analysis. The point at which the filter transmittance returns to its original value is defined as the split between organic and elemental carbon. Designation of the split in this manner allows assignment of pyrolyzed organic carbon to the organic fraction.

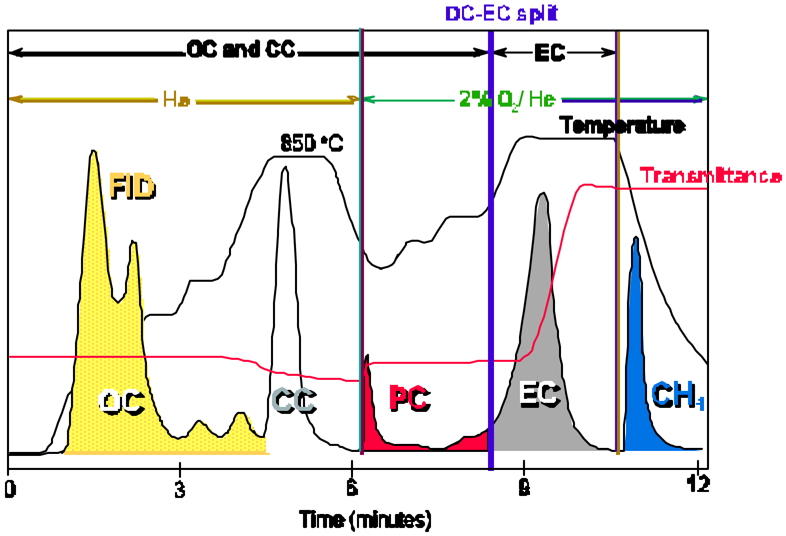


Figure A-4.. Sample Output of Thermal-Optical Method Showing Different Forms of Carbon

In general, thermal-optical methods classify carbon as >organic= or >elemental.= Organic carbon is non-light absorbing carbon that is volatilized in helium as the temperature is stepped to a preset maximum (850C). Elemental carbon is light-absorbing carbon (elemental or organic) and any non-light absorbing carbon evolved after pyrolysis correction. Depending on the sampling environment, carbonates [e.g., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] also may be present in the sample. Carbonate-source carbon is quantified as organic by NIOSH Method 5040, wherein the sample is exposed to 850C during the first part of the analysis (i.e., in helium only). Under these conditions, thermal decomposition of carbonate occurs. To quantify carbonate carbon, a second portion of the filter sample is analyzed after its acidification. Carbonate is taken as the difference between the pre- and post-acidification results (Note: the approach assumes a homogeneous filter deposit). Alternatively, carbonate carbon in a simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in >thermogram). The carbonate peak can be integrated separately within the instruments calculation software. This approach normally is taken when higher loadings of carbonate are present. In the case of the TOR method, carbonate in a filter portion is determined through on-line measurement of the carbon dioxide (CO_2) evolved upon acidification. Acid (0.04 M HCl) is injected directly onto the filter portion through an injection port. The sample oven is kept at ambient temperature while CO_2 is evolved, reduced to methane and quantified. (Note: This approach is subject to potential interference of adsorbed CO_2). Typically, carbonate carbon is not speciated in environmental samples because it has been found to constitute less than 5 percent of the total carbon in most samples (Chow et al., 1993).

It is important to remember that elemental and organic carbon have meaning only in the operational sense. That is, results reflect the method used and the appropriateness of a method depends on its purpose. Operational methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because elemental and organic carbon are defined operationally, the details of the measurement method must be rigorously prescribed.

Only one organic and one elemental carbon fraction are reported in NIOSH 5040 (total carbon is the sum of these two). In contrast, four types of organic carbon and three types of elemental are defined by the TOR technique. In both instances, different classes of carbon are evolved from the sample during the analysis. In the case of Method 5040, the division into two fractions reflects the purpose of the method (i.e., occupational monitoring of diesel particulate). For other applications (e.g., source apportionment), additional fractions may be appropriate provided that the applied temperature program is repeatable over time. Otherwise, relative information will not be meaningful because non-constant analytical parameters can affect the classification of carbon types.

7.3.2 Semi-volatile Organic Aerosols

Semi-volatile organic aerosols should not be considered on a routine basis due to the non-routine and research-oriented nature of measuring these species. Identification of the ideal denuder, filter combination, and sorbents and development of routine sampling and analytical methods is complicated due to the variety of semi-volatile organic aerosol compounds in the atmosphere and their varying absorptive properties.

The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon7-impregnated glass fiber filters. However, since many organic compounds are distributed between the gas and particle phases, additional sampling techniques are required to measure the particle phase semi-volatile organic compounds. This methodology is susceptible to negative (desorption of semi-volatile compounds from the particles on the filters) and positive (adsorption of gases by the filter material) artifacts. Considerable experimental and theoretical effort has been expended to understand and correct for these vaporization and condensation effects. Denuder technology has been employed to provide a less artifact-encumbered approach for accurate determination of semi-volatile species because the gas phase is removed prior to the particulate phase. A sorbent or denuder after the filter may also be employed to collect any semi-volatile material desorbed from the filter.

For quantification of individual organic compounds, the denuder, filter, and sorbent is extracted individually with a suitable organic solvent (or a combination of solvents). The extract is then analyzed by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

Appendix B

Standard Operating Procedures

Chemical Speciation Sampler Intercomparison Study

Standard Operating Procedures for this study have not been reproduced here to save paper, but can be found in the 4-City Study QAPP. A listing of the SOPs can be found in Table I-2.

Vanderpool, R. 1999. Quality Assurance Project Plan for the Four-City PM2.5 Chemical Speciation Sampler Evaluation Study. Prepared by Research Triangle Institute, RTI Project Number: 07263-030, EPA Funding Number: 68-D5-0040, WA III-30 and III-33. RTI, Research Triangle Park, NC.

Appendix C

Summary of Comments from Field and Laboratory Analysis Logbooks

Prepared by RTI
RTP, NC

Site	Date	Sampler	Repeat	Comments
1	01/06/99	AND	1	MgO denuders were not used in ch1. Sampler displays high flow rate ch4 (9.9 L/m).
1	01/06/99	AND	2	MgO denuders were not used in ch1. Sampler displays high flow rate ch4 (8.2 L/m).
1	01/09/99	AND	1	MgO denuders were not used in ch1. Sampler displays high Flow rate ch4 (9.9 L/m).
1	01/09/99	AND	2	Void-Sampler lost all calibrations.
1	01/15/99	AND	1	MgO denuders were used for remainder of study. Teflon filter (ch1) has a hole near the ring-did not affect mass conc. Hole occurred after sampling. Sampler displays high. Flow rate ch4 (8.9 L/m).
1	01/15/99	AND	2	MgO denuders were used for remainder of study. Andersen sent rep to site to re-calibrate prior to this run.Sampler displays high flow rate ch4 (7.6 L/m). XRF Data: "As" is below detection limits (BDL).
1	01/18/99	AND	1	Sampler displays low flow rate ch4 (6.6 L/m). XRF Data: "As" is BDL.
1	01/18/99	AND	2	Sampler displays low flow rate ch1 (6.0 L/m). Sampler displays high flow rate ch4 (7.8 L/m).
1	01/21/99	AND	1	Sampler displays low flow rate ch4 (4.1 L/m). XRF Data: "As" is BDL.
1	01/21/99	AND	2	Site op noted some water in the back near the top of the back panel. Sampler displays high flow rate ch2 (17.7 L/m) and ch4 (7.9 L/m). XRF Data: "Mn" is BDL.
1	01/24/99	AND	1	Sampler displays low flow rate ch4 (4.2 L/m).
1	01/24/99	AND	2	Sampler displays low flow rate ch1 (6.1 L/m). Sampler displays high flow rate ch2 (17.7 L/m) and ch 4 (7.9 L/m).
1	01/27/99	AND	1	Sampler displays high flow rate ch1 (7.6 L/m). Sampler displays low flow rate ch4 (4.2 L/m).
1	01/27/99	AND	2	Sampler displays low flow rate ch1 (6.3 L/m). Sampler displays high flow rate ch2 (17.9 L/m) and ch4 (8.0 L/m).
1	01/30/99	AND	1	Sampler displays low flow rate ch4 (4.3 L/m).
1	01/30/99	AND	2	Sampler displays low flow rate ch1 (5.8 L/m). Sampler displays high flow rate ch2 (18.0 L/m) and ch4 (7.9 L/m).
1	02/02/99	AND	1	Sampler displays low flow rate ch3 (15.6 L/m). Sampler displays high flow rate ch4 (7.7 L/m).
1	02/02/99	AND	2	Sampler displays low flow rate ch1 (6.4 L/m). Sampler displays high flow rate ch4 (7.7 L/m).
1	02/05/99	AND	1	Sampler displays low flow rate ch2 (16.0 L/m) and ch3 (15.5 L/m) and ch4 (7.0 L/m). XRF Data: "As" is BDL.
1	02/05/99	AND	2	Sampler displays low flow rate ch1 (6.1 L/m) and ch3 (16.0 L/m). High flow rate ch4 (7.7 L/m).
1	02/11/99	AND	1	Sampler displays high flow rate ch1 (7.8 L/m) and ch4 (7.9L/m). Sampler displays low flow rate ch3 (15.3 L/m). XRF Data: "Pb" is BDL.
1	02/11/99	AND	2	Sampler displays low flow rate ch1 (5.9 L/m). Sampler displays high flow rate ch4 (7.9 L/m). XRF Data: "Pb" and "As" are BDL.
1	02/14/99	AND	1	Sampler displays low flow rate ch2(16.0 L/m) and ch3 (15.4 L/m). XRF Data: "As" is BDL.
1	02/14/99	AND	2	Sampler displays low flow rate ch1 (6.3 L/m) and high flow flow rate ch4 (7.8 L/m).
1	02/17/99	AND	1	Sampler displays low flow rate ch2 (15.5 L/m) and ch4 (7.0 L/m).
1	02/17/99	AND	2	Sa in ch3-void SO4+2, NO3-, NH4+ data.
1	02/20/99	AND	1	Sampler displays low flow rate ch3 (15.6 L/m) and ch4 (7.0 L/m). XRF Data: "As" is BDL.
1	02/20/99	AND	2	Sampler displays low flow rate ch1 (6.2 L/m) and ch3 (16.0 L/m) and high flow rate ch4 (7.8 L/m). XRF Data: "As" is BDL.
1	02/23/99	AND	1	Large tear and 1 small hole in Teflon (Ch1) filter-did not affect mass conc. Tear/hole occurred after sampling.Sampler displays low flow rate ch3 (15.7 L/m). XRF Data: Did not analyze filter due to large tear.
1	02/23/99	AND	2	Sampler displays low flow rate ch1 (5.9 L/m) and ch3(16.0 L/m) and high flow rate ch4 (7.7 L/m).
1	02/26/99	AND	1	Sampler displays low flow rate ch1 (15.7 L/m) and ch4 (6.9 L/m). XRF Data: "As" is BDL.
1	02/26/99	AND	2	Sampler displays low flow rate ch1 (6.3 L/m) and ch3 (15.9 L/m) and ch4 (14.3 L/m). Site op verified ch4 flow, sampler reading 13.2 L/m with the pump off. XRF Data: "As" is BDL.
1	01/06/99	FRM-T	1	.
1	01/06/99	FRM-T	2	XRF Data: "As" is below detection limits (BDL).
1	01/09/99	FRM-T	1	.
1	01/09/99	FRM-T	2	Lab op noted 2 small holes--did not affect mass conc. Holes seems to have occurred subsequent to sampling. XRF Data: "As" is BDL.
1	01/15/99	FRM-T	1	.
1	01/15/99	FRM-T	2	XRF Data: "As" is BDL.
1	01/18/99	FRM-T	1	T.Miguel arrived at the site @0840 during the sample and found the filter in the down position. XRF Data: "As" is BDL.
1	01/18/99	FRM-T	2	.
1	01/21/99	FRM-T	1	Small puddles of H2O found inside on the impactor shelf and bottom of the cabinet. XRF Data: "As" is BDL.
1	01/21/99	FRM-T	2	XRF Data: "As" is BDL.
1	01/24/99	FRM-T	1	No sample-sample did not run because during the firmware upgrade the sampler shut down and would not power back up.

1	01/24/99	FRM-T	2	Firmware upgraded on 1/22. XRF Data: "As" is BDL.
1	01/27/99	FRM-T	1	No sample--sampler still will not power up.
1	01/27/99	FRM-T	2	.
1	01/30/99	FRM-T	1	T.Miguel was able to get the sampler running--firmware has not be upgraded.
1	01/30/99	FRM-T	2	.
1	02/02/99	FRM-T	1	.
1	02/02/99	FRM-T	2	.
1	02/05/99	FRM-T	1	Teflon filter appears to have been scratched w/ forceps-did not affect the mass conc. XRF Data: "As" is BDL.
1	02/05/99	FRM-T	2	.
1	02/11/99	FRM-T	1	XRF Data: "Cu" and "As" are BDL.
1	02/11/99	FRM-T	2	XRF Data: "Cu", "Pb", and "As" are BDL.
1	02/14/99	FRM-T	1	XRF Data: "As" is BDL.
1	02/14/99	FRM-T	2	XRF Data: "As" is BDL.
1	02/17/99	FRM-T	1	XRF Data: "As" is BDL.
1	02/17/99	FRM-T	2	.
1	02/20/99	FRM-T	1	XRF Data: "As" is BDL.
1	02/20/99	FRM-T	2	.
1	02/23/99	FRM-T	1	.
1	02/23/99	FRM-T	2	XRF Data: "As" is BDL.
1	02/26/99	FRM-T	1	Installed clean wins impactors. XRF Data: "As" is BDL.
1	02/26/99	FRM-T	2	Installed clean wins impacotrs. XRF Data: "Cu" and "As" are BDL.

1	01/06/99	FRM-Q	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/06/99	FRM-Q	2	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit. .
1	01/09/99	FRM-Q	1	.
1	01/09/99	FRM-Q	2	.
1	01/15/99	FRM-Q	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit. .
1	01/15/99	FRM-Q	2	.
1	01/18/99	FRM-Q	1	.
1	01/18/99	FRM-Q	2	.
1	01/21/99	FRM-Q	1	Small puddles of H2O found near the wins, near the locking mechanism and in the bottom of the cabinet.
1	01/21/99	FRM-Q	2	.
1	01/24/99	FRM-Q	1	Firmware upgraded on 1/22.
1	01/24/99	FRM-Q	2	No Sample-following the firmware upgrade, the sampler would not power up.
1	01/27/99	FRM-Q	1	Sampler ran 34 hours due to programming error.
1	01/27/99	FRM-Q	2	No Sample-sampler ran 3 seconds.
1	01/30/99	FRM-Q	1	.
1	01/30/99	FRM-Q	2	Sampler running again-firmware has not been upgraded.
1	02/02/99	FRM-Q	1	.
1	02/02/99	FRM-Q	2	No Sample-sampler did not run, may need new pump.
1	02/05/99	FRM-Q	1	.
1	02/05/99	FRM-Q	2	BGI sent a loaner FRM to replace downed unit. Checked for leaks, cleaned wins. Sampler was not audited.
1	02/11/99	FRM-Q	1	.
1	02/11/99	FRM-Q	2	Average flow rate is low (16.4 L/m).
1	02/14/99	FRM-Q	1	.
1	02/14/99	FRM-Q	2	.
1	02/17/99	FRM-Q	1	.
1	02/17/99	FRM-Q	2	.
1	02/20/99	FRM-Q	1	.
1	02/20/99	FRM-Q	2	.
1	02/23/99	FRM-Q	1	.
1	02/23/99	FRM-Q	2	.
1	02/26/99	FRM-Q	1	Installed clean wins impactor.
1	02/26/99	FRM-Q	2	Installed clean wins impactor.

1	01/06/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is below detection limits (BDL).
1	01/06/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL. Quartz filter was not transferred to DRI for EC/OC.
1	01/09/99	IMP	1	Void-large hole in filter. Hole seems to have occurred before/during sampling.
1	01/09/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	01/15/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	01/15/99	IMP	2	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/18/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Pump timer appears to be stuck at the off trigger.
1	01/18/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	01/21/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Timer for the pumps is broken. Site op is manually turning the sampler off and on. XRF Data: "As" is BDL.
1	01/21/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	01/24/99	IMP	1	Used avg flow rates from the site audits for 3 modules.

1	01/24/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	01/27/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	01/27/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	01/30/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	01/30/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/02/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	02/02/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/05/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	02/05/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/11/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "Pb" and "As" are BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	02/11/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "Cu", "Pb", and "As" are BDL.
1	02/14/99	IMP	1	Used avg flow rates from the site audits for 3 modules.XRF Data: "As" is BDL.
1	02/14/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/17/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	02/17/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/20/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
1	02/20/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	02/23/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit. XRF Data: "As" is BDL.
1	02/23/99	IMP	2	Used avg flow rates from the site audits for 3 modules.
1	02/26/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	02/26/99	IMP	2	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
1	01/06/99	MET	1	Void-pin hole near ring of Teflon (ch1). Hole seems to have occurred during/before sampling began. Sampler displays high sample volume on ch3(10.214 m^3) and ch4(10.605 m^3). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/06/99	MET	2	Sampler displays low sample volume ch3 (8.588 m^3) and ch4 (8.966 m^3). XRF Data: "As" is below detection limits (BDL). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral partilces in deposit.
1	01/09/99	MET	1	Sampler displays high sample volume ch1(10.791 m^3) and ch2 (10.720 m^3), ch4(10.676 m^3). XRF Data: "Pb" is BDL; and "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/09/99	MET	2	Sampler displays low sample volume ch3 (8.651m^3) and ch4 (9.101 m^3).XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/15/99	MET	1	Sampler displays low sample volume ch3 (8.651 m^3). XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis,indicative of mineral particles in deposit.
1	01/15/99	MET	2	Void-sampler ran 10.3 hours. (Sampler displays sample vol from the previous run.)
1	01/18/99	MET	1	Teflon filter (CH1) has a tear and small hole that seems to have been caused by the forceps. Did not affect mass conc. Sampler displays low sample vol ch3 (9.041 m^3). XRF Data: "As" is BDL.
1	01/18/99	MET	2	Sampler displays low sample vol ch3 (8.810 m^3) and ch4 (9.059 m^3). XRF Data: "As" is BDL.
1	01/21/99	MET	1	Sampler displays low sample vol ch3 (9.110 m^3). XRF Data: "Cu" is BDL; "As" is BDL.
1	01/21/99	MET	2	Suspect data. Suspect an error in the recording of the filter weights. Sampler displays low sample vol ch3 (8.840 m^3) and ch4 (9.070 m^3).
1	01/24/99	MET	1	Sampler displays low sample vol ch3 (9.063 m^3). XRF Data: "As" is BDL.
1	01/24/99	MET	2	Sampler displays low sample vol ch3 (8.822 m^3) and ch4 (9.067m^3).
1	01/27/99	MET	1	Sampler displays low sample vol ch3 (9.106 m^3).
1	01/27/99	MET	2	Sampler displays low sample vol ch3 (8.789 m^3) and ch4 (9.054 m^3).
1	01/30/99	MET	1	Sampler displays low sample vol ch3 (9.055 m^3).
1	01/30/99	MET	2	Sampler displays low sample vol ch3 (8.730 m^3) and ch4 (9.061 m^3).
1	02/02/99	MET	1	Large tear in Teflon (ch1)-did not affect mass conc. Appears hole occurred subsequent to sampling. Sampler displays low sample vol ch3 (9.098 m^3). XRF Data: "As" is BDL.
1	02/02/99	MET	2	Sampler displays low sample vol ch3 (8.739 m^3) and ch4 (9.109 m^3).
1	02/05/99	MET	1	Large tear in Teflon (ch1)-did not affect mass conc. Appears hole occurred subsequent to sampling. Sampler displays low sample vol ch3 (8.972 m^3). XRF Data: "Mn" is BDL.
1	02/05/99	MET	2	Sampler displays low sample vol ch3 (8.734 m^3) and ch4 (9.059 m^3). XRF Data: "As" is BDL.
1	02/11/99	MET	1	Sampler displays low sample vol ch3 (9.030 m^3). XRF Data: "Cu" and "Pb" are BDL.
1	02/11/99	MET	2	Sampler displays low sample vol ch3 (8.749 m^3) and ch4 (9.131 m^3). XRF Data: "As" is BDL.
1	02/14/99	MET	1	Sampler displays low sample vol ch3 (9.068 m^3).
1	02/14/99	MET	2	Sampler displays low sample vol ch3 (8.752 m^3) and ch4 (9.050 m^3). XRF Data: "As" is BDL.
1	02/17/99	MET	1	Tears @ ring Teflon (ch1)-did not affect mass conc. Appears hole occurred subsequent to sampling. Sampler displays low sample vol ch3 (9.042 m^3). XRF Data: "As" is BDL.
1	02/17/99	MET	2	Sampler displays low sample vol ch3 (8.698 m^3) and ch4 (9.036 m^3). XRF Data: "As" is BDL.
1	02/20/99	MET	1	Sampler displays low sample vol ch3 (9.089 m^3). XRF Data: "As" is BDL.
1	02/20/99	MET	2	Sampler displays low sample vol ch3 (8.473 m^3) and ch4 (9.059 m^3).
1	02/23/99	MET	1	Sampler displays low sample vol ch3 (9.036 m^3). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	02/23/99	MET	2	Sampler displays low sample vol ch3 (6.490 m^3) and ch4 (9.097 m^3). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	02/26/99	MET	1	Sampler displays low sample vol ch3 (9.007 m^3). XRF Data: "Cu", "Pb", and "As" are BDL.
1	02/26/99	MET	2	Fuzz on Teflon filter (ch1)-did not affect mass conc. Sampler displays low sample vol ch3 (8.690 m^3) and ch4 (9.056 m^3). XRF Data: "Mn", "Cu", and "Pb" are BDL.

1	01/06/99	URG	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/06/99	URG	2	FTP Flag-did not affect mass conc. Low sample volume on URG400 (22.591 m³). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/09/99	URG	1	.
1	01/09/99	URG	2	FTP Flag-did not affect mass conc. Low sample volume on URG400 (22.414 m³). XRF Data: "Cu" is below detection limits (BDL).
1	01/15/99	URG	1	.
1	01/15/99	URG	2	XRF Data: "As" is BDL.
1	01/18/99	URG	1	.
1	01/18/99	URG	2	Low sample volume on URG400 (22.604 m³). XRF Data: "As" is BDL.
1	01/21/99	URG	1	New Dry Gas Meter pumps installed and re-calibrated. Unable to locate Teflon filter. Filter was rec'd by RTI after sampling; but was not post-weighed.
1	01/21/99	URG	2	New Dry Gas Meter pumps installed and re-calibrated. XRF Data: "As" is BDL.
1	01/24/99	URG	1	Wins impactors cleaned before this run. XRF Data: "As" is BDL.
1	01/24/99	URG	2	Wins impactors cleaned before this run.
1	01/27/99	URG	1	Void-sample ran 10.5 hrs (URG400). Mass conc and Particulate NO3- data is void. Outer ring had slight split.
1	01/27/99	URG	2	.
1	01/30/99	URG	1	No sample-did not run (URG400). Mass conc and Particulate NO3- data is void. Problem with the display screen.
1	01/30/99	URG	2	Void-large tear in Teflon filter-affected mass conc. FTP Flag.
1	02/02/99	URG	1	Void-T.Miguel was working on the sampler and lost all data from this sample run when sampler was re-booted (URG400). Data was suspect anyway-sampler does not appear to have runned (Mass=1.00µg). Mass conc and particulate NO3- data is void.
1	02/02/99	URG	2	FTP Flag-did not affect mass conc. Medium-sized tear in Teflon filter-tear seems to have occurred after sampling.
1	02/05/99	URG	1	Void-sample ran 1 second (URG400). Mass conc and particulate NO3- data is void.
1	02/05/99	URG	2	Unable to locate Teflon filter. Filter was rec'd by RTI after sampling; but was not transferred for post-weight.
1	02/11/99	URG	1	Replaced pump and cleaned wins impactor before this run. XRF Data: "As" is BDL.
1	02/11/99	URG	2	XRF Data: "Cu" and "As" are BDL.
1	02/14/99	URG	1	.
1	02/14/99	URG	2	FTP Flag. XRF Data: "As" is BDL.
1	02/17/99	URG	1	XRF Data: "As" is BDL.
1	02/17/99	URG	2	FTP Flag.
1	02/20/99	URG	1	XRF Data: "As" is BDL.
1	02/20/99	URG	2	FTP Flag. XRF Data: "As" is BDL.
1	02/23/99	URG	1	Void-sample ran 2 seconds. TmFlo flag. Bad pump plug connection (URG400). Mass conc and particulate NO3- data is void.
1	02/23/99	URG	2	FTP Flag. XRF Data: "As" is BDL.
1	02/26/99	URG	1	2 small holes near ring of Teflon filter-did not affect mass conc. Holes appear to have occurred after sampling. Repaired pin on pump plug. Cleaned wins impactor before this run. XRF Data: "As" is BDL.
1	02/26/99	URG	2	Cleaned wins impactor before this run.

1	01/06/99	VAPS	1	Low sample volume ch1 (2.970 m³) and ch2 (19.058m³). Lab op dropped filter on floor. XRF Data: "As" is below detection limits (BDL). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/09/99	VAPS	1	Void-large hole in filter which affected mass conc--PM2.5 and PM10. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/15/99	VAPS	1	Void-filter pack was improperly put together. (Teflon filter was loaded downstream of Nylon filter.)Mass conc and NO3- data is void. The glass denuder (XAD) was received broken. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
1	01/18/99	VAPS	1	Void-ch2 (teflon)suspect that the weights were written down incorrectly. Ch3 low sample volume (17.031m³). XRF Data: "As" is BDL.
1	01/21/99	VAPS	1	Ch2 high sample volume (23.084m³). Ch3 low sample volume (19.412m³). XRF Data: "As" is BDL.
1	01/24/99	VAPS	1	.
1	01/27/99	VAPS	1	High sample vol ch1 (4.902 m³); Ch3 low sample volume (20.095m³).
1	01/30/99	VAPS	1	Nylon filter was not transferred to CEMQA for IC analyses. It appears that when an error occurred when unloading the filterpack--nylon filter was not kept refridgerated. Particulate NO3- data is void. XRF Data: "As" is BDL. Quartz filter was not transferred to DRI for EC/OC analysis.
1	02/02/99	VAPS	1	.
1	02/05/99	VAPS	1	XRF Data: "As" is BDL.
1	02/11/99	VAPS	1	XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysi, indicative of mineral particles in deposit.
1	02/14/99	VAPS	1	.
1	02/17/99	VAPS	1	Void-PM2.5 data is suspect.
1	02/20/99	VAPS	1	Suspect data-3 small holes appear to have caused by forceps. XRF Data: "As" is BDL.
1	02/23/99	VAPS	1	XRF Data: "As" is BDL.
1	02/26/99	VAPS	1	XRF Data: "As" is BDL.

2	01/06/99	AND	1	MgO denuders were not installed. Sampler displays low sample vol ch1-Nylon (9.504 m³) and ch2-Teflon (22.752 m³).
2	01/08/99	AND	1	MgO denuders were not installed. Sampler displays low sample vol ch1 (9.504 m³);ch2 (22.752 m³);ch3(22.896 m³).
2	01/14/99	AND	1	MgO denuders were installed. Sampler displays low sample vol ch1 (9.360 m³);ch2 (22.896 m³).

2	01/16/99	AND	1	Teflon (ch2) filter had large tear @ ring. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers. Sampler displays low sample vol ch1 (9.648 m^3);ch2 (22.896 m^3);ch3 (22.896 m^3).
2	01/18/99	AND	1	Teflon (ch2) filter had pin hole. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers. Sampler displays low sample vol ch1 (9.648 m^3).
2	01/20/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3).
2	01/22/99	AND	1	Sampler displays low sample vol ch1 (9.648 m^3). XRF Data: "As" is Below Detection Limit (BDL).
2	01/24/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3).
2	01/26/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3); ch3 (22.896 m^3).
2	01/28/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3); ch3 (22.896 m^3).
2	02/03/99	AND	1	Sampler displays low sample vol ch1 (9.360 m^3). Sampler displays high sample vol ch4 (11.232 m^3).
2	02/05/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3). Sampler displays high sample vol ch4 (11.232 m^3). XRF Data: "As" is BDL.
2	02/07/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3). Sampler displays high sample vol ch4 (11.232 m^3).
2	02/09/99	AND	1	Sampler displays low sample vol ch1 (9.504 m^3). XRF Data: "As" is BDL.
2	02/11/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3). Sampler displays high sample vol ch4 (11.520 m^3). XRF Data: "Mn" and "As" are BDL.
2	02/13/99	AND	1	Sampler displays low sample vol ch1 (9.648 m^3). XRF Data: "As" is BDL.
2	02/15/99	AND	1	Teflon (ch2) filter had a medium-sized tear. Site op noted pin hole on Teflon (ch3) filter. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers.
2	02/17/99	AND	1	Sampler displays low sample vol ch1 (9.360 m^3). XRF Data: "As" is BDL.
2	02/19/99	AND	1	Teflon (ch2) filter had small tear under ring. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers. Sampler displays low sample vol ch1 (9.216 m^3). XRF Data: "As" is BDL.
2	02/21/99	AND	1	Sampler displays low sample vol ch1 (9.360 m^3).

2	01/06/99	FRM-T	1	.
2	01/08/99	FRM-T	1	Lab operator noted large tear in filter. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers.
2	01/14/99	FRM-T	1	XRF Data: "As" is below detection limit (BDL).
2	01/16/99	FRM-T	1	.
2	01/18/99	FRM-T	1	Pin hole near ring. Site op replaced wins impactor well. Hole seems to have occurred subsequent to sampling b/c mass conc is in line with other samplers.
2	01/20/99	FRM-T	1	XRF Data: "As" is BDL.
2	01/22/99	FRM-T	1	XRF Data: "As" is BDL.

2	01/24/99	FRM-T	1	.
2	01/26/99	FRM-T	1	XRF Data: "As" is BDL.
2	01/28/99	FRM-T	1	XRF Data: "Mn" and "Pb" are BDL.
2	02/03/99	FRM-T	1	XRF Data: "As" is BDL.
2	02/05/99	FRM-T	1	XRF Data: "As" is BDL.
2	02/07/99	FRM-T	1	.
2	02/09/99	FRM-T	1	.
2	02/11/99	FRM-T	1	XRF Data: "Pb" is BDL.
2	02/13/99	FRM-T	1	XRF Data: "As" is BDL.
2	02/15/99	FRM-T	1	XRF Data: "As" is BDL.
2	02/17/99	FRM-T	1	XRF Data: "As" is BDL.
2	02/19/99	FRM-T	1	.
2	02/21/99	FRM-T	1	Void--Large hole poked in filter during unpacking.

2	01/06/99	FRM-Q	1	.
2	01/08/99	FRM-Q	1	.
2	01/14/99	FRM-Q	1	.
2	01/16/99	FRM-Q	1	.
2	01/18/99	FRM-Q	1	Site op replaced wins impactor well.
2	01/20/99	FRM-Q	1	.
2	01/22/99	FRM-Q	1	.
2	01/24/99	FRM-Q	1	.
2	01/26/99	FRM-Q	1	.
2	01/28/99	FRM-Q	1	.
2	02/03/99	FRM-Q	1	.
2	02/05/99	FRM-Q	1	.
2	02/07/99	FRM-Q	1	.
2	02/09/99	FRM-Q	1	.
2	02/11/99	FRM-Q	1	.
2	02/13/99	FRM-Q	1	.
2	02/15/99	FRM-Q	1	.
2	02/17/99	FRM-Q	1	.
2	02/19/99	FRM-Q	1	.
2	02/21/99	FRM-Q	1	.
2	01/06/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.

2	01/08/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/14/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit. Filter support grid upside down-deposit had widely spaced stripes.
2	01/16/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/18/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/20/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	01/22/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is below detection limits (BDL).
2	01/24/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	01/26/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	01/28/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	02/03/99	IMP	1	Used avg flow rates from the site audits for 3 modules. When Ch2 (Nylon) turned on it was very high (.80/11.5), couldn't see anything wrong. Filter pack looked ok--adj to .42. Ch3 (Quartz) hose on filter is loose, slip ring would not tighten. XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	02/05/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
2	02/07/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	02/09/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	02/11/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "Pb" and "As" are BDL.
2	02/13/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	02/15/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
2	02/17/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	02/19/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Elapsed timer did not record time on ch2 (Nylon). XRF Data: "As" is BDL.
2	02/21/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Large hole in Teflon filter (ch1)--void.

2	01/06/99	MET	1	Sample vol is low ch3-nylon (8.939 m^3) and ch4-quartz (9.084 m^3). XRF Data: "As" is below detection limits (BDL). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/08/99	MET	1	Sample vol is low ch3 (8.939 m^3) and ch4 (9.084 m^3). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/14/99	MET	1	MgO honeycomb denuder installed on Nylon filter channel. XRF Data: "As" is BDL.
2	01/16/99	MET	1	XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/18/99	MET	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/20/99	MET	1	Nylon NO3-Results are void;cannister assemblied with backing screen upstream of nylon filter. XRF Data: "As" is BDL.
2	01/22/99	MET	1	Sample vol is low ch3 (9.040 m^3). XRF Data: "Pb" is BDL, "As" is BDL.
2	01/24/99	MET	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	01/26/99	MET	1	.
2	01/28/99	MET	1	Void--Elapsed sample time = 1 second.
2	02/03/99	MET	1	Sample vol is low ch3 (8.969 m^3).
2	02/05/99	MET	1	Lower shield left down for this run to help determine why Met One PM2.5 conc are so high. Sample vol is low ch3 (9.017 m^3). XRF Data: "As" is BDL.
2	02/07/99	MET	1	Lower shield left down for this run to help determine why Met One PM2.5 conc are so high. Sample vol is low ch3 (8.994 m^3). XRF Data: "As" is BDL.
2	02/09/99	MET	1	Lower shield left down for this run to help determine why Met One PM2.5 conc are so high. Sample vol is low ch3 (9.122 m^3). XRF Data: "As" is BDL.
2	02/11/99	MET	1	Lower shield raised back up. XRF Data: "As" is BDL.
2	02/13/99	MET	1	EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	02/15/99	MET	1	XRF Data: "As" is BDL.
2	02/17/99	MET	1	Sample vol is low ch3 (9.023 m^3). XRF Data: "As" is BDL. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
2	02/19/99	MET	1	XRF Data: "As" is BDL.
2	02/21/99	MET	1	Teflon (Ch1) Data is void due to very high mass conc (~600 $\mu g/m^3$). XRF Data: "As" is BDL. Teflon (ch2) filter was not transferred to CEMQA for IC--appears to have been a mistake when unloading cannisters.

2	01/06/99	URG	1	URG400: VOID--Sample ran ~14hrs,Flags FTP, TM, F10. Mass conc and particulate NO3- data is void.
2	01/08/99	URG	1	URG400: VOID--Sample ran ~10hrs, URG sent modification kit for pump. Mass conc and NO3- data is void.
2	01/14/99	URG	1	URG400: Flag FTP
2	01/16/99	URG	1	URG400: Flag FTP
2	01/18/99	URG	1	URG400: Flag FTP,cleaned wins impactors
2	01/20/99	URG	1	URG400: Flag FTP
2	01/22/99	URG	1	URG400: Void-Nylon and Teflon filterpacks were cross- threaded. Mass conc and particulate NO3- data is void.
2	01/24/99	URG	1	URG400: Flag FTP
2	01/26/99	URG	1	URG400: Flag FTP
2	01/28/99	URG	1	URG400: Flag FTP
2	02/03/99	URG	1	URG400: Flag FTP, Double pump with DGM installed on 1/29. Bob M calibrated on 1/29. URG450: Bob M calibrated on 1/29.

				XRF Data: "As" is BDL.
2	02/05/99	URG	1	URG400: Flag FTP
2	02/07/99	URG	1	URG400: VOID--Flag FTP. Filter pack assemblied incorrectly- Teflon in bottom position and Nylon in top position. Mass conc and particulate NO3- data is void.
2	02/09/99	URG	1	URG400: VOID--Sampler ran 16 hrs 41 min, Flag FTP, Tm, Flo. Mass conc and particulate NO3- data is void.
2	02/11/99	URG	1	XRF Data: "As" is BDL.
2	02/13/99	URG	1	URG400: Void (Teflon filter)--appears filter weights were recorded incorrectly.
2	02/15/99	URG	1	URG400: Flag FTP. XRF Data: "As" is BDL.
2	02/17/99	URG	1	URG400: Flag FTP. XRF Data: "As" is BDL.
2	02/19/99	URG	1	URG400: Flag FTP. XRF Data: "As" is BDL.
2	02/21/99	URG	1	URG400: Flag FTP
2	01/06/99	VAPS	1	High sample volume on all channels. (Flow rates appear to be off.) Teflon (ch2) filter has started to tear @ ring.
2	01/08/99	VAPS	1	.
2	01/14/99	VAPS	1	Void--confusion w/ sample id#s. Ran Sample Day 4 filters on day 3
2	01/16/99	VAPS	1	Void--confusion w/ sample id#s. Sent additional filters renamed filters Day 4 (too)
2	01/18/99	VAPS	1	Sample vol high ch2-teflon (22.971 m^3).
2	01/20/99	VAPS	1	Void--Sample ran 36.4 hrs.
2	01/22/99	VAPS	1	.
2	01/24/99	VAPS	1	.
2	01/26/99	VAPS	1	.
2	01/28/99	VAPS	1	.
2	02/03/99	VAPS	1	.
2	02/05/99	VAPS	1	Void--Teflon (ch2-fine) filter weights appear to have been recorded incorrectly.
2	02/07/99	VAPS	1	XRF Data: "As" is BDL.
2	02/09/99	VAPS	1	.
2	02/11/99	VAPS	1	XRF Data: "Pb" and "As" are BDL.
2	02/13/99	VAPS	1	Void--Ch2 filterpack loaded incorrectly. Teflon loaded downstream of Nylon. Mass conc and particulate NO3- data is void.
2	02/15/99	VAPS	1	XRF Data: "As" is BDL.
2	02/17/99	VAPS	1	Void--Teflon (ch1-coarse)large hole in filter.
2	02/19/99	VAPS	1	Void--Ch2 filterpack loaded incorrectly. Nylon loaded upstream of Teflon. Mass conc and particulate NO3- data is void.
2	02/21/99	VAPS	1	Void--Teflon (ch2-fine) filter had a pin hole. Ch1 (PM10)-- filter was not post-weighed-error occurred when filterpack was unloaded.
3	01/17/99	AND	1	Ch2:pin hole near ring.Hole seems to have occurred sub- sequent to sampling b/c mass conc looks ok.
3	01/19/99	AND	1	XRF Data (from Teflon filter-ch2) "As" was BDL.
3	01/21/99	AND	1	Sampler displays low sample vol ch3-Teflon (22.464 m^3). XRF Data (from Teflon filter-ch2) "As" was BDL.
3	01/23/99	AND	1	Filters (ch1 and ch3) were loaded incorrectly. Nylon (ch1) was sampled in ch3. Sample volumes have been adjusted. XRF Data (from Teflon filter-ch2) "Si" and "Mn" and "As" was BDL.
3	01/25/99	AND	1	.
3	01/27/99	AND	1	Sampler displays low sample vol low ch1-Nylon (9.792 m^3) and in ch3 (22.608 m^3).
3	01/29/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3)
3	01/31/99	AND	1	.
3	02/02/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3).
3	02/04/99	AND	1	.
3	02/08/99	AND	1	Sampler displays low sample vol ch3 (22.608 m^3).
3	02/10/99	AND	1	Ch2(Teflon):filter appears to have scratched with finger- nail or forceps. Did not appear to effect mass conc.
3	02/12/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3) and ch3 (22.608 m^3).XRF Data: "As" is BDL.
3	02/14/99	AND	1	XRF Data: "As" and "Cu" are BDL.
3	02/16/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3).
3	02/18/99	AND	1	Ch4(Quartz):Void-site operator touched filter. Sampler displays low sample vol ch3 (22.608 m^3).
3	02/20/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3) and ch3 (22.608 m^3).
3	02/22/99	AND	1	Sampler displays low sample vol ch3 (22.608 m^3). XRF Data: "As" is BDL.
3	02/24/99	AND	1	XRF Data: "As" is BDL.
3	02/26/99	AND	1	Sampler displays low sample vol ch1 (9.792 m^3) and ch3 (21.744 m^3).
3	01/17/99	FRM-T	1	.
3	01/19/99	FRM-T	1	XRF Data: "As" was BDL
3	01/21/99	FRM-T	1	.
3	01/23/99	FRM-T	1	Void-H2O found on side of filter cassette and sides of impactor.When filter was unloaded there was moisture present.
3	01/25/99	FRM-T	1	Wins impactor cleaned and re-oiled before sample run.
3	01/27/99	FRM-T	1	.
3	01/29/99	FRM-T	1	.
3	01/31/99	FRM-T	1	.
3	02/02/99	FRM-T	1	Heavy rains. H2O droplets were observed on the sides of filter cassette. Filter observed to be ok. H2O seeped through the intersection of the downtube to the enclosure. Sampler parts were cleaned and prepared for next run.
3	02/04/99	FRM-T	1	XRF Data: "As" is BDL.

3	02/08/99	FRM-T	1	.
3	02/10/99	FRM-T	1	.
3	02/12/99	FRM-T	1	XRF Data: "As" is BDL.
3	02/14/99	FRM-T	1	.
3	02/16/99	FRM-T	1	.
3	02/18/99	FRM-T	1	.
3	02/20/99	FRM-T	1	XRF Data: "As" is BDL.
3	02/22/99	FRM-T	1	XRF Data: "As" is BDL.
3	02/24/99	FRM-T	1	XRF Data: "As" is BDL.
3	02/26/99	FRM-T	1	XRF Data: "As" is BDL.
3	01/17/99	FRM-Q	1	.
3	01/19/99	FRM-Q	1	.
3	01/21/99	FRM-Q	1	.
3	01/23/99	FRM-Q	1	.
3	01/25/99	FRM-Q	1	.
3	01/27/99	FRM-Q	1	.
3	01/29/99	FRM-Q	1	.
3	01/31/99	FRM-Q	1	.
3	02/02/99	FRM-Q	1	.
3	02/04/99	FRM-Q	1	.
3	02/08/99	FRM-Q	1	.
3	02/10/99	FRM-Q	1	.
3	02/12/99	FRM-Q	1	.
3	02/14/99	FRM-Q	1	.
3	02/16/99	FRM-Q	1	.
3	02/18/99	FRM-Q	1	.
3	02/20/99	FRM-Q	1	Bob M had to change filter cassette. (filter had been loaded into the wrong filter cassette.)
3	02/22/99	FRM-Q	1	.
3	02/24/99	FRM-Q	1	.
3	02/26/99	FRM-Q	1	.
3	01/17/99	IMP	1	Sample did not run due to short in electrical system.
3	01/19/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Nylon/Quartz modules:Adj Mag Reading from 0.44" H2O to 0.46" H2O after 10.4 hrs into run. XRF Data: "As" was BDL.
3	01/21/99	IMP	1	Used avg flow rates from the site audits for 3 modules. All channels flow was set to 0.52 b/c gauge was misread.
3	01/23/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Nylon channel vacuum gauge is faulty. XRF Data: "Pb" was BDL.
3	01/25/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Teflon filter has a hole which seems to have occurred subsequent to sampling b/c mass conc is ok.
3	01/27/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
3	01/29/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	01/31/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/02/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Filter support grid upside down-deposit had widely spaced stripes or grid pattern.
3	02/04/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/08/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/10/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/12/99	IMP	1	Used avg flow rates from the site audits for 3 modules. Suspect Data Teflon channel-sampler appears to have run ok-no reason to invalidate. XRF Data: "Si", "Pb", and "As" are BDL.
3	02/14/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
3	02/16/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
3	02/18/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/20/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/22/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/24/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	02/26/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
3	01/17/99	MET	1	No sample vol recorded for any channels.
3	01/19/99	MET	1	Low sample vol ch3-nylon (8.933 m^3). XRF Data: "As" was Below detection limits (BDL).
3	01/21/99	MET	1	Quartz (Ch5): Mask shin was not installed. Analysis results corrected numerically to adjust for the actual deposition area. Low sample vol ch3 (8.948 m^3).
3	01/23/99	MET	1	Low sample vol ch3 (8.970 m^3). XRF Data: "Si" was BDL. "Cu" was BDL. "As" was BDL.
3	01/25/99	MET	1	Low sample vol ch3 (9.042 m^3).
3	01/27/99	MET	1	Low sample vol ch3 (8.908 m^3).
3	01/29/99	MET	1	Low sample vol ch3 (8.913 m^3).
3	01/31/99	MET	1	Low sample vol ch3 (8.882 m^3). Backing screen found in petri dish of Teflon (ch1)
3	02/02/99	MET	1	Low sample vol ch3 (8.921 m^3).
3	02/04/99	MET	1	Low sample vol ch3 (8.935 m^3).
3	02/08/99	MET	1	Low sample vol ch3 (9.095 m^3). XRF Data: "Cu" and "As" are BDL.

3	02/10/99	MET	1	Low sample vol ch3 (9.033 m^3).
3	02/12/99	MET	1	Low sample vol ch3 (8.919 m^3). XRF Data: "As" is BDL.
3	02/14/99	MET	1	Low sample vol ch3 (8.949 m^3). XRF Data: "Mn" and "As" are BDL.
3	02/16/99	MET	1	Low sample vol ch3 (8.930 m^3). EC/OC Data: Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
3	02/18/99	MET	1	XRF Data: "Cu" is BDL.
3	02/20/99	MET	1	Low sample vol ch3 (8.819 m^3). EC/OC Data: Void due to suspect data. XRF Data: "As" is BDL.
3	02/22/99	MET	1	Small hole near ring-did not appear to effect mass conc. Hole seems to have occurred subsequent to sampling. Low sample vol ch3 (8.878 m^3). XRF Data: "Cu" and "As" are BDL.
3	02/24/99	MET	1	Void--Sample ran 15 hrs 4 min.
3	02/26/99	MET	1	Low sample vol ch3 (8.919 m^3). XRF Data: "Mn" and "As" are BDL.

3	01/17/99	URG	1	Quartz filter holder observed to be too loose--sample is invalid. Particulate NO3- data is void.
3	01/19/99	URG	1	.
3	01/21/99	URG	1	XRF Data: "As" was below detection limits (BDL).
3	01/23/99	URG	1	XRF Data: "As" was BDL.
3	01/25/99	URG	1	Teflon filter has large tear--did not appear to effect mass conc. Tear seems to have occurred subsequent to sampling. XRF Data: "As" was BDL.
3	01/27/99	URG	1	.
3	01/29/99	URG	1	.
3	01/31/99	URG	1	Teflon filter has a hole-did not appear to effect mass conc. Hole seems to have occurred subsequent to sampling. XRF Data: "Mn" and "As" are BDL.
3	02/02/99	URG	1	.
3	02/04/99	URG	1	.
3	02/08/99	URG	1	XRF Data: "As" is BDL.

3	02/10/99	URG	1	XRF Data: "As" is BDL.
3	02/12/99	URG	1	Teflon filter has a pin hole-did not appear to effect mass conc. Hole seems to have occurred subsequent to sampling. XRF Data: "As" is BDL.
3	02/14/99	URG	1	XRF Data: "Si", "Cu" and "As" are BDL.
3	02/16/99	URG	1	.
3	02/18/99	URG	1	.
3	02/20/99	URG	1	.
3	02/22/99	URG	1	XRF Data: "Mn" and "As" are BDL.
3	02/24/99	URG	1	XRF Data: "As" is BDL.
3	02/26/99	URG	1	XRF Data: "As" is BDL.

3	01/17/99	VAPS	1	Low sample vol ch2 (20.128 m^3).XRF Data: "As" is Below Detection Limits (BDL).
3	01/19/99	VAPS	1	Low sample vol ch2 (19.853 m^3).
3	01/21/99	VAPS	1	Low sample vol ch2 (19.814 m^3). XRF Data: "As" is BDL.
3	01/23/99	VAPS	1	Ch2 (Teflon) is void-appears filter weights were recorded incorrectly.
3	01/25/99	VAPS	1	Void-Sample Duration = 33.2 hours. XAD denuder was found to contain a very small piece of glass while unpacking the cooler. A small crack on one of the ends of the denuder is suspected.
3	01/27/99	VAPS	1	.
3	01/29/99	VAPS	1	XRF Data: "Cu" is BDL.
3	01/31/99	VAPS	1	Ch3 (quartz) has high sample volume (29.367 m^3). XRF Data: "Mn" and "As" were BDL.
3	02/02/99	VAPS	1	.
3	02/04/99	VAPS	1	.
3	02/08/99	VAPS	1	.
3	02/10/99	VAPS	1	.
3	02/12/99	VAPS	1	Void-Ch2 (Teflon-fine) filter has several pin holes. Appears pin holes were present before sampling.
3	02/14/99	VAPS	1	Ch2 (Teflon-fine) filter has 1 small hole present which seems to have occurred subsequent to sampling b/c mass conc looks ok. XRF Data: "Mn", "Cu", and "As" are BDL.
3	02/16/99	VAPS	1	.
3	02/18/99	VAPS	1	Nylon filter was not transferred to CEMQA for analyses-- believe an error occurred when unloading filter packs. Particulate NO3- data is void.
3	02/20/99	VAPS	1	XRF Data: "Mn" is BDL.
3	02/22/99	VAPS	1	Void-Ch2 filter has 1 pin hole. Appears pin hole was present before sampling. Low sample vol ch3-quartz (20.237 m^3).Ch1 (PM10): filter weights were recorded incorrectly.
3	02/24/99	VAPS	1	Void-Negative mass (PM2.5). Believe that lap operator wrote down the initial weights incorrectly.
3	02/26/99	VAPS	1	XRF Data: "As" is BDL.

4	01/15/99	AND	1	XRF Data: "Mn" is below detection limits (BDL); "As" is BDL.
4	01/17/99	AND	1	XRF Data: "Mn" is BDL; "Cu" is BDL.
4	01/19/99	AND	1	XRF Data: "As" is BDL.
4	01/21/99	AND	1	Sampler displays low sample vol ch1-Nylon (9.648 m^3).
4	01/23/99	AND	1	Site op noted a problem with the o-rings. Sampler displays low sample vol ch1 (9.792 m^3). XRF Data: "Cu" is BDL; "As" is BDL.
4	01/25/99	AND	1	.

4	01/27/99	AND	1	.
4	01/29/99	AND	1	.
4	01/31/99	AND	1	Suspect data(Teflon filter-ch2)-fuzz and other unidentified particles present on the filter-affected the mass conc. XRF Data: "Mn" is BDL.
4	02/02/99	AND	1	Sampler displays low sample vol ch1 (9.648 m³). XRF Data: "Mn" and "As" are BDL.
4	02/06/99	AND	1	.
4	02/08/99	AND	1	XRF Data: "As" is BDL.
4	02/10/99	AND	1	XRF Data: "As" is BDL.
4	02/12/99	AND	1	Sampler displays low sample vol ch1 (9.792 m³).
4	02/14/99	AND	1	XRF Data: "As" is BDL.
4	02/16/99	AND	1	XRF Data: "As" is BDL.
4	02/18/99	AND	1	Fuzz present on filter(Teflon filter-ch2)-did not appear to affect mass conc. Sampler displays low sample vol ch1 (9.792 m³). XRF Data: "As" is BDL.
4	02/20/99	AND	1	.
4	02/22/99	AND	1	XRF Data: "As" is BDL.
4	02/24/99	AND	1	Average flow rates were recorded 2/25/99 @ 1200.
4	01/15/99	FRM-T	1	XRF Data: "As" is below detection limits (BDL).
4	01/17/99	FRM-T	1	.
4	01/19/99	FRM-T	1	XRF Data: "As" is BDL.
4	01/21/99	FRM-T	1	XRF Data: "As" is BDL.
4	01/23/99	FRM-T	1	2 pin holes in Teflon filter-did not affect mass conc. Appears hole occurred subsequent to sampling. XRF Data: "Cu" is BDL; "Pb" is BDL; "As" is BDL.
4	01/25/99	FRM-T	1	.
4	01/27/99	FRM-T	1	.
4	01/29/99	FRM-T	1	No sample-did not run due to malfunctioning filter exchange mechanism.
4	01/31/99	FRM-T	1	XRF Data: "Mn" is BDL.
4	02/02/99	FRM-T	1	No sample-did not run due to malfunctioning filter exchange mechanism.
4	02/06/99	FRM-T	1	.
4	02/08/99	FRM-T	1	XRF Data: "As" is BDL.
4	02/10/99	FRM-T	1	.
4	02/12/99	FRM-T	1	XRF Data: "Cu" and "As" are BDL.
4	02/14/99	FRM-T	1	Sampler's Avg Temperature readings are incorrect. XRF Data: "Cu" and "As" are BDL.
4	02/16/99	FRM-T	1	.
4	02/18/99	FRM-T	1	XRF Data: "As" is BDL.
4	02/20/99	FRM-T	1	Fuzz present on Teflon filter-did not appear to affect mass conc. XRF Data: "As" is BDL.
4	02/22/99	FRM-T	1	Small tear @ ring-did not affect mass conc. Appears hole occurred subsequent to sampling.
4	02/24/99	FRM-T	1	.
4	01/15/99	FRM-Q	1	.
4	01/17/99	FRM-Q	1	.
4	01/19/99	FRM-Q	1	.
4	01/21/99	FRM-Q	1	.
4	01/23/99	FRM-Q	1	.
4	01/25/99	FRM-Q	1	.
4	01/27/99	FRM-Q	1	.
4	01/29/99	FRM-Q	1	.
4	01/31/99	FRM-Q	1	.
4	02/02/99	FRM-Q	1	.
4	02/06/99	FRM-Q	1	.
4	02/08/99	FRM-Q	1	.
4	02/10/99	FRM-Q	1	EC/OC Data: Quartz filter was not transferred to DRI.
4	02/12/99	FRM-Q	1	.
4	02/14/99	FRM-Q	1	Sampler's Avg Temperature readings are incorrect.
4	02/16/99	FRM-Q	1	.
4	02/18/99	FRM-Q	1	.
4	02/20/99	FRM-Q	1	.
4	02/22/99	FRM-Q	1	.
4	02/24/99	FRM-Q	1	.
4	01/15/99	IMP	1	XRF Data:"Mn" is below the detection limits(BDL)."As" is BDL Used avg flow rates from the site audits for 3 modules.
4	01/17/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
4	01/19/99	IMP	1	XRF Data" "As" is BDL. Used avg flow rates from the site audits for 3 modules
4	01/21/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
4	01/23/99	IMP	1	Slight tear in Teflon filter-did not affect mass conc. Appears tear occurred after sampling. Ch2 is void-moisture found inside this channel. Filter and housing saturated with H2O. Valve would not turn on. Used avg flow rates from the site audits for 3 modules. XRF Data: "Mn" is BDL; "Cu" is BDL; "As" is BDL.
4	01/25/99	IMP	1	Void-Water found inside Ch2. Used avg flow rates from the site audits for 3 modules.
4	01/27/99	IMP	1	No sample-filters were not installed in cartridges.

4	01/29/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
4	01/31/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "Mn" is BDL. EC/OC Data: Quartz filter was not transferred to DRI.
4	02/02/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "Mn" is BDL.
4	02/06/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
4	02/08/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
4	02/10/99	IMP	1	Used avg flow rates from the site audits for 3 modules.
4	02/12/99	IMP	1	Ch2 timer did not record any elapsed time. Though it appears to have run as programmed. Pressure drop was approx double all previous runs. Used avg flow rates from the site audits for 3 modules. XRF Data: "Pb" is BDL.
4	02/14/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "Cu" is BDL.
4	02/16/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
4	02/18/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Filter support grid upside down-deposit has widely spaced stripes or grid pattern. XRF Data: "As" is BDL.
4	02/20/99	IMP	1	Used avg flow rates from the site audits for 3 modules. EC/OC Data: Filter support grid upside down-deposit has widely spaced stripes or grid pattern.
4	02/22/99	IMP	1	Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
4	02/24/99	IMP	1	Medium-sized tear in Teflon filer-did not affect mass conc. Appears tear occurred after sampling. Ch2 timer displays 0.0 hrs for elapsed time. Site op noted that it appears to have run as programmed. Used avg flow rates from the site audits for 3 modules. XRF Data: "As" is BDL.
4	01/15/99	MET	1	Void-due to sample duration (sample began @ 1400.)
4	01/17/99	MET	1	Sampler displaying incorrect sample volume. (Sampler reading 1/2 the acutal volume.) Site op verified volume. In the database, the mass conc has been calculated using ~9.0 m^3. XRF Data: "Cu" is below detection limits (BDL).
4	01/19/99	MET	1	Sampler displaying incorrect sample volume. (Sampler reading 1/2 the acutal volume.) Site op verified volume. In the database, the mass conc has been calculated using ~9.0 m^3 XRF Data: "Pb" is BDL; "As" is BDL.
4	01/21/99	MET	1	Sample volume was calculated using the flow measured by site op. Nylon filter was crimped-possible leak or improperly put together. XRF Data: "As" is BDL.
4	01/23/99	MET	1	New pump installed on 1/22/99. Low sample vol ch3-nylon (8.586 m^3). XRF Data: "Si" is BDL; "Mn" is BDL; "Cu" is BDL; "As" is BDL.
4	01/25/99	MET	1	Flow check performed by site operator. Low sample vol ch1- Teflon (9.092 m^3) and ch3 (8.568 m^3).
4	01/27/99	MET	1	Low sample vol ch3 (8.507 m^3).
4	01/29/99	MET	1	Low sample vol ch3 (8.544 m^3). XRF Data: "Pb" is BDL.
4	01/31/99	MET	1	Low sample vol ch3 (9.082 m^3).
4	02/02/99	MET	1	Low sample vol ch3 (8.468 m^3). XRF Data: "Mn", "Cu", "Pb", and "As" are BDL.
4	02/06/99	MET	1	Cooling fan was turned off to try to identify high PM conc as compared to the FRM. Was to determine if aspiration of PM2.5 is affected by cooling fan. Low sample vol ch3 (8.651 m^3). XRF Data: "Cu" is BDL.
4	02/08/99	MET	1	Low sample vol ch3 (8.765 m^3). XRF Data: "Pb" and "As" are BDL.
4	02/10/99	MET	1	Low sample vol ch3 (8.607 m^3). XRF Data: "Pb" and "As" are BDL.
4	02/12/99	MET	1	Low sample vol ch3 (8.550 m^3). XRF Data: "Si" and "As" are BDL.
4	02/14/99	MET	1	Low sample vol ch3 (8.531 m^3). XRF Data: "Cu" and "As" are BDL.
4	02/16/99	MET	1	.
4	02/18/99	MET	1	Void-sample ran for 1 second. (However, the volumes reported by the sampler look as if the sampler ran as programmed.)
4	02/20/99	MET	1	Low sample vol ch3 (8.492 m^3). XRF Data: "As" is BDL.
4	02/22/99	MET	1	Low sample vol ch3 (8.456 m^3). XRF Data: "As" is BDL.
4	02/24/99	MET	1	Low sample vol ch3 (8.479 m^3). XRF Data: "As" is BDL.
4	01/15/99	URG	1	XRF Data: "Mn" is below detection limits (BDL).
4	01/17/99	URG	1	Both URG400 and URG450 are displaying temps ~4°C higher than the other samplers--did not affect the data.
4	01/19/99	URG	1	XRF Data: "Pb" is BDL; "As" is BDL.
4	01/21/99	URG	1	XRF Data: "As" is BDL.
4	01/23/99	URG	1	XRF Data: "Mn" is BDL; "As" is BDL.
4	01/25/99	URG	1	Max meter drop reading = 199.4 mm Hg;No average flow or temp recorded. Did not affect mass conc.
4	01/27/99	URG	1	.
4	01/29/99	URG	1	.
4	01/31/99	URG	1	XRF Data: "Mn" and "As" are BDL.
4	02/02/99	URG	1	XRF Data: "Mn", "Cu", and "As" are BDL.
4	02/06/99	URG	1	XRF Data: "As" is BDL.
4	02/08/99	URG	1	XRF Data: "As" is BDL.
4	02/10/99	URG	1	.
4	02/12/99	URG	1	URG400: Void--does not appear that sampler ran as programmed.
4	02/14/99	URG	1	XRF Data: "Cu" and "As" are BDL.
4	02/16/99	URG	1	Wins impactor cleaned before this sample run. XRF Data: "As" is BDL.
4	02/18/99	URG	1	XRF Data: "As" is BDL.
4	02/20/99	URG	1	.
4	02/22/99	URG	1	.
4	02/24/99	URG	1	XRF Data: "As" is BDL.
4	01/15/99	VAPS	1	XRF Data: "Mn" is below detection limits (BDl); "As" is BDL.

4	01/17/99	VAPS	1	Low sample volume ch2 (20.512 m^3) and ch3 (19.890 m^3); XRF Data: "Mn" is BDL.
4	01/19/99	VAPS	1	XRF Data: "As" is BDL.
4	01/21/99	VAPS	1	Low sample volume ch3 (19.698 m^3).
4	01/23/99	VAPS	1	Low sample volume ch3 (19.430 m^3).XRF Data: "Mn" is BDL; "Pb" is BDL; "As" is BDL.
4	01/25/99	VAPS	1	Low sample volume ch2 (20.531 m^3).XRF Data: "Mn" and "Cu" and "Pb" and "As" are BDL.
4	01/27/99	VAPS	1	Void--Sample duration = 34.7hrs.
4	01/29/99	VAPS	1	Low sample volume ch2 (19.989 m^3) and ch3 (19.964 m^3). EC/OC Data: Non-white carbon punch, after carbon analysis, indicative of mineral particles in deposit.
4	01/31/99	VAPS	1	Low sample volume ch2 (19.879 m^3) and ch3 (20.514 m^3). XRF Data: "Pb" is BDL.
4	02/02/99	VAPS	1	Low sample volume ch2 (19.744 m^3) and ch3 (19.240 m^3). XRF Data: "Mn" and "As" are BDL.
4	02/06/99	VAPS	1	Low sample volume ch2 (20.021 m^3) and ch3 (19.188 m^3). XRF Data: "As" is BDL.
4	02/08/99	VAPS	1	No sample--did not run due to programming error.
4	02/10/99	VAPS	1	Void-Teflon and Nylon filters. Filterpack was assemblied incorrectly (Teflon loaded downstream of Nylon filter.) Low sample volume ch3 (18.991 m^3). Mass conc and particulate NO3- data are void.
4	02/12/99	VAPS	1	Low sample vol ch2 (20.208 m^3) and ch3 (18.073 m^3). XRF Data: "Cu" and "As" are BDL.
4	02/14/99	VAPS	1	Void-Teflon and Nylon filters. Filterpack was assembled incorrectly (Teflon loaded downstream of Nylon filter.) Low sample volume ch3 (20.108 m^3). Mass conc and particulate NO3- data are void.
4	02/16/99	VAPS	1	Low sample volume ch2 (19.717 m^3) and ch3 (19.389 m^3). XRF Data: "Cu" is BDL.
4	02/18/99	VAPS	1	Void-Sample duration = 38.4 hrs
4	02/20/99	VAPS	1	Low sample volume ch2 (20.138 m^3) and ch3 (20.199 m^3).
4	02/22/99	VAPS	1	Two small holes-did not affect mass conc. Holes occurred after sampling. Low sample vol ch2 (20.103 m^3). XRF Data: "As" is BDL.
4	02/24/99	VAPS	1	EC/OC Data: Quartz filter was not transferred to DRI. XRF Data: "Mn" and "As" are BDL.

Appendix D

Final Data Archive, By Species, Site, Date, and Sampler for the 4-City Study

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of PM-2.5 (µg/m3)		Sampler[1]					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	32.7	35.3	34.7	71.26	34.9	36.9
	1/9/1999	6.7	7.7	**7.9**	21.6	7.7	
	1/15/1999	26.8	28.6	26.3	66.2	32.9	
	1/18/1999	85.1	74.3	87.5	93.0	105.1	
	1/21/1999	13.3	14.9	13.2	13.3	**16.8**	32.5
	1/24/1999	30.1	**29.4**	27.0	33.4	38.7	57.5
	1/27/1999	2.7	**3.0**	2.8	3.0	**3.1**	4.9
	1/30/1999	22.0	29.5	16.4	33.4		49.7
	2/2/1999	5.4	5.6	5.7	14.2	**5.1**	12.6
	2/5/1999	18.0	21.0	19.7	19.3		26.2
	2/11/1999	2.2	2.2	2.6	9.5	2.5	9.1
	2/14/1999	34.2	35.6	34.2	41.6	53.5	74.8
	2/17/1999	59.0	59.0	58.7	65.7	80.5	
	2/20/1999	31.2	29.1	32.8	38.9	39.8	54.2
	2/23/1999	17.4	17.6	16.0	32.0	**22.3**	36.4
	2/26/1999	22.6	23.6	22.6	25.2	35.1	63.4
2	1/6/1999	26.4	26.8	22.3	91.5		29.8
	1/8/1999	21.3	21.2	18.3	45.0		33.4
	1/14/1999	21.9	22.0	15.7	38.0	19.0	
	1/16/1999	25.6	25.3	21.2	46.8	24.5	
	1/18/1999	24.6	24.4	22.6	43.7	23.5	26.3
	1/20/1999	12.9	12.7	10.7	26.7	11.6	
	1/22/1999	9.1	9.0	8.9	20.6		9.1
	1/24/1999	20.6	19.8	14.7	38.0	19.5	21.7
	1/26/1999	8.4	7.6	6.9	9.8	8.1	10.2
	1/28/1999	4.4	4.1	4.1		4.0	4.1
	2/3/1999	17.1	17.3	15.5	34.2	16.1	17.5
	2/5/1999	11.0	11.5	10.1	12.1	12.7	
	2/7/1999	22.3	23.3	18.2	28.7		32.3
	2/9/1999	13.6	13.8	12.0	21.1		13.6
	2/11/1999	4.2	3.9	3.9	6.4	3.4	3.8
	2/13/1999	12.3	12.4	13.2	25.2		
	2/15/1999	12.6	12.8	12.2	26.0	11.7	12.2
	2/17/1999	20.2	20.3	17.4	36.2	20.8	21.5
	2/19/1999	13.5	13.4	12.4	28.9	13.5	
	2/21/1999	12.9			26.7	11.3	
3	1/17/1999	21.4	20.6			21.0	24.4
	1/19/1999	9.0	9.2	9.0	11.5	9.4	9.8
	1/21/1999	25.3	25.8	26.7	25.0	25.0	33.2
	1/23/1999	9.4		9.1	7.9	8.7	
	1/25/1999	19.3	19.4	18.8	20.4	21.2	
	1/27/1999	38.5	37.6	38.6	40.7	40.9	47.4
	1/29/1999	15.0	15.0	14.7	15.5	15.4	16.6
	1/31/1999	11.8	12.4	11.7	10.9	12.3	13.5
	2/2/1999	13.9	13.8	13.6	13.3	14.0	16.2
	2/4/1999	25.8	25.8	25.7	25.1	26.4	34.6
	2/8/1999	16.9	16.5	16.6	16.4	16.5	18.6
	2/10/1999	11.8	11.9	11.4	12.8	11.7	14.9
	2/12/1999	15.5	15.6		15.6	15.3	
	2/14/1999	5.1	5.2	5.4	5.5	5.2	3.5
	2/16/1999	32.5	32.2	30.3	38.6	31.6	41.5
	2/18/1999	24.9	24.9	25.1	24.4	24.4	25.4
	2/20/1999	11.0	10.5	10.5	12.3	11.3	13.2
	2/22/1999	5.3	5.0	5.7	6.5	5.9	
	2/24/1999	10.8	10.8	10.8		11.7	
	2/26/1999	14.8	14.4	14.4	15.9	15.0	17.0
4	1/15/1999	6.4	8.6	6.2		5.9	
	1/17/1999	9.4	9.7	9.5	10.0	9.4	10.7
	1/19/1999	4.2	4.4	5.0	5.0	4.2	4.6
	1/21/1999	23.1	23.8	23.0	24.4	24.6	25.4
	1/23/1999	6.2	6.5	5.7	6.0	6.2	8.2
	1/25/1999	8.5	8.3	8.5	9.6	8.4	9.4
	1/27/1999	15.7	15.3		15.9	16.1	
	1/29/1999	18.3		18.6	18.8	18.8	20.9
	1/31/1999	10.7	8.7	7.2	8.3	9.1	10.5
	2/2/1999	7.0		7.0	7.1	7.8	8.4
	2/6/1999	9.4	10.4	9.1	11.0	9.9	12.5
	2/8/1999	6.1	6.6	6.2	6.8	7.2	
	2/10/1999	11.0	11.5	11.2	12.9	12.0	
	2/12/1999	12.4	12.8	12.6	13.6		16.3
	2/14/1999	5.7	6.5	6.2	6.7	7.2	
	2/16/1999	19.7	20.5	20.4	23.7	21.3	24.5
	2/18/1999	9.5	9.8	9.9		11.0	
	2/20/1999	13.9	13.9	14.2	15.4	15.2	16.1
	2/22/1999	5.0	5.2	5.0	5.6	5.5	5.4
	2/24/1999	11.9	12.0	11.4	12.3	13.1	15.1

[1] **Shaded values are from replicate sampler used to increase n for mass statistics at Rubidoux.**

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of SO4-T (µg/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	0.6		0.6	1.0		
	1/9/1999	0.2		0.2	0.5		
	1/15/1999	0.5		0.5	1.0		
	1/18/1999	6.1		5.4	6.0		
	1/21/1999	1.6		1.6	1.7		
	1/24/1999	1.8		1.7	1.8		
	1/27/1999	0.2		0.2	0.3		
	1/30/1999	0.5		0.5	0.7		
	2/2/1999	0.3		0.3	0.4		
	2/5/1999	0.7		0.7	0.8		
	2/11/1999	0.3		0.3	0.4		
	2/14/1999	1.7		1.6	1.7		
	2/17/1999	3.8		3.6	3.6		
	2/20/1999	2.2		2.0	2.1		
	2/23/1999	0.5		0.4	0.8		
	2/26/1999	2.1		1.9	1.9		
2	1/6/1999	0.6		0.6	0.9		
	1/8/1999	0.9		0.89	1.2		
	1/14/1999	0.7		0.7	1.0		
	1/16/1999	0.9		0.91	1.2		
	1/18/1999	1.7		1.64	1.9		
	1/20/1999	1.1		1.06	1.3		
	1/22/1999	0.2		0.18	0.4		
	1/24/1999	0.6		0.54	0.8		
	1/26/1999	0.3		0.29	0.4		
	1/28/1999	0.4		0.39			
	2/3/1999	0.6		0.59	0.8		
	2/5/1999	0.4		0.38	0.5		
	2/7/1999	0.6		0.63	0.7		
	2/9/1999	1.0		1.1	1.3		
	2/11/1999	0.2		0.22	0.3		
	2/13/1999	0.6		0.62	0.9		
	2/15/1999	1.0		1.02	1.2		
	2/17/1999	1.2		1.15	1.5		
	2/19/1999	1.0		1.05	1.3		
	2/21/1999	1.1		1.15			
3	1/17/1999	3.0					
	1/19/1999	1.5		1.6	1.7		
	1/21/1999	4.0		4.2	4.3		
	1/23/1999	1.3		2.8	2.5		
	1/25/1999	6.7		6.7	6.8		
	1/27/1999	8.2		8.1	8.4		
	1/29/1999	4.0		4.0	4.0		
	1/31/1999	1.7		1.7	1.8		
	2/2/1999	2.9		3.0	3.0		
	2/4/1999	5.4		5.4	5.4		
	2/8/1999	4.1		4.1	4.2		
	2/10/1999	2.4		2.5	2.5		
	2/12/1999	4.2		4.2	4.4		
	2/14/1999	1.2		1.2	1.3		
	2/16/1999	6.3		6.1	6.5		
	2/18/1999	7.1		6.9	7.0		
	2/20/1999	3.6		3.6	3.6		
	2/22/1999	1.1		1.1	1.2		
	2/24/1999	1.7		1.7			
	2/26/1999	2.6		2.5	2.5		
4	1/15/1999	1.9		1.9			
	1/17/1999	1.3		1.3	1.3		
	1/19/1999	0.7		0.7	0.7		
	1/21/1999	5.3		5.3	5.1		
	1/23/1999	1.8			1.8		
	1/25/1999	3.4			3.5		
	1/27/1999	5.5			5.7		
	1/29/1999	6.1		6.2	6.2		
	1/31/1999	3.1		3.3	3.3		
	2/2/1999	2.8		2.7	2.8		
	2/6/1999	1.8		1.8	1.8		
	2/8/1999	2.5		2.6	2.5		
	2/10/1999	2.3		2.4	2.4		
	2/12/1999	5.6		5.3	5.6		
	2/14/1999	2.5		2.4	2.5		
	2/16/1999	2.0		1.9	1.5		
	2/18/1999	2.8		2.7			
	2/20/1999	6.2		6.1	6.1		
	2/22/1999	1.9		1.6	1.9		
	2/24/1999	2.8		2.8	2.8		

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of SO4Q (µg/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999		0.7			0.7	0.7
	1/9/1999		0.3			0.4	0.5
	1/15/1999		0.6			0.5	0.9
	1/18/1999		6.0			6.6	6.7
	1/21/1999		1.6			1.7	1.9
	1/24/1999		1.9			2.0	2.0
	1/27/1999					0.3	0.3
	1/30/1999		0.6			0.7	0.7
	2/2/1999		0.3			0.4	0.4
	2/5/1999		1.2			0.7	0.8
	2/11/1999		0.4			0.4	0.4
	2/14/1999		1.8			1.9	1.8
	2/17/1999		3.7			3.8	3.7
	2/20/1999		1.6			1.9	2.3
	2/23/1999		0.4			0.5	0.7
	2/26/1999		2.0			2.0	2.1
2	1/6/1999		0.7				0.6
	1/8/1999		1.0			1.0	1.0
	1/14/1999		0.8			0.7	
	1/16/1999		1.0			1.0	
	1/18/1999		1.8			1.8	1.7
	1/20/1999		1.2			1.1	
	1/22/1999		0.2			0.2	0.2
	1/24/1999		0.6			0.6	0.6
	1/26/1999		0.3			0.4	0.3
	1/28/1999		0.5			0.4	0.4
	2/3/1999		0.7			0.7	0.7
	2/5/1999		0.4			0.4	0.4
	2/7/1999		0.7			0.7	0.7
	2/9/1999		1.2			1.3	1.1
	2/11/1999		0.3			0.3	0.3
	2/13/1999		0.7			0.7	0.7
	2/15/1999		1.1			1.1	1.0
	2/17/1999		1.6			1.2	1.1
	2/19/1999		1.2			1.2	1.1
	2/21/1999		1.2			1.3	1.2
3	1/17/1999		3.1				2.6
	1/19/1999		1.8			1.6	1.3
	1/21/1999		4.0			4.1	3.6
	1/23/1999		2.6			2.3	2.3
	1/25/1999		6.7			6.8	
	1/27/1999		8.4			8.4	7.5
	1/29/1999		4.4			4.2	3.5
	1/31/1999		2.0			1.8	1.4
	2/2/1999		3.0			2.8	2.6
	2/4/1999		5.7			5.9	4.9
	2/8/1999		4.0			3.9	3.4
	2/10/1999		2.7			2.6	2.3
	2/12/1999		4.1			4.0	3.5
	2/14/1999		1.5			1.4	1.2
	2/16/1999		6.5			6.6	5.8
	2/18/1999		7.3			6.8	6.5
	2/20/1999		3.7			3.9	3.3
	2/22/1999		1.5			1.4	1.2
	2/24/1999		2.0			2.0	1.7
	2/26/1999		2.7			2.5	2.6
4	1/15/1999		1.9			2.0	1.8
	1/17/1999		1.3			1.4	1.3
	1/19/1999		0.7			0.7	0.7
	1/21/1999		5.2			5.0	4.9
	1/23/1999		1.7			1.8	1.8
	1/25/1999		3.5			3.7	3.3
	1/27/1999		5.4			5.6	
	1/29/1999		6.2			6.4	6.6
	1/31/1999		3.3			3.2	3.4
	2/2/1999		2.8			2.7	2.8
	2/6/1999		2.0			1.9	1.9
	2/8/1999		2.6			2.5	
	2/10/1999		2.3			2.4	2.3
	2/12/1999		5.5			5.5	5.4
	2/14/1999		2.6			2.7	2.1
	2/16/1999		2.2			2.4	2.1
	2/18/1999		2.8			2.9	
	2/20/1999		5.9			6.1	6.2
	2/22/1999		2.0			2.3	1.7
	2/24/1999		2.9			2.6	3.0

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of NO3T (µg/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	10.5			10.8		
	1/9/1999	0.8			0.9		
	1/15/1999	8.3			9.5		
	1/18/1999	38.0			38.8		
	1/21/1999	3.1			3.1		
	1/24/1999	11.6			11.6		
	1/27/1999	0.2			0.2		
	1/30/1999	7.7			8.9		
	2/2/1999	0.2			0.4		
	2/5/1999	7.4			7.4		
	2/11/1999	0.1			0.1		
	2/14/1999	15.3			15.7		
	2/17/1999	26.2			26.1		
	2/20/1999	12.3			13.2		
	2/23/1999	5.6			6.0		
	2/26/1999	9.1			8.9		
2	1/6/1999	4.3			5.3		
	1/8/1999	3.8			4.6		
	1/14/1999	2.8			3.1		
	1/16/1999	3.8			4.7		
	1/18/1999	1.7			2.8		
	1/20/1999	1.6			2.7		
	1/22/1999	0.6			0.4		
	1/24/1999	0.6			1.1		
	1/26/1999	0.9			1.3		
	1/28/1999	0.1					
	2/3/1999	2.5			3.4		
	2/5/1999	1.2			1.4		
	2/7/1999	4.5			5.4		
	2/9/1999	1.2			1.8		
	2/11/1999	0.1			0.1		
	2/13/1999	0.2			0.3		
	2/15/1999	0.9			1.4		
	2/17/1999	3.7			4.8		
	2/19/1999	1.7			3.2		
	2/21/1999	0.6					
3	1/17/1999	3.7					
	1/19/1999	1.4			1.2		
	1/21/1999	5.4			5.3		
	1/23/1999	0.6			1.2		
	1/25/1999	4.3			4.3		
	1/27/1999	8.2			8.1		
	1/29/1999	2.8			2.7		
	1/31/1999	2.9			3.0		
	2/2/1999	2.6			2.5		
	2/4/1999	6.2			5.6		
	2/8/1999	3.2			3.1		
	2/10/1999	1.8			1.6		
	2/12/1999	1.9			1.7		
	2/14/1999	0.6			0.6		
	2/16/1999	5.9			5.9		
	2/18/1999	3.6			3.3		
	2/20/1999	1.1			1.2		
	2/22/1999	0.5			0.5		
	2/24/1999	3.0					
	2/26/1999	5.4			4.6		
4	1/15/1999	0.1					
	1/17/1999	0.2			0.2		
	1/19/1999	0.1			0.1		
	1/21/1999	0.4			0.4		
	1/23/1999	0.3			0.3		
	1/25/1999	0.1			0.1		
	1/27/1999	0.3			0.4		
	1/29/1999	0.4			0.5		
	1/31/1999	0.9			0.8		
	2/2/1999	0.3			0.2		
	2/6/1999	0.1			0.2		
	2/8/1999	0.1			0.1		
	2/10/1999	0.2			0.2		
	2/12/1999	0.1			0.2		
	2/14/1999	0.2			0.3		
	2/16/1999	0.6			0.7		
	2/18/1999	0.4					
	2/20/1999	0.5			0.5		
	2/22/1999	0.3			0.3		
	2/24/1999	1.7			1.7		

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of NO3P (µg/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	10.24	11.91	10.68	10.94	12.22	13.15
	1/9/1999	0.88	1.05	0.90	1.11	1.14	1.28
	1/15/1999	8.28	9.64	7.76	10.19	9.53	
	1/18/1999	34.65	38.03	34.58	40.42	41.78	42.34
	1/21/1999	3.22	3.06	3.51	3.82	6.52	4.16
	1/24/1999	10.92	12.13	11.62	12.47	12.59	13.31
	1/27/1999	0.61		0.65	0.76		1.19
	1/30/1999	7.98	9.69	8.37	9.71		
	2/2/1999	0.39	0.44	0.41	0.49		0.62
	2/5/1999	6.95	9.52	7.88	8.32		8.58
	2/11/1999	0.10	0.13	0.08	0.17	0.15	0.16
	2/14/1999	14.24	16.71	15.39	16.94	17.86	17.43
	2/17/1999	24.14	25.83	25.85	27.29	26.71	27.04
	2/20/1999	14.04	12.22	14.83	16.27	17.91	20.25
	2/23/1999	5.14	6.20	6.03	6.52		6.81
	2/26/1999	9.14	9.70	9.68	10.50	10.53	11.13
2	1/6/1999	5.55	5.81	4.36	6.26		7.88
	1/8/1999	4.73	4.98	4.03	5.44		5.96
	1/14/1999	4.18	3.46	2.65	4.63	6.00	
	1/16/1999	5.06	5.33	4.42	5.75	7.34	
	1/18/1999	3.50	2.55	2.74	3.97	4.46	4.29
	1/20/1999	3.61	3.71	2.90		5.27	
	1/22/1999	0.40	0.45	0.41	0.55		0.53
	1/24/1999	1.29	1.37	1.25	1.59	1.86	1.75
	1/26/1999	1.93	1.99	1.91	1.55	3.09	2.57
	1/28/1999	0.41	0.44	0.37		0.67	0.62
	2/3/1999	4.08	4.42	3.52	4.56	5.95	5.96
	2/5/1999	2.14	2.23	2.10	2.24	3.07	4.26
	2/7/1999	7.02	7.43	6.28	7.42		9.11
	2/9/1999	4.18	4.24	3.51	4.07		4.59
	2/11/1999	0.16	0.20	0.14	0.19	0.24	0.20
	2/13/1999	0.28	0.29	0.25	0.37	0.52	
	2/15/1999	2.36	2.36	1.83	2.57	3.78	3.85
	2/17/1999	6.44	6.81	4.43	6.84	9.30	8.77
	2/19/1999	5.39	5.47	3.51	5.82	8.73	
	2/21/1999	2.51	2.42	1.99	2.82	4.34	4.29
3	1/17/1999	3.78	4.11				5.97
	1/19/1999	1.71	1.90	1.93	1.90	2.27	2.96
	1/21/1999	5.31	5.46	5.91	5.69	5.73	6.31
	1/23/1999	3.99	1.63	1.91	1.71	1.94	3.23
	1/25/1999	4.32	4.62	4.78	4.67	5.03	
	1/27/1999	7.95	8.64	8.30	8.57	8.84	8.07
	1/29/1999	2.90	3.39	3.12	3.18	3.67	3.00
	1/31/1999	2.80	3.46	3.06	3.14	3.12	2.40
	2/2/1999	2.64	2.71	2.79	2.77	2.58	3.30
	2/4/1999	5.90	6.53	6.30	6.34	6.97	6.86
	2/8/1999	3.03	3.14	3.33	3.36	3.23	3.22
	2/10/1999	1.97	2.18	2.07	2.15	2.61	1.99
	2/12/1999	2.60	2.62	2.68	2.73	3.07	2.78
	2/14/1999	0.65	0.92	0.68	0.73	0.74	0.73
	2/16/1999	6.32	6.14	5.51	6.91	8.28	7.93
	2/18/1999	3.50	3.86	3.74	2.34	3.75	
	2/20/1999	1.36	1.59	1.42	1.51	1.84	1.73
	2/22/1999	0.53	1.07	0.54	0.61	0.73	0.62
	2/24/1999	2.85	3.84	3.03		3.35	3.53
	2/26/1999	5.13	6.09	5.32	5.60	6.02	6.40
4	1/15/1999	0.23	0.22	0.26		0.25	0.24
	1/17/1999	0.46	0.43	0.43	0.53	0.56	0.64
	1/19/1999	0.14	0.13	0.12	0.24	0.17	0.20
	1/21/1999	1.10	1.00	1.08	0.72	1.58	1.34
	1/23/1999	0.44	0.25		0.49	0.31	0.42
	1/25/1999	0.27	0.23		0.34	0.39	0.40
	1/27/1999	1.33	1.01		1.57	2.07	
	1/29/1999	1.07	1.07	1.09	1.36	1.62	1.76
	1/31/1999	1.54	1.47	1.62	1.69	2.30	2.68
	2/2/1999	0.66	0.67	0.69	0.76	0.95	1.02
	2/6/1999	0.44	0.25	0.40	0.51	0.70	0.80
	2/8/1999	0.16	0.17	0.14	0.19	0.21	
	2/10/1999	0.57	0.29	0.59	0.71	0.61	
	2/12/1999	0.35	0.11	0.33	0.39		0.41
	2/14/1999	0.52	0.34	0.55	0.64	0.73	
	2/16/1999	1.60	1.75	1.28	0.28	3.13	2.82
	2/18/1999	0.76	0.73	0.72		1.01	
	2/20/1999	1.67	1.14	1.59	1.92	2.49	3.25
	2/22/1999	0.53	0.40	0.58	0.64	0.76	0.86
	2/24/1999	2.30	2.25	2.40	2.76	3.08	2.68

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of NH4 (µg/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	3.21	3.69	2.75	3.13	3.61	3.50
	1/9/1999	0.28	0.39	0.16	0.16	0.43	0.24
	1/15/1999	2.45	3.00	1.85	2.65	2.96	1.29
	1/18/1999	13.20	13.20	10.60	13.48	14.34	13.31
	1/21/1999	1.13	1.49	0.92	1.31	1.58	1.46
	1/24/1999	4.00	4.56	3.43	4.43	4.86	4.35
	1/27/1999	0.10		0.10	0.05	0.32	0.24
	1/30/1999	2.45	3.04	2.10	2.94	3.45	2.84
	2/2/1999	0.11	0.26	0.06	0.08	0.37	0.15
	2/5/1999	2.44	2.76	2.19	2.66	2.99	2.55
	2/11/1999	0.12	0.14	0.10	0.08	0.17	0.06
	2/14/1999	4.90	5.41	4.24	5.31	5.98	4.79
	2/17/1999	9.00	9.34	7.83	9.27	9.42	8.39
	2/20/1999	4.18	4.24	4.35	4.69	5.32	4.91
	2/23/1999	1.69	1.81	1.48	1.58	2.09	1.57
	2/26/1999	2.88	3.21	2.69	3.39	3.85	3.48
2	1/6/1999	1.38	1.65	0.87	1.71	1.86	1.89
	1/8/1999	1.40	1.73	1.01	1.68	1.74	1.80
	1/14/1999	0.98	1.19	0.36	1.09	1.25	
	1/16/1999	1.37	1.87	1.04	1.66	1.71	
	1/18/1999	1.02	1.31	0.83	1.31	1.14	1.49
	1/20/1999	0.79	1.50	0.69	0.97	1.36	
	1/22/1999	0.06	0.20	0.06	0.10	0.02	0.17
	1/24/1999	0.24	0.51	0.25	0.32	0.37	0.50
	1/26/1999	0.33	0.70	0.39	0.38	0.64	0.70
	1/28/1999	0.16	0.23	0.15		0.20	0.25
	2/3/1999	0.89	1.55	0.70	1.23	1.18	1.59
	2/5/1999	0.47	0.86	0.40	0.53	0.79	0.86
	2/7/1999	1.48	2.52	1.56	1.94	2.24	2.42
	2/9/1999	0.74	1.69	0.95	0.99	0.81	0.85
	2/11/1999	0.05	0.13	0.06	0.08	0.20	0.12
	2/13/1999	0.21	0.26	0.20	0.25	0.27	0.27
	2/15/1999	0.57	1.12	0.49	0.67	1.08	1.11
	2/17/1999	1.42	2.44	0.99	1.56	2.24	2.14
	2/19/1999	0.77	1.93	0.65	1.22	2.01	1.91
	2/21/1999	0.52	1.13	0.52		1.18	1.05
3	1/17/1999	2.22	2.39				1.87
	1/19/1999	1.00	1.21	0.95	1.09	1.23	0.89
	1/21/1999	3.22	3.10	3.07	3.56	3.40	2.63
	1/23/1999	1.18	1.38	1.08	1.34	1.30	1.24
	1/25/1999	3.76	3.66	3.53	4.09	4.03	
	1/27/1999	5.53	5.78	5.00	5.64	5.83	4.91
	1/29/1999	2.35	2.59	2.14	2.53	2.61	2.09
	1/31/1999	1.56	1.80	1.40	1.75	1.57	1.17
	2/2/1999	1.96	2.05	1.63	2.13	1.83	1.55
	2/4/1999	3.82	4.03	3.56	3.96	4.26	3.45
	2/8/1999	2.55	2.43	2.32	2.75	2.44	1.98
	2/10/1999	1.50	1.72	1.36	1.58	1.68	1.35
	2/12/1999	2.09	2.38	1.96	2.11	2.35	1.90
	2/14/1999	0.59	0.78	0.51	0.66	0.63	0.57
	2/16/1999	3.97	4.02	3.04	4.24	4.49	3.84
	2/18/1999	3.68	3.86	3.34	3.80	3.64	3.42
	2/20/1999	1.72	1.83	1.52	1.89	1.83	1.46
	2/22/1999	0.55	0.89	0.49	0.67	0.69	0.53
	2/24/1999	1.47	1.97	1.29		1.66	1.42
	2/26/1999	2.52	2.82	2.08	2.44	2.46	2.45
4	1/15/1999	0.65	0.58	0.41		0.73	0.71
	1/17/1999	0.51	0.53	0.35	0.52	0.65	0.58
	1/19/1999	0.24	0.23	0.12	0.23	0.28	0.27
	1/21/1999	1.82	1.88	1.59	1.89	1.93	1.80
	1/23/1999	0.49	0.42		0.53	0.45	0.46
	1/25/1999	1.30	1.21		1.28	1.50	1.29
	1/27/1999	2.03	1.99		2.14	2.37	
	1/29/1999	2.31	2.26	2.16	2.42	2.59	2.78
	1/31/1999	1.34	1.45	1.23	1.26	1.56	1.64
	2/2/1999	1.08	1.15	0.95	0.99	1.23	1.36
	2/6/1999	0.70	0.64	0.62	0.58	0.82	0.81
	2/8/1999	0.89	0.85	0.89	0.86	0.94	
	2/10/1999	0.96	0.86	0.88	0.89	1.00	1.07
	2/12/1999	1.62	1.50	1.44	1.47	1.75	1.92
	2/14/1999	0.90	0.91	0.84	0.90	1.02	0.90
	2/16/1999	0.93	1.26	0.80	0.80	1.52	1.28
	2/18/1999	1.16	1.13	0.98		1.40	
	2/20/1999	2.38	2.30	2.30	2.29	2.54	2.85
	2/22/1999	0.79	0.77	0.75	0.72	0.98	0.82
	2/24/1999	1.50	1.78	1.34	1.41	1.70	1.79

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of OC (µg/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	**10.26**	8.69	7.85	8.81	8.01	5.75
	1/9/1999		4.58	2.98	5.86	4.18	2.80
	1/15/1999	**10.04**	7.72	4.16	9.37	6.81	14.99
	1/18/1999	**14.21**	10.01	5.26	10.42	11.49	14.50
	1/21/1999	**4.28**	2.98	1.75	3.43	3.08	3.57
	1/24/1999	**8.13**	6.89	2.97	7.60	5.72	7.65
	1/27/1999	**2.46**		1.25	3.41	2.64	1.66
	1/30/1999	**7.71**	7.78	3.28	7.78	6.39	
	2/2/1999	**4.79**	4.58	2.56	3.79	3.24	2.51
	2/5/1999	**5.89**	4.65	3.98	4.29	3.83	3.62
	2/11/1999	**1.96**	2.05	1.58	2.35	1.66	1.16
	2/14/1999	**6.97**	5.53	5.86	7.57	5.86	5.68
	2/17/1999	**8.34**	5.69	6.45	5.46	6.40	6.70
	2/20/1999	**8.26**	6.93	5.91	7.82	6.32	6.23
	2/23/1999	**6.67**	5.50	4.58	7.38	5.17	4.82
	2/26/1999	**3**	4.19	3.83	4.64	3.94	5.45
2	1/6/1999	11.22	11.75	7.65	12.32	7.78	6.76
	1/8/1999	9.49	7.86	5.80	10.05	6.38	4.76
	1/14/1999	12.03	9.48	6.72	1.64	7.64	
	1/16/1999	14.63	11.79	9.42	12.71	8.33	
	1/18/1999	12.13	10.14	10.21	13.32	8.63	8.32
	1/20/1999	7.60	5.60	4.04	5.51	4.05	
	1/22/1999	6.87	6.23	5.45	5.42	4.21	3.28
	1/24/1999	14.71	12.51	10.11	12.11	9.19	7.84
	1/26/1999	5.78	4.34	3.96	4.85	3.69	2.94
	1/28/1999	4.73	3.96	3.25		2.16	1.72
	2/3/1999	10.37	8.98	8.10	10.77	9.23	5.51
	2/5/1999	7.23	5.60	4.45	5.72	5.61	4.04
	2/7/1999	10.78	9.67	7.61	10.35	9.72	7.10
	2/9/1999	9.21	7.69	6.58	9.30	4.91	4.54
	2/11/1999	5.54	3.99	3.51	4.52	3.72	1.81
	2/13/1999	8.50	7.29	5.79	10.41	5.64	4.68
	2/15/1999	8.53	7.34	6.09	7.64	6.95	4.08
	2/17/1999	10.25	8.34	7.50	9.59	7.21	4.21
	2/19/1999	8.25	6.45	5.64	1.41	6.56	2.96
	2/21/1999	8.82	7.75	6.12	8.49	6.38	3.98
3	1/17/1999	8.85	7.59				3.92
	1/19/1999	5.94	4.89	2.16	5.51	3.90	1.89
	1/21/1999	6.36	5.17	5.82	2.64	4.72	4.12
	1/23/1999	3.13	2.31	1.93	2.54	1.97	1.99
	1/25/1999	3.55	2.80	2.29	2.86	2.10	
	1/27/1999	9.14	9.57	7.83	8.00	7.57	6.06
	1/29/1999	5.68	4.05	3.82	3.98	3.48	2.34
	1/31/1999	4.60	4.13	3.95	3.95	3.64	1.88
	2/2/1999	6.11	3.10	2.74	3.24	2.93	2.26
	2/4/1999	6.76	5.32	4.54	4.44	4.48	3.84
	2/8/1999	4.04	3.40	3.24	3.75	3.07	2.45
	2/10/1999	4.79	4.46	3.74	4.14	3.36	2.42
	2/12/1999	6.56	4.60	3.71	4.23	3.64	2.46
	2/14/1999	3.62	2.31	1.92	2.02	1.53	1.31
	2/16/1999	11.01	8.54	7.83	10.14	8.29	5.65
	2/18/1999	6.82	4.41	4.71	4.39	4.20	3.30
	2/20/1999	3.10	2.78	2.39	0.39	2.16	1.62
	2/22/1999	3.72	2.77	2.98	2.39	2.20	1.24
	2/24/1999	4.69	3.66	3.71		3.06	2.07
	2/26/1999	3.95	3.30	3.10	3.07	3.21	2.33
4	1/15/1999	2.83	3.10	2.26		1.89	2.42
	1/17/1999	5.52	4.42	3.04	4.62	3.38	2.94
	1/19/1999	2.67	2.79	2.01	2.65	1.72	1.46
	1/21/1999	7.43	7.27	5.99	7.20	6.22	5.56
	1/23/1999	2.32	2.49	1.79	2.80	0.89	2.02
	1/25/1999	2.45	2.40	1.83	2.83	1.74	1.64
	1/27/1999	4.00	3.78		3.83	4.22	
	1/29/1999	5.59	4.66	3.97	5.33	4.04	6.85
	1/31/1999	3.11	2.39	1.78		2.06	1.86
	2/2/1999	2.96	2.00	1.72	2.86	1.95	1.80
	2/6/1999	3.85	3.75	2.83	4.01	2.96	3.06
	2/8/1999	1.70	2.21	1.29	2.44	1.68	
	2/10/1999	4.89		2.76	3.51	2.87	3.13
	2/12/1999	3.96	3.32	2.47	4.15	2.69	2.99
	2/14/1999	2.54	1.81	1.62	2.27	1.51	1.17
	2/16/1999	10.07	8.51	7.51	10.33	7.95	7.34
	2/18/1999	3.31	3.37	2.25		2.72	
	2/20/1999	2.76	3.11	2.31	3.06	2.09	2.25
	2/22/1999	2.02	1.46	1.58	1.77	1.47	1.19
	2/24/1999	3.75	3.24	2.69	3.62	2.87	

[1] **Shaded values are from replicate sampler to replace missing primary OC data.**

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of EC (µg/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	**6.1**	6.51	4.55	5.68	5.90	6.08
	1/9/1999		1.65	0.81	2.18	1.40	1.50
	1/15/1999	**4.77**	5.22	1.49	4.95	4.17	5.48
	1/18/1999	**5.69**	7.70	1.85	7.23	6.73	5.72
	1/21/1999	**1.64**	1.61	0.37	1.56	1.50	1.55
	1/24/1999	**3.05**	3.22	0.73	2.76	2.78	2.95
	1/27/1999	**0.57**		0.35	0.58	0.87	0.76
	1/30/1999	**3.6**	4.44	1.13	2.99	3.77	
	2/2/1999	**1.45**	1.59	0.85	1.46	1.31	1.39
	2/5/1999	**2.08**	2.50	2.45	2.67	2.44	2.63
	2/11/1999	**0.21**	0.56	0.46	0.51	0.54	0.39
	2/14/1999	**2.29**	2.86	2.47	2.99	3.28	2.55
	2/17/1999	**4.54**	5.43	4.24	4.03	4.97	4.53
	2/20/1999	**3.51**	3.08	2.86	3.38	3.98	3.19
	2/23/1999	**3.31**	2.64	2.38	3.01	3.37	3.10
	2/26/1999	**0.96**	1.90	1.68	1.64	2.03	1.92
2	1/6/1999	5.18	5.01	5.12	5.48	5.87	5.74
	1/8/1999	4.23	3.86	3.74	4.30	3.81	4.42
	1/14/1999	4.72	4.56	3.92	0.10	4.26	
	1/16/1999	5.16	4.82	4.77	4.50	4.47	
	1/18/1999	5.43	5.71	4.26	4.93	5.37	5.19
	1/20/1999	1.98	2.29	1.49	2.03	2.05	
	1/22/1999	2.21	2.37	1.96	2.11	2.61	2.02
	1/24/1999	4.09	5.03	3.78	3.90	4.89	4.32
	1/26/1999	1.38	1.86	1.41	1.54	1.92	1.66
	1/28/1999	1.26	1.53	1.12		1.30	1.20
	2/3/1999	2.98	4.56	3.54	4.32	3.96	3.49
	2/5/1999	2.32	3.26	2.66	2.96	3.36	2.76
	2/7/1999	3.20	4.28	3.81	4.36	4.23	3.91
	2/9/1999	2.41	3.28	2.93	3.33	2.94	2.68
	2/11/1999	0.99	1.47	1.41	1.67	1.53	1.13
	2/13/1999	1.93	2.70	2.26	2.84	2.39	2.23
	2/15/1999	2.73	2.99	2.49	2.76	2.87	2.41
	2/17/1999	3.77	3.98	3.33	4.14	3.61	3.22
	2/19/1999	2.60	2.37	1.97	0.12	2.35	1.95
	2/21/1999	2.65	2.64	2.45	2.85	2.46	2.26
3	1/17/1999	3.69	3.62				2.33
	1/19/1999	1.01	2.10	0.58	1.97	1.91	1.64
	1/21/1999	1.59	3.54	2.32	1.47	3.60	2.85
	1/23/1999	5.35	0.82	0.77	0.79	0.77	0.64
	1/25/1999	2.13	1.64	1.43	1.67	1.68	
	1/27/1999	1.55	5.21	4.71	4.93	4.56	4.73
	1/29/1999	2.13	2.07	2.01	2.13	2.09	1.72
	1/31/1999	1.53	1.73	1.82	1.80	1.80	0.93
	2/2/1999	2.25	1.91	1.79	1.80	2.20	1.60
	2/4/1999	3.50	3.35	2.95	3.13	3.47	2.80
	2/8/1999	1.94	2.45	2.10	1.76	2.07	1.50
	2/10/1999	1.91	2.42	1.97	2.06	2.15	1.81
	2/12/1999	2.35	2.71	2.08	2.17	2.08	2.04
	2/14/1999	1.11	1.16	1.11	0.91	0.98	1.22
	2/16/1999	5.28	5.73	4.45	6.25	5.48	5.33
	2/18/1999	3.28	3.43	3.38	2.77	3.34	3.09
	2/20/1999	1.45	1.63	1.70	0.00	1.41	1.53
	2/22/1999	1.46	1.71	1.83	1.37	1.39	1.60
	2/24/1999	1.51	1.91	1.60		1.46	1.34
	2/26/1999	1.59	1.57	1.42	1.34	1.50	1.03
4	1/15/1999	0.77	1.30	0.99		1.05	1.07
	1/17/1999	1.57	2.17	1.29	1.36	1.61	1.83
	1/19/1999	0.87	1.41	0.96	1.12	1.20	1.09
	1/21/1999	2.96	3.70	2.21	3.12	3.36	3.58
	1/23/1999	0.38	0.76	0.36	0.52	0.37	0.38
	1/25/1999	0.88	1.16	0.88	1.01	1.20	0.94
	1/27/1999	2.08	2.51		2.20	2.22	
	1/29/1999	2.41	2.84	2.24	2.70	2.70	4.52
	1/31/1999	0.68	0.90	0.64		0.81	0.68
	2/2/1999	0.90	0.96	0.76	0.99	0.93	0.81
	2/6/1999	1.83	1.60	1.42	1.60	2.04	1.91
	2/8/1999	0.83	0.78	0.65	0.73	0.92	
	2/10/1999	2.29		1.86	1.72	2.29	1.97
	2/12/1999	0.99	0.82	0.80	0.75	0.96	0.66
	2/14/1999	0.57	0.55	0.56	0.42	0.59	0.41
	2/16/1999	2.66	3.06	2.40	2.71	2.94	2.37
	2/18/1999	1.16	1.20	1.00		1.20	
	2/20/1999	1.21	1.06	1.08	1.13	1.25	1.07
	2/22/1999	0.62	0.65	0.76	0.75	0.83	0.75
	2/24/1999	1.25	1.43	1.21	1.17	1.02	

[1] **Shaded values are from replicate sampler to replace missing primary EC data.**

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of S (ng/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	256	247	237		260	273
	1/9/1999	93	102		164	1100	
	1/15/1999	208	205	199	331	205	
	1/18/1999	2235	1928	2119	2288	2310	
	1/21/1999	624	606	570	664		672
	1/24/1999	706		580	784	814	779
	1/27/1999	84		98	106		106
	1/30/1999	210	242	147	292		269
	2/2/1999	104	111	89	152		130
	2/5/1999	315	311	306	353		344
	2/11/1999	119	121	113	128	131	146
	2/14/1999	636	645	605	704	665	651
	2/17/1999	1473	1392	1359	1439	1457	
	2/20/1999	802	646	760	836	818	862
	2/23/1999		175	143	286		162
	2/26/1999	751	788	718	807	798	839
2	1/6/1999	268	256	228	374		266
	1/8/1999	392	375	344	484		363
	1/14/1999	301	300	328	359	298	
	1/16/1999	357	366	301	454	358	
	1/18/1999	631	643	880	784	654	597
	1/20/1999	403	386	362	431	384	
	1/22/1999	84	71	73	127		151
	1/24/1999	222	238	159	296	221	218
	1/26/1999	129	122	124	175	126	121
	1/28/1999	148	162	143		143	138
	2/3/1999	237	227	234	313	238	227
	2/5/1999	166	177	170	149	158	
	2/7/1999	268	285	268	315		265
	2/9/1999	401	402	364	447		424
	2/11/1999	80	85	72	92	77	77
	2/13/1999	237	237	229	284		
	2/15/1999	402	407	377	461	392	346
	2/17/1999	459	480	425	448	463	436
	2/19/1999	399	435	394	490	412	
	2/21/1999	434			553	440	
3	1/17/1999	1114	1131			1219	1372
	1/19/1999	567	575	620	639	651	654
	1/21/1999	1541	1323	1500	1665	1480	1567
	1/23/1999	980		935	905	1010	
	1/25/1999	2363	2233	2124	2523	2503	
	1/27/1999	2953	2794	2756	3138	3239	3034
	1/29/1999	1454	1430	1326	1464	1520	1416
	1/31/1999	628	640	617	674	694	681
	2/2/1999	1072	1033	959	1113	1102	1031
	2/4/1999	1942	2027	1752	2049	2071	2000
	2/8/1999	1461	1481	612	1636	1509	1619
	2/10/1999	876	900	837	961	927	867
	2/12/1999	1454	1474		1558	1492	
	2/14/1999	434	441	407	461	440	335
	2/16/1999	2154	2203	1995	2287	2182	2170
	2/18/1999	2467	2411	2226	2519	2482	
	2/20/1999	1270	1290		1339	1337	1257
	2/22/1999	395	394	397	451	432	
	2/24/1999	578	590	557		663	
	2/26/1999	941	892	870	987	969	915
4	1/15/1999	714	698	646		752	778
	1/17/1999	509	506	463	554	547	537
	1/19/1999	259	262	241	289	280	254
	1/21/1999	1884	1821	1742	1870	1949	1899
	1/23/1999	622	612	570	632	655	624
	1/25/1999	1258	1231	1148	1364	1289	1332
	1/27/1999	1946	2004		2086	2094	
	1/29/1999	2247		2010	2366	2329	2313
	1/31/1999	1184	1171	972	1188	1276	356
	2/2/1999	1037		934	1026	1080	1018
	2/6/1999	638	692	563	717	755	690
	2/8/1999	890	867	920	905	921	
	2/10/1999	865	861	809	870	892	
	2/12/1999	1828	1953	1841	2102		1969
	2/14/1999	833	889	855	888	954	
	2/16/1999	689	712	693	709	790	732
	2/18/1999	999	1007	1017		1070	
	2/20/1999	2130	2084	2180	2079	2267	2304
	2/22/1999	657	678	619	715	764	686
	2/24/1999	1012	1046	931	1122	1065	1131

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Si (ng/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	492	420	621		430	805
	1/9/1999	264	218		1715	195	
	1/15/1999	449	378	609	2409	339	
	1/18/1999	166	217	206	509	116	
	1/21/1999	67	16	24	130		341
	1/24/1999	86		41	208	53	407
	1/27/1999	0		30	53		177
	1/30/1999	140	150	116	694		1025
	2/2/1999	166	146	166	915		888
	2/5/1999	65	43	37	77		191
	2/11/1999	179	101	150	792	110	988
	2/14/1999	174	121	171	672	126	794
	2/17/1999	332	236	284	642	244	
	2/20/1999	170	119	135	613	106	916
	2/23/1999		280	341	1627		2270
	2/26/1999	113	72	81	134	83	585
2	1/6/1999	532	461	478	2732		648
	1/8/1999	510	500	503	2530		634
	1/14/1999	469	467	560	1752	341	
	1/16/1999	501	475	472	2918	377	
	1/18/1999	450	403	632	2573	295	491
	1/20/1999	472	417	406	1236	301	
	1/22/1999	274	212	257	1409		3958
	1/24/1999	474	444	353	1749	314	585
	1/26/1999	179	133	162	671	90	196
	1/28/1999	88	75	115		43	113
	2/3/1999	450	334	464	2347	315	480
	2/5/1999	60	56	127	104	42	
	2/7/1999	95	94	103	578		157
	2/9/1999	225	172	213	530		266
	2/11/1999	72	50	94	371	47	70
	2/13/1999	475	395	452	1636		
	2/15/1999	390	312	411	1341	267	390
	2/17/1999	475	375	430	1466	294	468
	2/19/1999	446	320	487	1573	300	
	2/21/1999	342			1134	206	
3	1/17/1999	70	57			78	85
	1/19/1999	53	45	38	99	40	76
	1/21/1999	67	52	83	93	61	51
	1/23/1999	0		21	0	15	
	1/25/1999	34	49	48	77	39	
	1/27/1999	84	97	71	192	85	112
	1/29/1999	60	41	35	83	44	47
	1/31/1999	35	31	45	64	41	16
	2/2/1999	46	25	45	0	48	57
	2/4/1999	89	59	64	175	90	70
	2/8/1999	29	40	71	62	4	34
	2/10/1999	32	24	41	75	34	45
	2/12/1999	40	19		149	32	
	2/14/1999	10	26	14	38	0	3
	2/16/1999	126	133	153	318	131	143
	2/18/1999	64	25	64	66	50	
	2/20/1999	48	22		67	31	13
	2/22/1999	36	32	49	235	26	
	2/24/1999	71	61	45		46	
	2/26/1999	76	72	81	208	86	97
4	1/15/1999	31	51	53		32	88
	1/17/1999	72	30	43	66	44	65
	1/19/1999	69	71	67	98	76	69
	1/21/1999	208	195	205	226	185	258
	1/23/1999	41	23	38	0	29	315
	1/25/1999	30	34	53	100	29	109
	1/27/1999	67	38		73	66	
	1/29/1999	100		104	228	115	120
	1/31/1999	35	24	27	30	9	290
	2/2/1999	23		33	48	20	35
	2/6/1999	47	72	24	157	83	78
	2/8/1999	35	36	28	58	38	
	2/10/1999	71	77	65	153	57	
	2/12/1999	36	19	14	0		51
	2/14/1999	39	42	24	57	42	
	2/16/1999	164	227	161	286	143	258
	2/18/1999	26	42	41		53	
	2/20/1999	100	101	116	34	104	106
	2/22/1999	33	41	42	16	54	65
	2/24/1999	91	106	67	105	77	116

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Ca (ng/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	500	397	587		409	715
	1/9/1999	217	168		1606	169	
	1/15/1999	473	360	567	2407	324	
	1/18/1999	261	343	282	751	155	
	1/21/1999	56	34	57	89		207
	1/24/1999	106		83	198	72	426
	1/27/1999	27		30	68		125
	1/30/1999	141	140	101	703		921
	2/2/1999	293	246	284	1697		1565
	2/5/1999	76	52	64	66		330
	2/11/1999	86	64	87	386	64	465
	2/14/1999	177	112	166	728	112	746
	2/17/1999	187	125	159	321	122	
	2/20/1999	164	80	138	711	98	753
	2/23/1999		243	285	1784		1836
	2/26/1999	77	61	79	89	49	344
2	1/6/1999	238	209	219	1231		286
	1/8/1999	233	213	215	1171		278
	1/14/1999	233	219	256	815	170	
	1/16/1999	213	188	185	1262	148	
	1/18/1999	184	159	262	1087	119	212
	1/20/1999	178	151	167	559	110	
	1/22/1999	118	89	122	640		1747
	1/24/1999	194	167	138	697	127	237
	1/26/1999	63	40	58	312	34	72
	1/28/1999	39	26	50		24	39
	2/3/1999	207	149	214	1115	140	225
	2/5/1999	38	29	68	51	28	
	2/7/1999	52	39	49	238		51
	2/9/1999	87	65	87	224		96
	2/11/1999	44	33	63	221	30	53
	2/13/1999	143	124	144	506		
	2/15/1999	164	130	173	610	114	165
	2/17/1999	206	158	190	656	123	196
	2/19/1999	167	116	177	637	103	
	2/21/1999	142			432	76	
3	1/17/1999	35	32			33	48
	1/19/1999	32	31	36	81	40	41
	1/21/1999	67	53	48	51	46	55
	1/23/1999	20		25	14	17	
	1/25/1999	24	24	23	41	18	
	1/27/1999	73	59	67	136	65	69
	1/29/1999	26	24	24	66	22	24
	1/31/1999	25	27	25	51	26	19
	2/2/1999	31	25	27	23	23	25
	2/4/1999	43	48	38	104	34	42
	2/8/1999	16	17	36	42	13	16
	2/10/1999	33	28	31	60	24	26
	2/12/1999	45	66		83	37	
	2/14/1999	13	13	13	16	10	4
	2/16/1999	127	107	124	316	102	122
	2/18/1999	27	23	25	27	23	
	2/20/1999	19	14		41	16	17
	2/22/1999	25	20	26	92	20	
	2/24/1999	32	28	30		29	
	2/26/1999	33	23	32	63	22	27
4	1/15/1999	13	22	20		15	20
	1/17/1999	14	14	16	18	12	18
	1/19/1999	15	17	17	36	19	18
	1/21/1999	158	146	172	168	140	182
	1/23/1999	29	27	21	25	21	23
	1/25/1999	17	16	15	30	16	16
	1/27/1999	26	17		23	19	
	1/29/1999	61		65	68	43	52
	1/31/1999	16	14	11	19	10	121
	2/2/1999	6		7	8	5	6
	2/6/1999	36	44	21	59	33	40
	2/8/1999	11	13	10	23	11	
	2/10/1999	25	29	27	58	22	
	2/12/1999	15	17	19	16		18
	2/14/1999	13	14	14	15	14	
	2/16/1999	77	88	75	119	70	100
	2/18/1999	12	14	12		12	
	2/20/1999	20	17	17	17	14	19
	2/22/1999	19	21	20	23	17	25
	2/24/1999	15	18	12	15	12	18

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Fe (ng/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	520.3	435.7	573.3		466.9	688.6
	1/9/1999	149.2	140.5		724.5	134.9	
	1/15/1999	482.1	385.9	486.3	1336	363	
	1/18/1999	292.2	239.4	324	401	228.1	
	1/21/1999	73.5	54.6	66.8	110.2		253.5
	1/24/1999	136.8		105.4	184.9	112	368.4
	1/27/1999	31.5		39.6	50.3		100
	1/30/1999	204.9	220.1	150.7	504.2		787.9
	2/2/1999	124.7	113.8	120.8	426.7		470.7
	2/5/1999	80.3	72.2	75.1	67.5		195.2
	2/11/1999	68.2	58	68.9	310.8	51.5	406.3
	2/14/1999	241.4	166.2	203.4	498.9	171.7	596
	2/17/1999	282.1	209.9	233.5	362.8	213.6	
	2/20/1999	193	125.7	190.3	413.2	159.1	618.6
	2/23/1999		276.6	291.4	928.7		1137
	2/26/1999	110.7	92.5	101.9	132.2	85.6	390.7
2	1/6/1999	445.8	404	396.8	1217.5		498.5
	1/8/1999	366.3	354.1	333.4	1098.8		415.6
	1/14/1999	453.6	420.6	473.2	871.3	362.6	
	1/16/1999	360.1	337.6	310.1	1186.3	279.1	
	1/18/1999	340.9	330.3	485.6	1164.2	259.6	402
	1/20/1999	208.8	186	185.2	480.8	138.4	
	1/22/1999	212.5	173.7	205	597.7		1618.5
	1/24/1999	342.7	304.8	227.7	777.9	258.3	398.7
	1/26/1999	128.1	94.5	109.6	292.2	74.7	134.8
	1/28/1999	69.7	57.1	77		44.1	76.7
	2/3/1999	324.9	270.3	323.4	971.4	259.1	350.2
	2/5/1999	94.9	73.3	125.4	100.3	65.5	
	2/7/1999	171.4	141.5	160.8	338.8		161.4
	2/9/1999	218	174	214.1	316.3		249.8
	2/11/1999	77.9	59.8	122.8	241.9	67.5	78
	2/13/1999	286.8	257.3	283.9	643.6		
	2/15/1999	244.1	200.8	249.2	559.6	180.1	222.7
	2/17/1999	372.6	298.4	331	672.4	248	344.1
	2/19/1999	234.4	190.2	251.5	578.3	171.5	
	2/21/1999	228.5			420	143.4	
3	1/17/1999	163.2	158.1			161	212.9
	1/19/1999	102.6	105.6	99.4	131.1	106.4	113.9
	1/21/1999	158	101.8	144.1	169.6	133.5	159.5
	1/23/1999	33.5		40.8	17.7	25.9	
	1/25/1999	74.6	69.4	67.7	70	67.5	
	1/27/1999	286.3	256.3	287	352.7	272.3	286.4
	1/29/1999	74.6	67.1	70.3	102.4	67.8	70.6
	1/31/1999	64.1	69.3	62.6	83	58.3	26
	2/2/1999	83.7	89.3	84.6	74.1	77.9	73.6
	2/4/1999	206.7	221.5	194.1	278.9	217.6	209.7
	2/8/1999	84.2	68.8	74.1	92.3	58.4	77.6
	2/10/1999	114.8	92.3	96.8	153.3	103.9	105.1
	2/12/1999	140.4	138		189.6	132.4	
	2/14/1999	19.1	18.1	16.6	24.2	15.9	9.9
	2/16/1999	317.8	303.3	310.3	509.1	282.4	311.7
	2/18/1999	90.2	76.4	75.1	85.7	74.6	
	2/20/1999	35.9	24		60.7	30.4	31.5
	2/22/1999	39.4	34	44.9	83.5	35	
	2/24/1999	57.2	56.2	54.5		59.1	
	2/26/1999	71.6	53.2	66.5	102.2	53.6	57.2
4	1/15/1999	38.9	36.7	39.2		33.8	48.9
	1/17/1999	36.4	36.6	55	45.5	34.4	44.9
	1/19/1999	50.4	65.5	53.6	84	51.2	60.9
	1/21/1999	133.3	124.6	131.8	147.2	120.4	148.6
	1/23/1999	15.5	12	7.2	7.7	8.6	7.7
	1/25/1999	41.6	32.7	36.3	48.8	32.7	42
	1/27/1999	49.9	45.5		58.6	40.4	
	1/29/1999	94.9		90	123.9	77.2	86
	1/31/1999	26.6	21.5	17.3	31.4	21.2	95.2
	2/2/1999	15.8		20.2	12.3	14.1	25.6
	2/6/1999	75.8	84	70.3	121.6	78.2	101.5
	2/8/1999	43.1	54.6	46.2	58.7	44	
	2/10/1999	101.4	103.1	94	123.1	83.9	
	2/12/1999	16.9	10.9	14.2	14.7		16.5
	2/14/1999	27.5	31.9	29.7	35.8	23.8	
	2/16/1999	62.4	82.2	66.3	122.4	68.4	85.3
	2/18/1999	28.5	40.3	31		31	
	2/20/1999	36	34.6	36.6	37.4	35.5	44
	2/22/1999	39.6	40.8	39.2	49.1	41.9	56.7
	2/24/1999	41.6	45.5	32.2	46.6	31.3	52.9

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Zn (ng/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	243.9	244.2	240		257.1	250.3
	1/9/1999	7.4	9.2		17.3	11.9	
	1/15/1999	251.7	254.8	246.3	265.5	270	
	1/18/1999	159.5	85.4	163	163.2	174	
	1/21/1999	8.1	8.2	9.1	11.9		12.7
	1/24/1999	13.8		10.7	14.8	16	21.5
	1/27/1999	3.9		4.6	2.8		6.9
	1/30/1999	24.4	25.5	18.9	41.7		32.9
	2/2/1999	136.9	139.2	115.4	140		133.5
	2/5/1999	75	78.8	71.6	73.2		79.8
	2/11/1999	4.5	3.9	4.3	5.8	2.3	9.8
	2/14/1999	17.4	17.4	16.3	61.2	16.4	21.8
	2/17/1999	53.9	47.1	44.4	55.7	54.2	
	2/20/1999	19.5	15.9	16.5	22	19.5	24.6
	2/23/1999		156.1	116.9	180.1		62.5
	2/26/1999	12.1	12	11	12.7	13.2	17.8
2	1/6/1999	29.9	30.6	27.6	51.3		32.2
	1/8/1999	27.9	30.3	25.4	51.5		28.4
	1/14/1999	30.5	47.5	28.4	42.4	29	
	1/16/1999	24.4	25.8	20.1	45.5	25.6	
	1/18/1999	27.8	25.1	39.8	53.4	25.1	28
	1/20/1999	28.4	25	25.6	30.2	25.1	
	1/22/1999	11	11.4	9.9	18.7		32.6
	1/24/1999	24.4	24.8	18.5	37.9	24.2	24.6
	1/26/1999	17.1	15.7	17	19.9	15.9	16.9
	1/28/1999	3.7	1.5	4.1		1.9	4.2
	2/3/1999	18	19.2	19	38.1	20.2	19.8
	2/5/1999	8.3	11.8	10.3	11.1	8.5	
	2/7/1999	12.6	10.1	10.8	18		10.4
	2/9/1999	17.3	15.7	14.3	18.4		20.3
	2/11/1999	4.4	3.8	4.6	6.4	3.3	2
	2/13/1999	17.1	16.5	16.5	26.2		
	2/15/1999	17.2	15	16.1	24.3	15.4	10.6
	2/17/1999	20.1	22.9	16.9	26.9	18.9	19
	2/19/1999	16.7	14.9	14.7	27	13.4	
	2/21/1999	12.8			15.4	11.1	
3	1/17/1999	37	40			43.2	50.9
	1/19/1999	27.8	25.1	28.7	31.4	33	34
	1/21/1999	80.2	65.1	79.6	75.5	76.9	86.8
	1/23/1999	7.6		7.5	6.1	8	
	1/25/1999	25	21.2	19.6	21.7	21.5	
	1/27/1999	95.3	83.3	90.6	98.2	101.3	98.9
	1/29/1999	19.1	19.8	16	18.4	19.5	17.4
	1/31/1999	15.6	16.8	16.9	14.5	17.7	15.5
	2/2/1999	23.6	22.4	20.3	25.8	24	19.9
	2/4/1999	43.9	48.7	39.2	51.3	48.2	45.9
	2/8/1999	32.6	30.4	12.4	33.7	33.9	36.2
	2/10/1999	25.9	22.9	21.7	23.9	23.3	25.5
	2/12/1999	20	35.4		24.4	21.9	
	2/14/1999	4.9	5.2	4.9	4.9	5	3
	2/16/1999	64.4	67.8	63.3	64.8	63.1	61.7
	2/18/1999	37.8	35.6	35.4	31.3	42	
	2/20/1999	9.8	10.6		9.6	11.4	9.1
	2/22/1999	8.6	6.7	8.7	10.6	8.5	
	2/24/1999	29.7	30.8	30.9		33.1	
	2/26/1999	14.9	15.4	15.4	12.9	14.6	14.8
4	1/15/1999	5.4	3.8	5		5.1	4.5
	1/17/1999	9.5	11.9	10.6	11.8	11.2	11.8
	1/19/1999	15.7	18.7	16.1	16	19.2	18
	1/21/1999	46.9	43.4	36.5	45.5	44	47.6
	1/23/1999	6.5	5.8	3.7	6.3	6.5	4
	1/25/1999	8.6	7.6	7.7	7.9	6.2	5.3
	1/27/1999	23.7	17.8		20.1	21.4	
	1/29/1999	21.7		16.8	3.1	23.7	24.9
	1/31/1999	12.8	54.9	1.1	12.2	13.1	5
	2/2/1999	4.4		0.9	3.6	6.8	5.4
	2/6/1999	14.4	16.7	36.5	14.1	14	13
	2/8/1999	8	6.4	9.6	9.5	9.5	
	2/10/1999	11.8	11.8	12.7	11.8	13	
	2/12/1999	3.3	5.3	5.6	3.3		5.3
	2/14/1999	10.2	11.1	10.8	9.7	11.3	
	2/16/1999	13.1	14.6	14.4	13.6	16.8	15.9
	2/18/1999	13.5	14	12.7		14.4	
	2/20/1999	13.5	13.2	13.7	11.6	13.3	16.2
	2/22/1999	7.5	7.9	6.9	6.5	8.7	10.2
	2/24/1999	9.8	9.9	8.6	10.5	14.1	13

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of K (ng/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	139.3	130.9	156.2		127.5	193.3
	1/9/1999	66.9	63.6		330.1	65.2	
	1/15/1999	135.8	121	143.8	473.9	125.9	
	1/18/1999	161.9	122.5	162	231.5	164	
	1/21/1999	53.9	40.1	53.7	65.7		116.7
	1/24/1999	112.5		87.9	146.8	122.3	181.1
	1/27/1999	16		18.9	25.7		32.9
	1/30/1999	104.8	124.7	72.7	200.4		246.9
	2/2/1999	52.1	48.4	43.7	167.1		147.7
	2/5/1999	63.8	62.5	60.8	60.7		86.2
	2/11/1999	30.8	23.5	30.2	130.8	24.6	149.5
	2/14/1999	99.7	93.4	95.1	186.8	94.6	200.2
	2/17/1999	132.3	112	115	175.7	114.4	
	2/20/1999	90.9	77.1	82.9	170.3	85.5	218.4
	2/23/1999		80.7	79.7	320.9		374.4
	2/26/1999	58.4	49.9	56	71.2	47.2	184.6
2	1/6/1999	158.5	150.9	139.2	491.9		177.7
	1/8/1999	155.7	150.2	141.3	492.8		167.6
	1/14/1999	194	194.5	211.2	379.3	177.8	
	1/16/1999	225.2	225.6	194.5	628.3	213.5	
	1/18/1999	232.9	237.2	327.4	561.3	226.8	238
	1/20/1999	192.1	181.1	173.5	325.1	165.9	
	1/22/1999	87.2	81.9	86.6	268.2		610.1
	1/24/1999	237.1	244.8	172.8	450.5	229.1	264.6
	1/26/1999	70.6	62.4	68.8	149.8	58.6	69.7
	1/28/1999	30.3	29.5	34.3		24.7	32.9
	2/3/1999	138.7	124.2	138.2	436.3	124.5	145.9
	2/5/1999	59.9	58.8	65.3	60.4	55.3	
	2/7/1999	116.5	123.6	117.3	196.2		117.6
	2/9/1999	91.1	83.5	87.3	148.3		95.8
	2/11/1999	32.3	31.5	38.3	81.9	31.3	35.2
	2/13/1999	144.7	134.6	137.3	337.6		
	2/15/1999	133	127.2	136.6	292.9	122.1	130.2
	2/17/1999	163.3	159.7	153.2	326.4	143.6	166.1
	2/19/1999	193.2	188.2	191.3	376.7	177.4	
	2/21/1999	131.7			230	117.1	
3	1/17/1999	91.6	95.3			100.4	115.9
	1/19/1999	33.6	31.4	34.2	36.6	36.9	43.3
	1/21/1999	61.5	53.9	62.7	57.7	68.7	66.5
	1/23/1999	26.4		28	23.3	23.3	
	1/25/1999	38.4	35.7	35.8	46.6	35.3	
	1/27/1999	119.1	111.9	111.4	137.7	125.6	128.4
	1/29/1999	46.8	44.2	43.4	60.1	49.6	44.8
	1/31/1999	57.6	58.6	58.9	65.4	65.9	62.1
	2/2/1999	37.9	36.1	36.8	36	38.3	36.3
	2/4/1999	66.3	71	58.6	75.1	65.7	68.9
	2/8/1999	45	48.5	70.5	55.6	45.9	52.6
	2/10/1999	49.5	45.5	46.7	59.1	46.8	49
	2/12/1999	56.9	57.4		64.2	58.3	
	2/14/1999	28.9	31.1	28.4	35.6	29	19
	2/16/1999	116.4	115.1	105	147.1	115.3	122.8
	2/18/1999	68	63.9	62.5	68.8	71.2	
	2/20/1999	42.1	40.2		51.8	43.3	39.2
	2/22/1999	33.8	28.5	34.1	62.9	34.6	
	2/24/1999	38.3	37.5	35		38.5	
	2/26/1999	54.3	51.9	52.6	73.7	54.5	53.7
4	1/15/1999	42	39.9	38.2		43.6	46.2
	1/17/1999	85.2	80.5	79.3	91.2	87.7	90.4
	1/19/1999	28.7	32.5	31.4	45.4	34.5	33.3
	1/21/1999	183	176.9	179.9	189.8	190.6	204.6
	1/23/1999	43.8	38.7	45.4	43.6	36.8	47.8
	1/25/1999	35.9	35.2	33.6	46.8	38.4	36.9
	1/27/1999	75.6	77.1		79.1	77.2	
	1/29/1999	91.4		81.4	99.3	92.5	94.8
	1/31/1999	49.5	44.6	40.3	52.3	48.3	66.3
	2/2/1999	34.7		35.8	31.5	34.1	37.6
	2/6/1999	68.5	74.9	48.1	85.9	80.8	77
	2/8/1999	32.7	31.9	34	45	32	
	2/10/1999	57.4	58.1	54.6	75.8	56.2	
	2/12/1999	69.1	72.3	66.8	77.5		72.9
	2/14/1999	35.7	36.5	36.4	39.9	39.6	
	2/16/1999	134.6	146.4	137.5	167.2	149.3	155.9
	2/18/1999	43.9	49.1	46.8		49.6	
	2/20/1999	69.2	69.6	66.5	62.9	68.1	72.7
	2/22/1999	30	31.7	30.8	32.6	35.2	34.4
	2/24/1999	87.6	95.2	78.6	93.9	90.8	95

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Mn (ng/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	11.1	9.8	12.0		10.2	13.1
	1/9/1999	1.7	1.5		17.8	3.0	
	1/15/1999	9.0	10.6	8.7	31.5	7.6	
	1/18/1999	6.4	8.1	6.1	10.9	6.4	
	1/21/1999	1.0	1.2	1.1	2.6		3.6
	1/24/1999	2.6		2.2	3.9	3.3	4.7
	1/27/1999	1.3		1.3	3.9		1.6
	1/30/1999	3.9	4.5	2.5	7.9		11.7
	2/2/1999	2.0	2.7	2.0	4.8		9.8
	2/5/1999	0.6	1.6	1.7	0.0		1.9
	2/11/1999	1.1	1.7	1.9	9.0	1.1	9.7
	2/14/1999	4.5	3.3	3.6	7.1	2.3	8.7
	2/17/1999	7.9	6.0	5.9	8.8	8.2	
	2/20/1999	4.5	2.3	3.7	10.8	3.1	13.1
	2/23/1999		7.0	6.7	24.7		21.8
	2/26/1999	3.7	2.6	3.1	4.4	2.9	7.8
2	1/6/1999	7.4	8.3	7.5	24.1		9.4
	1/8/1999	6.0	5.7	7.2	24.4		7.9
	1/14/1999	7.5	6.6	6.5	18.1	7.3	
	1/16/1999	7.0	6.5	4.5	25.1	4.2	
	1/18/1999	5.1	4.7	7.8	23.8	3.3	5.6
	1/20/1999	5.5	4.1	5.5	13.2	5.0	
	1/22/1999	3.8	2.8	3.8	13.4		32.3
	1/24/1999	4.8	3.7	2.7	14.4	2.9	5.3
	1/26/1999	3.4	2.3	2.5	4.8	1.8	3.0
	1/28/1999	1.3	0.0	1.6		1.4	0.8
	2/3/1999	6.6	4.7	6.9	18.2	7.0	6.9
	2/5/1999	1.8	0.0	2.1	2.9	0.7	
	2/7/1999	1.8	2.6	2.3	7.5		4.0
	2/9/1999	4.9	3.6	3.4	5.1		3.4
	2/11/1999	0.0	0.9	2.5	6.6	1.7	1.4
	2/13/1999	3.1	4.5	3.4	10.1		
	2/15/1999	4.2	5.3	4.0	14.7	4.2	5.4
	2/17/1999	5.2	5.6	5.7	16.8	4.0	5.6
	2/19/1999	3.8	3.8	3.8	11.3	4.6	
	2/21/1999	3.0			8.4	2.4	
3	1/17/1999	2.6	2.3			1.7	1.1
	1/19/1999	1.6	1.7	1.8	3.6	2.4	1.1
	1/21/1999	7.4	4.9	3.4	1.5	4.6	3.6
	1/23/1999	0.0		0.4	2.3	1.6	
	1/25/1999	3.3	2.0	0.9	4.8	2.1	
	1/27/1999	7.6	6.0	7.8	7.0	8.8	8.1
	1/29/1999	1.1	2.4	2.6	2.4	2.5	0.7
	1/31/1999	1.3	0.0	1.7	1.8	0.0	0.0
	2/2/1999	2.1	2.6	2.5	3.8	2.4	2.9
	2/4/1999	5.0	3.9	5.1	4.3	4.6	5.3
	2/8/1999	1.9	1.9	1.1	2.2	3.4	1.7
	2/10/1999	3.1	4.1	3.4	6.5	3.9	2.7
	2/12/1999	3.9	5.2		9.5	3.9	
	2/14/1999	1.2	2.1	1.1	0.0	1.0	0.0
	2/16/1999	6.1	7.1	6.6	8.0	5.7	8.1
	2/18/1999	4.7	2.6	2.4	5.0	3.7	
	2/20/1999	0.8	1.3		3.3	1.4	0.0
	2/22/1999	1.6	0.6	1.2	4.6	0.0	
	2/24/1999	3.2	2.2	2.7		2.2	
	2/26/1999	3.2	2.6	2.6	0.0	2.7	2.4
4	1/15/1999	0.0	1.0	0.0		0.0	0.0
	1/17/1999	0.0	0.7	0.8	1.7	0.9	0.0
	1/19/1999	2.3	2.3	3.2	2.1	2.7	2.1
	1/21/1999	6.4	7.1	5.4	6.2	7.7	6.4
	1/23/1999	1.6	1.2	0.0	0.0	0.0	0.0
	1/25/1999	1.0	1.0	0.0	2.4	0.8	0.0
	1/27/1999	0.0	1.6		0.0	1.5	
	1/29/1999	1.9		3.1	5.3	3.7	3.7
	1/31/1999	0.0	0.0	0.0	2.3	0.0	4.0
	2/2/1999	0.0		0.0	0.0	0.0	0.0
	2/6/1999	1.6	2.1	1.8	2.3	1.9	3.6
	2/8/1999	1.1	0.6	1.4	2.9	2.8	
	2/10/1999	2.0	1.7	2.1	3.9	3.1	
	2/12/1999	2.1	1.4	1.9	2.7		1.6
	2/14/1999	2.8	0.8	1.9	2.0	2.8	
	2/16/1999	2.0	3.2	2.6	7.4	3.6	5.5
	2/18/1999	1.1	2.4	0.7		1.1	
	2/20/1999	4.7	2.2	2.7	2.0	2.1	4.4
	2/22/1999	1.8	1.8	0.9	2.1	2.7	1.1
	2/24/1999	1.4	1.2	1.1	0.9	1.8	0.0

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Cu (ng/m3)		Sampler					
Site	Date	AND	FRM	IMP	MET	URG	VAPS
1	1/6/1999	16.3	11.4	15.3		15.1	22
	1/9/1999	2.4	2.3		4.1	2.3	
	1/15/1999	10.5	8.9	7.6	11.4	7.8	
	1/18/1999	10.8	30.7	9.2	8.1	9.8	
	1/21/1999	1.7	1.1	1.2	0		4.2
	1/24/1999	5.2		3	3.1	6.6	14
	1/27/1999	0		1.4	0		2.3
	1/30/1999	4.5	5.6	5.8	9.5		15
	2/2/1999	2.9	2.5	1.6	4.8		5.1
	2/5/1999	6.4	4	3	7.1		6.4
	2/11/1999	1.7	0	0.6	0	1.5	0.9
	2/14/1999	3.5	4.6	4.1	6.8	3.4	7.5
	2/17/1999	10.1	7	7.5	12.2	10.2	
	2/20/1999	4.7	3	5.2	3.7	4.8	9.5
	2/23/1999		10.1	8.5	15.1		9.9
	2/26/1999	2.8	2.1	2.1	0	1.3	2.8
2	1/6/1999	17.8	17	16.2	30.6		22.2
	1/8/1999	18.6	15.8	16.1	26.8		16.4
	1/14/1999	11.6	37.6	12.7	17.5	9	
	1/16/1999	13.9	11.7	10.5	22.8	9	
	1/18/1999	22.9	19	29.4	34.6	19.4	22.6
	1/20/1999	7.6	6.7	6.4	6.5	6.3	
	1/22/1999	3.9	2.9	3.3	3.9		15.2
	1/24/1999	15.2	14.1	13.2	19	13.4	16.5
	1/26/1999	1.6	3.1	2.5	9.9	2.8	5.3
	1/28/1999	1.9	2.2	1		0.8	2.2
	2/3/1999	9.1	7.4	10.4	15.9	7.5	10.9
	2/5/1999	3	2.9	2.9	0	0.7	
	2/7/1999	5	6.1	5.3	7.5		4.7
	2/9/1999	12.6	9.3	11.8	14.6		15.6
	2/11/1999	1.5	1.6	1.2	2.2	1.6	1.2
	2/13/1999	9.9	9.7	8.9	14.2		
	2/15/1999	5.6	4.5	5.4	6	2.8	5.4
	2/17/1999	11.3	12.5	8.3	16.4	8.8	10.7
	2/19/1999	5.3	4.7	5.2	10.1	4.8	
	2/21/1999	11.2			13.7	10.6	
3	1/17/1999	6.9	3.8			4.9	9
	1/19/1999	2.8	2.9	3.5	4.3	4	2.8
	1/21/1999	6.1	6.3	4.8	5.8	5.4	6.5
	1/23/1999	2.3		1.3	0	2.6	
	1/25/1999	6.1	5.8	6.6	5.7	7.6	
	1/27/1999	12.8	11.2	12.2	15.6	12.3	11.3
	1/29/1999	3.4	1.7	2.9	0	2.3	0
	1/31/1999	4.4	2.7	1.8	0	3.1	4.8
	2/2/1999	1.2	2.7	3.6	2	3.6	3.2
	2/4/1999	10.8	12.7	10.4	11.9	11.2	11.1
	2/8/1999	2.7	3.8	2.7	0	3.4	2.7
	2/10/1999	5.2	4.7	4	6.2	3.6	5.2
	2/12/1999	3.5	6		4	3.6	
	2/14/1999	0	1.1	1.5	3.6	0	0
	2/16/1999	10.8	13.3	12.8	18.1	12.2	11.4
	2/18/1999	4.4	6.5	3	0	5.9	
	2/20/1999	1.9	0.9		2.6	2.3	1.7
	2/22/1999	1.2	2.9	1.5	0	2	
	2/24/1999	2.6	3.1	3		3.5	
	2/26/1999	2.8	6	4.9	2.1	4.6	4.3
4	1/15/1999	1.9	2.3	2.2		2	3.3
	1/17/1999	0	3.1	3.3	0	1.2	2.9
	1/19/1999	2.3	2.8	2.6	3.6	1.7	1.7
	1/21/1999	64	64.3	57.3	69.9	65	64.8
	1/23/1999	0	0	0	0	1.7	0.9
	1/25/1999	2.7	1.5	0.5	0	1.4	0
	1/27/1999	2.9	2.3		3.7	1.7	
	1/29/1999	2.6		3.4	0	2.9	5.2
	1/31/1999	5.8	7.9	5.8	9	5.9	6.1
	2/2/1999	0.8		1.5	0	0	1.6
	2/6/1999	3.6	3.9	4.2	0	4.6	4.5
	2/8/1999	9.8	9.5	8.5	11.9	8	
	2/10/1999	6.3	7.9	7.2	9	5.2	
	2/12/1999	0.7	0	1.5	3.1		0
	2/14/1999	1.5	0	0	0	0	
	2/16/1999	1.4	0.7	2.8	3.3	1.3	0
	2/18/1999	5.8	5	6.2		4.6	
	2/20/1999	3.2	2.7	3.9	1.9	4.1	4.3
	2/22/1999	9.4	8.9	8.1	13.3	9.9	10.6
	2/24/1999	6.2	7.1	5.9	4	4.7	4.3

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of Pb (ng/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	49.7	49.3	47.7		52.0	50.5
	1/9/1999	3.9	3.9		0.0	8.3	
	1/15/1999	12.6	11.2	9.8	16.8	10.7	
	1/18/1999	35.3	18.5	37.2	41.7	35.2	
	1/21/1999	3.3	6.2	4.0	5.5		7.8
	1/24/1999	11.1		8.1	13.9	13.5	13.0
	1/27/1999	0.0		2.8	0.0		2.4
	1/30/1999	8.3	11.2	5.5	11.6		9.8
	2/2/1999	12.9	12.3	8.9	17.7		10.0
	2/5/1999	25.2	26.4	25.1	21.7		25.5
	2/11/1999	0.0	2.0	0.0	0.0	1.8	3.4
	2/14/1999	10.1	7.7	8.1	5.6	7.1	7.4
	2/17/1999	15.5	14.6	15.8	16.1	16.3	
	2/20/1999	6.0	3.1	6.3	11.4	10.8	7.4
	2/23/1999		49.6	34.8	47.7		13.6
	2/26/1999	2.9	1.8	4.2	0.0	1.9	5.4
2	1/6/1999	11.0	10.3	6.2	14.0	4.9	
	1/8/1999	10.8	10.3	8.0	21.7	12.4	
	1/14/1999	4.7	10.5	14.1	14.4	12.7	58.1
	1/16/1999	7.6	8.0	3.3	7.0	3.8	
	1/18/1999	7.9	4.8	2.8	0.0		12.0
	1/20/1999	4.3	21.9	17.4	28.2	23.5	25.1
	1/22/1999	3.7	2.1	1.4	4.6	0.0	1.9
	1/24/1999	23.0	0.0	0.0		1.8	3.0
	1/26/1999	3.0	4.8	6.0	5.4	6.0	4.5
	1/28/1999	3.3	2.9	4.1	7.1	2.1	
	2/3/1999	5.4	3.2	5.0	5.6		4.6
	2/5/1999	1.6	6.3	6.6	12.9		8.2
	2/7/1999	4.3	0.0	0.0	3.2	4.6	0.0
	2/9/1999	12.0	4.2	3.2	4.1		
	2/11/1999	2.9	8.6	7.1	8.1	7.0	5.2
	2/13/1999	4.4	8.8	7.9	9.0	8.1	4.6
	2/15/1999	5.8	5.6	6.1	9.9	9.1	
	2/17/1999	9.2				6.6	
	2/19/1999	6.0					
	2/21/1999	6.9	8.0	17.6	12.0	11.9	
3	1/17/1999	17.7	15.8	17.0	12.8	18.9	16.3
	1/19/1999	3.5		0.0	9.6	3.4	
	1/21/1999	11.6	7.9	7.5	8.0	11.4	
	1/23/1999	37.7	35.9	32.1	36.9	40.0	37.5
	1/25/1999	9.0	11.0	8.2	14.6	10.9	9.7
	1/27/1999	3.2	5.7	3.3	0.0	4.0	3.5
	1/29/1999	4.9	6.9	3.5	4.8	7.0	3.9
	1/31/1999	31.1	38.7	29.2	31.2	32.9	34.1
	2/2/1999	9.0	10.9	2.6	11.4	10.9	10.9
	2/4/1999	8.4	6.3	7.9	7.8	13.4	7.2
	2/8/1999	4.2	3.7		5.5	5.6	
	2/10/1999	4.3	3.5	5.4	8.8	5.7	3.4
	2/12/1999	14.2	20.2	16.0	21.7	17.8	20.1
	2/14/1999	9.3	7.2	7.9	3.7	7.4	
	2/16/1999	5.7	6.5		12.6	6.2	5.4
	2/18/1999	2.3	2.6	2.0	4.4	2.5	
	2/20/1999	7.2	7.9	7.4		7.2	
	2/22/1999	8.4	8.3	4.4	10.3	7.8	10.0
	2/24/1999						
	2/26/1999	9.1			10.0	13.3	
4	1/15/1999	1.4	1.1	2.4		0.0	1.5
	1/17/1999	4.1	3.9	2.5	0.0	0.0	3.2
	1/19/1999	15.9	15.8	14.5	17.7	17.4	14.9
	1/21/1999	1.9	0.0	3.0	3.2	0.0	0.0
	1/23/1999	2.8	1.3	2.0	3.2	3.1	0.0
	1/25/1999	3.9	4.4		8.6	4.3	
	1/27/1999	5.1		5.1	8.0	6.4	4.5
	1/29/1999	3.7	4.4	2.4	0.0	5.1	0.0
	1/31/1999	1.8		1.1	0.0	1.7	5.6
	2/2/1999	3.3	4.0	11.7	4.4	6.6	6.2
	2/6/1999	2.6	5.2	2.7	0.0	1.7	
	2/8/1999	5.4	1.8	3.0	0.0	2.7	
	2/10/1999	1.3	2.5	0.0	3.4		2.3
	2/12/1999	3.7	3.5	2.5	0.0	4.5	
	2/14/1999	6.5	4.1	5.1	3.4	5.2	3.8
	2/16/1999	3.7	3.8	3.9		5.4	
	2/18/1999	6.4	7.5	4.8	7.7	5.3	4.8
	2/20/1999	3.3	2.9	3.3	5.7	4.0	4.8
	2/22/1999	1.5	2.9	2.6	5.5	3.3	0.0
	2/24/1999						

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of As (ng/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999	1.90	2.30	0.00		2.20	0.00
	1/9/1999	1.00	1.30		0.00	0.80	
	1/15/1999	0.70	1.40	1.70	0.00	1.30	
	1/18/1999	0.00	0.00	0.00	0.00	3.00	
	1/21/1999	0.00	0.00	0.00	0.00		0.00
	1/24/1999	0.70		1.10	0.00	0.00	1.10
	1/27/1999	1.30		0.00	0.00		0.00
	1/30/1999	0.00	0.00	0.00	0.00		0.00
	2/2/1999	0.00	0.00	0.50	0.00		1.10
	2/5/1999	0.00	0.00	0.00	3.00		0.00
	2/11/1999	0.90	0.00	0.00	2.30	0.00	0.00
	2/14/1999	0.00	0.00	0.00	2.00	1.20	1.10
	2/17/1999	1.70	0.00	0.90	0.00	0.00	
	2/20/1999	0.00	1.40	1.10	0.00	0.00	0.00
	2/23/1999		1.10	0.00	1.10		0.00
	2/26/1999	0.00	0.00	0.00	0.00	0.00	0.00
2	1/6/1999	1.40	0.00	1.30	0.00	1.70	
	1/8/1999	3.20	2.00	0.50	0.00	0.80	
	1/14/1999	1.20	3.40	4.00	3.30	1.00	13.00
	1/16/1999	2.50	0.00	1.70	0.00	2.00	
	1/18/1999	4.90	0.00	0.00	0.00		1.80
	1/20/1999	1.30	3.50	2.40	4.10	2.60	2.30
	1/22/1999	0.00	0.00	0.00	0.00	0.00	0.00
	1/24/1999	3.50	0.70	0.00		0.00	0.00
	1/26/1999	0.00	0.00	0.00	2.10	0.00	1.90
	1/28/1999	0.00	0.00	0.00	0.00	0.00	
	2/3/1999	1.70	1.20	0.90	0.00		0.00
	2/5/1999	0.00	3.30	3.00	0.00		2.10
	2/7/1999	0.80	2.10	0.00	0.00	0.00	0.00
	2/9/1999	0.00	0.00	1.30	2.90		
	2/11/1999	0.00	0.00	0.70	0.00	0.00	0.00
	2/13/1999	0.00	0.00	0.00	0.00	0.00	1.00
	2/15/1999	1.70	1.70	0.00	0.00	0.00	
	2/17/1999	0.00				1.20	
	2/19/1999	0.00					
	2/21/1999	1.90	2.40	0.00	0.00	1.50	
3	1/17/1999	0.00	0.00	1.80	3.70	0.00	0.00
	1/19/1999	0.00		1.10	0.00	0.00	
	1/21/1999	0.00	2.00	0.90	0.00	0.00	
	1/23/1999	1.80	0.00	2.60	0.00	1.50	0.80
	1/25/1999	1.70	0.00	1.60	0.00	1.30	2.10
	1/27/1999	0.00	0.00	0.50	4.20	0.00	0.00
	1/29/1999	0.00	0.00	0.00	0.00	0.00	1.50
	1/31/1999	1.10	0.00	1.80	3.10	3.60	2.20
	2/2/1999	1.30	0.90	1.00	0.00	0.00	1.60
	2/4/1999	1.10	2.70	1.40	3.20	0.00	1.50
	2/8/1999	0.00	0.00		0.00	0.00	
	2/10/1999	0.00	1.00	0.00	0.00	0.00	0.00
	2/12/1999	4.40	1.70	2.60	2.10	1.70	1.00
	2/14/1999	1.10	3.60	1.30	2.20	3.40	
	2/16/1999	1.80	0.00		0.00	1.20	1.10
	2/18/1999	0.00	0.00	0.90	0.00	0.00	
	2/20/1999	0.00	0.00	1.10		0.00	
	2/22/1999	1.60	0.00	1.20	0.00	0.00	0.00
	2/24/1999						
	2/26/1999	1.90			1.00	0.00	
4	1/15/1999	0.00	0.00	0.00		1.30	0.00
	1/17/1999	0.00	0.00	0.00	0.00	0.00	0.00
	1/19/1999	3.20	0.00	0.60	0.00	0.00	3.10
	1/21/1999	0.00	0.00	0.00	0.00	0.70	0.00
	1/23/1999	0.00	0.70	0.00	0.00	0.00	0.00
	1/25/1999	0.00	0.00		0.00	0.00	
	1/27/1999	1.10		1.20	0.00	0.00	2.00
	1/29/1999	2.00	1.00	0.70	2.30	0.00	0.80
	1/31/1999	0.00		1.00	0.00	0.00	0.00
	2/2/1999	1.00	0.80	0.00	2.50	0.00	0.00
	2/6/1999	0.00	0.00	0.00	0.00	0.00	
	2/8/1999	0.00	2.90	0.90	0.00	0.90	
	2/10/1999	0.70	0.00	0.70	0.00		0.00
	2/12/1999	0.00	0.00	0.60	0.00	0.00	
	2/14/1999	0.00	0.80	0.00	2.50	0.00	2.90
	2/16/1999	0.00	0.00	0.00		0.00	
	2/18/1999	0.70	0.00	1.10	0.00	1.40	2.20
	2/20/1999	0.00	1.00	0.00	0.00	1.70	0.00
	2/22/1999	1.10	1.20	0.00	0.00	0.00	2.30
	2/24/1999						

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study

Average of PM-10 (µg/m3)		Sampler					
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**	**VAPS**
1	1/6/1999						82.0
	1/9/1999						
	1/15/1999						7.3
	1/18/1999						19.0
	1/21/1999						33.7
	1/24/1999						59.7
	1/27/1999						6.7
	1/30/1999						51.3
	2/2/1999						14.9
	2/5/1999						27.0
	2/11/1999						10.5
	2/14/1999						75.8
	2/17/1999						62.6
	2/20/1999						59.0
	2/23/1999						44.4
	2/26/1999						65.9
2	1/6/1999						60
	1/8/1999						66.63
	1/14/1999						
	1/16/1999						
	1/18/1999						55.84
	1/20/1999						
	1/22/1999						23.56
	1/24/1999						47.87
	1/26/1999						20.98
	1/28/1999						10.57
	2/3/1999						45.35
	2/5/1999						
	2/7/1999						41.47
	2/9/1999						29.37
	2/11/1999						9.12
	2/13/1999						17.26
	2/15/1999						30.32
	2/17/1999						
	2/19/1999						19.41
	2/21/1999						
3	1/17/1999						29.0
	1/19/1999						38.4
	1/21/1999						3.8
	1/23/1999						
	1/25/1999						55.3
	1/27/1999						21.1
	1/29/1999						15.4
	1/31/1999						18.5
	2/2/1999						39.3
	2/4/1999						20.3
	2/8/1999						18.7
	2/10/1999						7.9
	2/12/1999						5.0
	2/14/1999						52.5
	2/16/1999						27.3
	2/18/1999						15.0
	2/20/1999						
	2/22/1999						34.9
	2/24/1999						23.0
	2/26/1999						
4	1/15/1999						
	1/17/1999						67.1
	1/19/1999						8.0
	1/21/1999						34.3
	1/23/1999						13.5
	1/25/1999						11.6
	1/27/1999						
	1/29/1999						26.9
	1/31/1999						12.9
	2/2/1999						10.5
	2/6/1999						15.6
	2/8/1999						
	2/10/1999						7.7
	2/12/1999						20.0
	2/14/1999						1.8
	2/16/1999						32.2
	2/18/1999						
	2/20/1999						17.6
	2/22/1999						7.3
	2/24/1999						19.2

Appendix D1

Final Data Archive, By Species, Site, Date, and Sampler for Replicate No. 2 Measurements at Rubidoux

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99	32.52	34.26	33.99	71.26	38.29
	01/09/99		7.42	7.94	21.93	8.57
	01/15/99	28.44	27.68	28.77		31.84
	01/18/99	87.47	84.58	89.44	98.49	111.18
	01/21/99	12.69	12.59	13.28		16.77
	01/24/99	29.7	29.36	32.34	34.69	38.3
	01/27/99	2.41	2.96	2.7	3.14	3.09
	01/30/99	21.29	21.35	13.28	31.01	
	02/02/99	5.07	5.04	4.77	15.48	5.12
	02/05/99	19.5	19.4	19.48	19.94	
	02/11/99	2.26	2.58	2.67	8.25	2.58
	02/14/99	34.59	34.01	32.01	41.86	41.3
	02/17/99	60.06	57.99	57.34	64.38	71.99
	02/20/99	34.08	29.98	30.12	40.68	35.97
	02/23/99	18.06	17.07	18.1	41.57	22.34
	02/26/99	23.23	22.65	21.67	25.14	35.39

Average of SO4-T (µg/m3)		Sampler				
Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99	0.58		0.61	1.14	
	01/09/99			0.29	0.47	
	01/15/99	0.51		0.52		
	01/18/99	6.08		5.92	6.09	
	01/21/99	1.61		1.67	1.7	
	01/24/99	1.74		1.77	1.87	
	01/27/99	0.23		0.24	0.29	
	01/30/99	0.52		0.53	0.7	
	02/02/99	0.25		0.12	0.43	
	02/05/99	0.7		0.68	0.82	
	02/11/99	0.32		0.34	0.42	
	02/14/99	1.65		1.6	1.81	
	02/17/99			3.64	3.79	
	02/20/99	2.03		2.04	2.2	
	02/23/99	0.48		0.43	0.84	
	02/26/99	1.93		1.94	1.99	

Average of SO4Q (µg/m3)		Sampler				
Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99		0.64			0.67
	01/09/99		0.28			0.42
	01/15/99		0.57			0.64
	01/18/99		5.69			5.76
	01/21/99		1.58			1.57
	01/24/99					1.71
	01/27/99					0.29
	01/30/99					0.59
	02/02/99					0.42
	02/05/99		0.48			0.75
	02/11/99		0.42			0.46
	02/14/99		1.88			1.68
	02/17/99		4.08			3.69
	02/20/99		1.81			1.9
	02/23/99		0.53			0.52
	02/26/99		2.2			1.91

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

Average of NO3T (µg/m3)		Sampler				
Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99	10.4			12.31	
	01/09/99				0.94	
	01/15/99	8.86				
	01/18/99	38.63			39.51	
	01/21/99	3.3			3.37	
	01/24/99	11.57			12.34	
	01/27/99	0.24			0.24	
	01/30/99	8.25			9.15	
	02/02/99	0.24			0.37	
	02/05/99	7.68			7.82	
	02/11/99	0.07			0.11	
	02/14/99	15.64			16.14	
	02/17/99				26.65	
	02/20/99	13.56			13.8	
	02/23/99	5.78			6.34	
	02/26/99	8.93			8.97	

Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99	11.35	11.74	10.82	12.52	12.58
	01/09/99		0.99	0.96	1.19	1.22
	01/15/99	10.51	9.63	9.16		10.81
	01/18/99	44.07	36.17	37.43	40	36.78
	01/21/99	3.84	2.95	3.63	3.64	3.21
	01/24/99	13.31		12.1	12.25	11.11
	01/27/99	0.77		0.69	0.75	1.33
	01/30/99	10.62		8.44	9.57	10.9
	02/02/99	0.45		0.19	0.52	0.62
	02/05/99	8.68	4.13	7.69	8.21	16.27
	02/11/99	0.13	0.11	0.08	0.14	0.23
	02/14/99	17.27	17.72	15.27	16.6	16.37
	02/17/99	30.21	28.49	25.91	27.01	26.82
	02/20/99	16.8	13.88	14.87	16.61	17.17
	02/23/99	6.91	7.27	6.18	8.6	7
	02/26/99	10.56	10.51	10.02	10.31	9.47

Average of NH4 (µg/m3)		Sampler				
Site	Date	AND	FRM	IMP	MET	URG
1	01/06/99	3.07	3.38	2.77	3.68	3.75
	01/09/99		0.33	0.18	0.2	0.46
	01/15/99	2.54	2.81	2.23		3.25
	01/18/99	13.24	13.05	11.55	13.95	12.87
	01/21/99	1.29	1.33	0.93	1.42	1.44
	01/24/99	4		3.56	4.6	4.24
	01/27/99	0.1		0.1	0.06	0.29
	01/30/99	2.55		2.08	2.97	3.16
	02/02/99	0.11		0.02	0.08	0.29
	02/05/99	2.46	1.2	2.12	2.81	3
	02/11/99	0.11	0.16	0.09	0.08	0.15
	02/14/99	4.87	6	4.23	5.53	5.45
	02/17/99		10.26	7.86	9.65	9.41
	02/20/99	4.51	4.68	4.28	4.82	4.85
	02/23/99	1.68	2.22	1.54	1.71	2.14
	02/26/99	2.99	3.91	2.75	3.45	3.6

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

Average of OC (μg/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	10.26	8.71	#DIV/0!	11.32	7.08
	01/09/99		4.2	4.22	4.03	3.43
	01/15/99	10.04	7.41	7.09		7.71
	01/18/99	14.21	12.86	9.79	11.68	10.92
	01/21/99	4.28	4.02	3.05	3.12	2.77
	01/24/99	8.13		6.88	6.39	6.18
	01/27/99	2.46		2.09	2.68	2.26
	01/30/99	7.71	6.41	6.3	8.72	7.67
	02/02/99	4.79		3.3	3.23	2.99
	02/05/99	5.89	4.5	3.8	4.12	4.31
	02/11/99	1.96	2.11	1.42	2.33	2.06
	02/14/99	6.97	6.35	5.31	6.66	5.3
	02/17/99	8.34	7.28	6.89	7.51	8.33
	02/20/99	8.26	7.11	6.15	8.58	6.79
	02/23/99	6.67	5.25	6.19	8.29	5.49
	02/26/99	3	4.13	3.84	5.63	4.13

Average of EC (μg/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	6.1	5.93	4.5	6.68	6.38
	01/09/99		1.43	1.35	1.47	1.53
	01/15/99	4.77	4.58	4.4		4.77
	01/18/99	5.69	6.79	6.27	7.16	6.65
	01/21/99	1.64	1.75	1.35	1.45	1.31
	01/24/99	3.05		3.09	2.72	2.91
	01/27/99	0.57		0.86	0.87	0.8
	01/30/99	3.6	4	3.37	4.02	4.34
	02/02/99	1.45		1.5	1.35	1.44
	02/05/99	2.08	1.36	2.48	2.62	2.71
	02/11/99	0.21	0.73	0.4	0.49	0.48
	02/14/99	2.29	3.29	2.35	2.9	2.79
	02/17/99	4.54	5.69	4.74	4.44	4.18
	02/20/99	3.51	3.69	3.13	3.28	3.43
	02/23/99	3.31	3.6	2.99	3.23	3.21
	02/26/99	0.96	1.89	1.48	1.88	1.83

Average of S (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	237.6	258.9	251.5	418.6	273.2
	01/09/99		99.1	103.8	178.4	108.1
	01/15/99	203.6	195.1	210.9		224.1
	01/18/99	2233.1	2271	6409.4	2417.3	2395.7
	01/21/99	584.5	562.6	546.6		682
	01/24/99	703.2	599.3	631.1	754	798.6
	01/27/99	94.1	94.3	98.6	109	99.6
	01/30/99	194.6	213.6	135.6	284.7	
	02/02/99	104.9	111.2		164.1	104.5
	02/05/99	301.4	306.7	306.6	353.6	
	02/11/99	102.7	113	103.5	156.7	127.5
	02/14/99	616.8	634.2	585.4	698.4	639.4
	02/17/99	1453.2	1412.8	1363.8	1528.2	1437
	02/20/99	776.5	628.2	748.5	936.3	785.4
	02/23/99	170.2	172.5	169.4	317.3	160.1
	02/26/99	790.4	790.9	723	791.4	792.7

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

Average of Si (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	481.6	494.7	672.5	3329.6	501.6
	01/09/99		244.7	316.3	1743.9	214.9
	01/15/99	477.4	345.1	645.2		422.9
	01/18/99	145.3	115.2	600.8	445.1	152.3
	01/21/99	45.4	95.8	34.6		54.5
	01/24/99	63.7	105.5	58.6	137.1	56.1
	01/27/99	22.1	60.5	37.5	58.7	17.3
	01/30/99	132.7	326.3	107.2	613.2	
	02/02/99	162.4	132.1		905.3	132.4
	02/05/99	38.3	24.8	39.3	104.2	
	02/11/99	122.7	101.6	144.6	473.7	168.3
	02/14/99	148	123.4	133	445.7	146.2
	02/17/99	305.3	255.1	319	681.5	286.1
	02/20/99	145.7	93.7	169.7	717.3	194.5
	02/23/99	386.9	289.2	463.7	2513.9	319.3
	02/26/99	89.1	75.7	102.3	266.2	57.1

Average of K (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	129.2	139.6	161.5	674.3	151.5
	01/09/99		70.9	85.6	331.5	68
	01/15/99	133.3	117.7	155.7		136.8
	01/18/99	156.2	163.5	472	231.4	164.3
	01/21/99	45.6	53.8	45.8		45.5
	01/24/99	109.4	104.8	102.2	132.6	126.9
	01/27/99	16.2	18.1	18.6	27.1	21.7
	01/30/99	99.5	130.2	66.4	215.4	
	02/02/99	48.5	45.3		168.8	43.9
	02/05/99	63.1	64.6	62.2	74	
	02/11/99	25.2	24.1	29	78.3	32
	02/14/99	95.2	86.9	93.5	156	96
	02/17/99	121.2	109	121.6	186.4	121.7
	02/20/99	84.1	72.4	81.6	200	92.3
	02/23/99	91.7	77.6	106.2	456.8	86.4
	02/26/99	58.4	58.2	56.9	89.6	51.9

Average of Ca (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	462.1	446.4	630.2	3453.8	493.5
	01/09/99		187	293.8	1589.2	186.3
	01/15/99	434.6	330.7	565.1		352.2
	01/18/99	203.4	154.2	757.2	736.3	170.5
	01/21/99	46.4	77.5	51.3		38.5
	01/24/99	85.5	137.3	93.3	136.9	75.7
	01/27/99	22.3	45.2	28.3	58.2	24.2
	01/30/99	119.1	260.9	90.6	686.6	
	02/02/99	255.8	224.1		1837.1	212.3
	02/05/99	62.7	51.8	65.6	136.4	
	02/11/99	72.7	58.2	79.6	275.3	88.9
	02/14/99	135.1	106.5	140.5	479.5	121
	02/17/99	164.8	124.5	163.6	343.7	138.9
	02/20/99	137.5	80	148.3	803.4	131.9
	02/23/99	330.5	233.8	393	2439.1	260.4
	02/26/99	68.5	62.9	73.5	152.1	54

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

Average of Mn (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	10	11.8	13.9	39.1	12.4
	01/09/99		3.9	3.8	14.7	2.6
	01/15/99	8.9	7.2	11.4		9.3
	01/18/99	8.3	5.9	21.8	10.2	6.9
	01/21/99	0	1	1.1		0.6
	01/24/99	2.2	2.1	2.8	3.4	1.6
	01/27/99	0	1.2	1	0	1.2
	01/30/99	2.7	5.4	1.7	9.9	
	02/02/99	2.4	2.4		5.9	2.6
	02/05/99	0.7	1.5	2.1	4.5	
	02/11/99	2.6	1.2	2.5	5.1	2
	02/14/99	2.7	2.7	3.1	6.7	2.3
	02/17/99	6.5	5.8	5.5	8.6	6.5
	02/20/99	4.4	4.7	3.8	8.1	3.5
	02/23/99	8.1	6.4	8.7	32.1	7.9
	02/26/99	2.8	2.1	3.2	0	3

Average of Fe (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	457.5	480.1	580.3	1799.4	532.1
	01/09/99		150	200.4	734	144
	01/15/99	430.7	360.6	498.7		413.3
	01/18/99	268	217.3	886.8	423.7	249.5
	01/21/99	59.7	89.8	64.2		53.9
	01/24/99	116.7	153.8	116	156.6	111.2
	01/27/99	40	60.4	40	48	59.4
	01/30/99	191.2	302.6	134.3	515.4	
	02/02/99	116.4	99.5		427.5	104.9
	02/05/99	78.1	70.8	76.9	95.1	
	02/11/99	57.6	49.6	64.4	203.8	77.9
	02/14/99	199.5	152.5	196.6	379	177.7
	02/17/99	243.8	216.3	249.6	393.5	225.8
	02/20/99	180.6	125.6	180.5	446.8	180
	02/23/99	330.3	259.1	365	1234.1	282.3
	02/26/99	100.2	93.3	103.7	172.3	92.6

Average of Cu (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	16.5	17.2	14.2	21.8	17.5
	01/09/99		2.7	2	3.9	0
	01/15/99	10	8.5	8.5		8.1
	01/18/99	9.2	7.2	29.2	10.4	15.3
	01/21/99	1.4	11.2	1.7		1.7
	01/24/99	6.7	16.4	4.8	5	6.8
	01/27/99	1.6	13.6	0.5	0	2.1
	01/30/99	6.6	28.1	2.4	8.6	
	02/02/99	3.1	3.8		8.9	
	02/05/99	6.4	4.2	4.1	4.1	
	02/11/99	0.8	0	0	3.3	0
	02/14/99	4.6	1.7	4	2.8	4.4
	02/17/99	7.5	10.1	8.5	10.6	14
	02/20/99	3.5	4.7	3.5	7.1	5.2
	02/23/99	11.9	11.1	9.7	15.1	9
	02/26/99	1	0	1.6	0	1.6

Appendix D. Final Data Archive, By Species, Site, Date, Sampler for the 4 City Study, Measurements at Rubidoux.

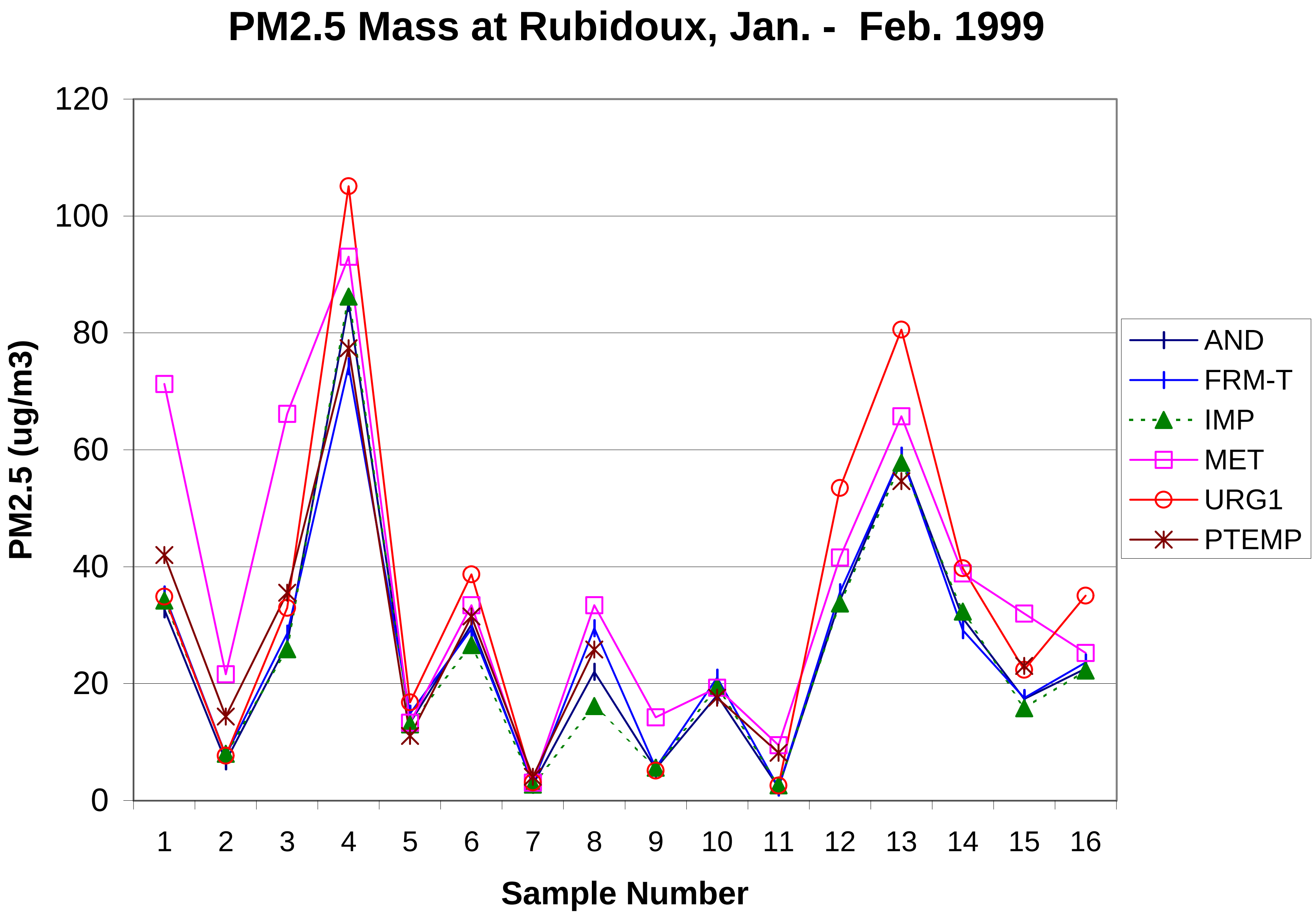
Average of Zn (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	234.9	246.1	225.9	283.7	277.2
	01/09/99		7.7	9.8	19.6	12.5
	01/15/99	264	240	229.7		294.1
	01/18/99	151.3	164.2	461	168.6	177.2
	01/21/99	6.8	9.5	7.4		8.8
	01/24/99	14.3	16.2	12.8	16.2	14.4
	01/27/99	5.5	5.1	5.7	3.4	6.1
	01/30/99	21.9	24.8	15	32.2	
	02/02/99	133.3	127.7		147.1	134.3
	02/05/99	77.7	76.5	69.4	78.4	
	02/11/99	3.5	3.7	3	6.9	4.2
	02/14/99	16.1	15.8	15.6	27.4	17.4
	02/17/99	53.2	52.7	50	51.8	53.2
	02/20/99	20	10.4	14.7	21.7	17.3
	02/23/99	162.3	148	149.1	176	149
	02/26/99	12.8	11.5	13.1	12	10.6

Average of Pb (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	45.1	50	50.1	67.3	51.7
	01/09/99		5.3	4.5	5.7	6.3
	01/15/99	16.1	10.2	11.7		13.9
	01/18/99	33.1	32.3	99.8	36.3	39.6
	01/21/99	2.2	4.6	5		5.7
	01/24/99	7.9	9.3	11.5	4.9	12.2
	01/27/99	0	1.5	0	0	0
	01/30/99	6.8	8.4	4.9	12.3	
	02/02/99	12.6	13.8		8.8	15.5
	02/05/99	24.2	23.4	23.1	27.3	
	02/11/99	0	0	0.1	6.7	3.2
	02/14/99	7.7	10.6	7.4	10.5	12.1
	02/17/99	13.7	15.6	14.9	16.4	17
	02/20/99	6.6	5.3	5.4	5.1	7.1
	02/23/99	45	46.9	43.6	39.5	44.8
	02/26/99	4.4	4.2	3.4	0	2.1

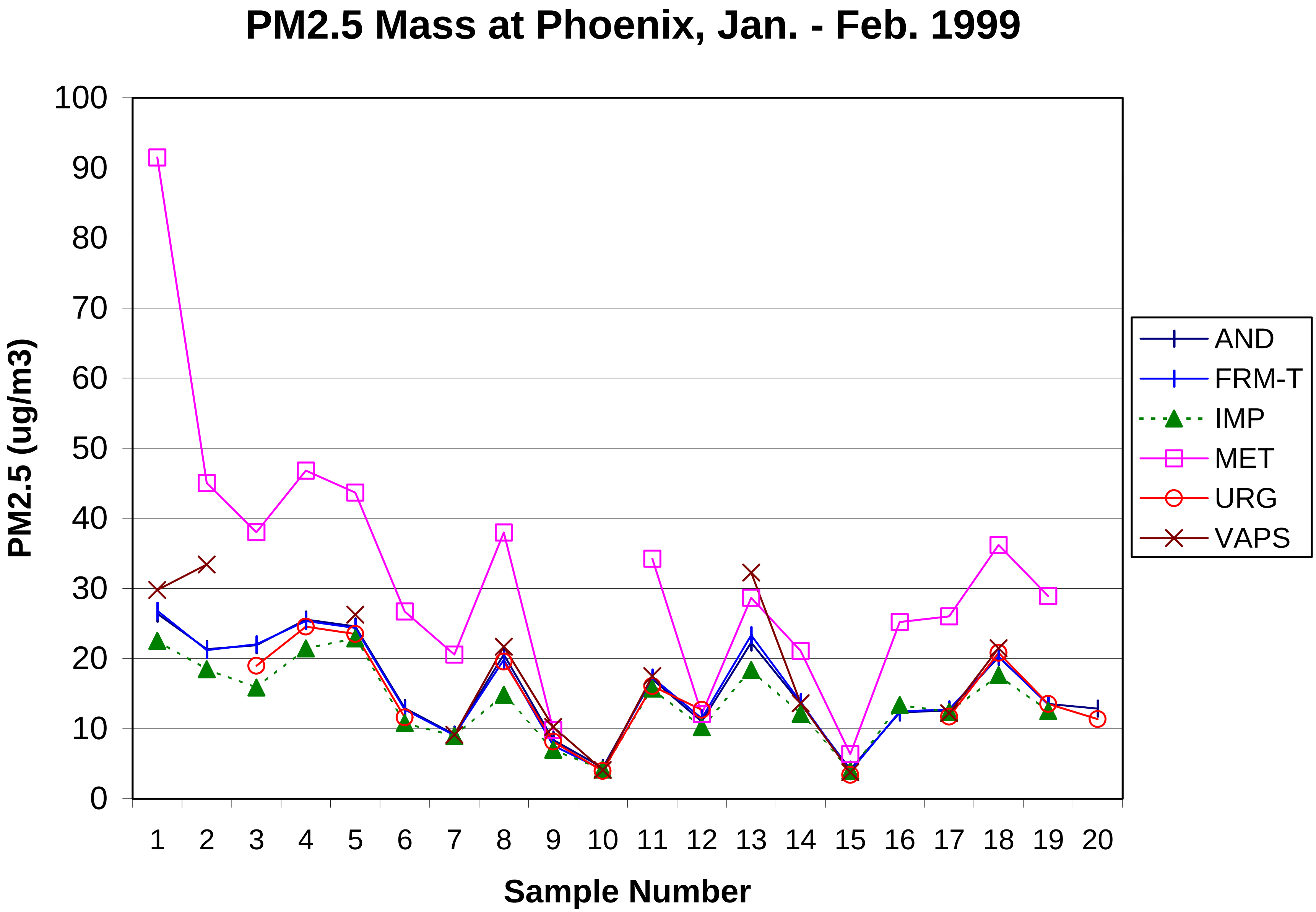
Average of As (ng/m3)		Sampler				
Site	**Date**	**AND**	**FRM**	**IMP**	**MET**	**URG**
1	01/06/99	2.3	0	0	0	2
	01/09/99		0	1.2	0	1.4
	01/15/99	0	0	0.9		0
	01/18/99	2.4	4	4.2	0	0
	01/21/99	1.2	0	0		0
	01/24/99	1.2	0	0	2.8	0.9
	01/27/99	0	0	0	0	0.8
	01/30/99	0.8	0	0	0	
	02/02/99	0	0		0	0
	02/05/99	0.9	1.5	1.3	0	
	02/11/99	0	0	0	0	0
	02/14/99	0.8	0	1	0	0
	02/17/99	1.8	1.1	1.8	0	1.3
	02/20/99	0	0	0	1.1	0
	02/23/99	1.3	0	1.3	2	0
	02/26/99	0	0	0	2.6	1.4

Appendix E

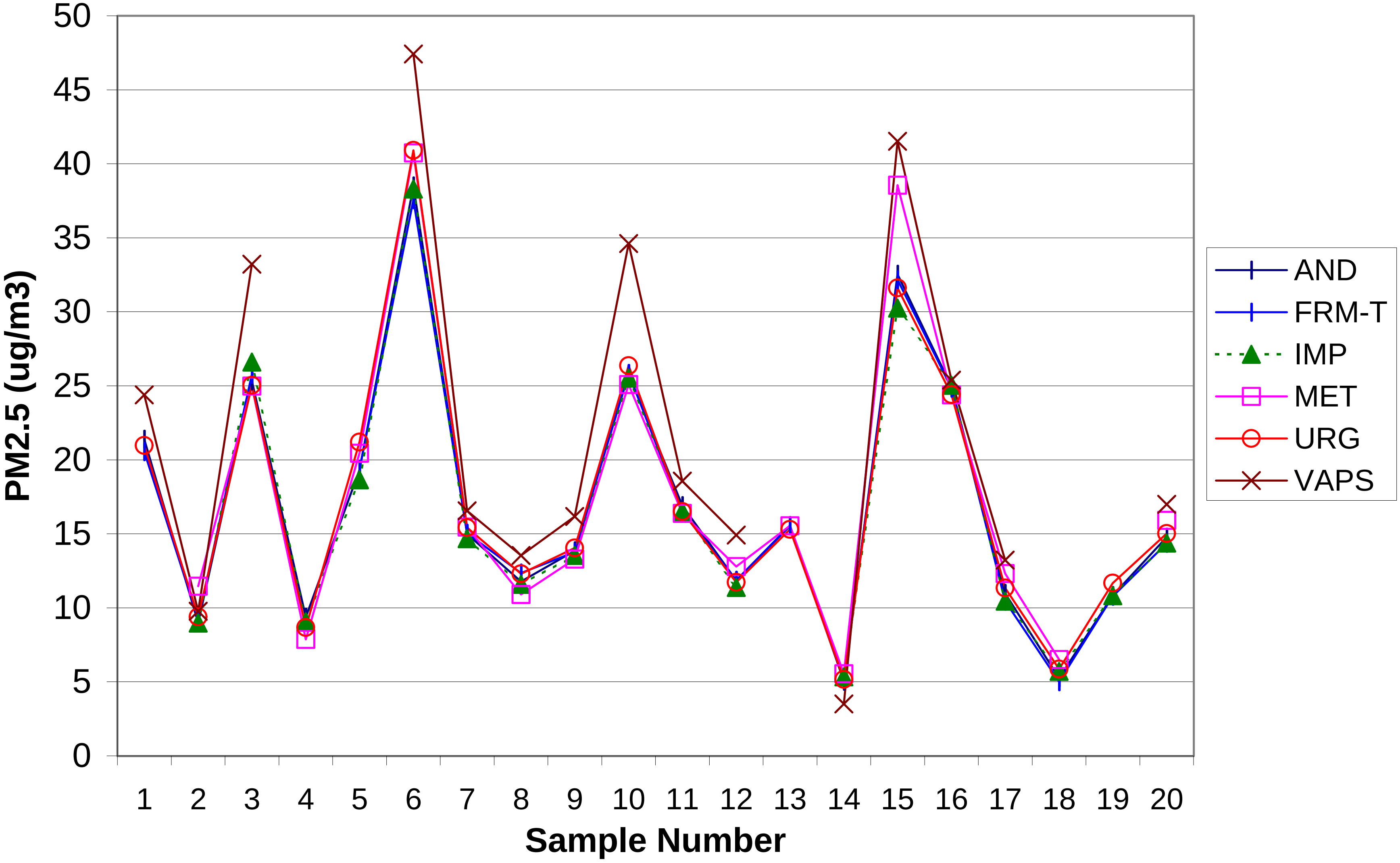
Time Series Plots for All Species Measured in the 4-City Study

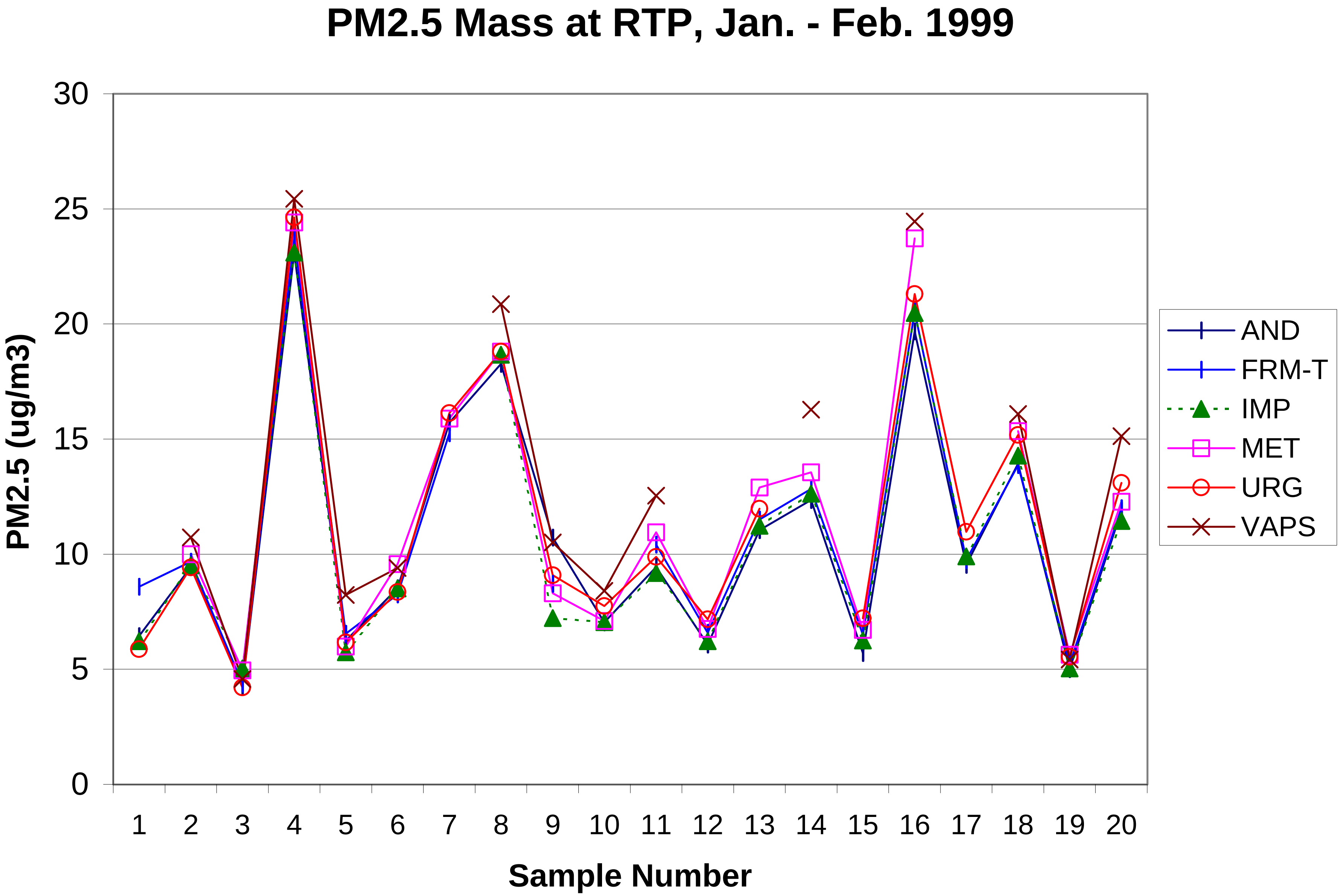


PM2.5 Mass at Rubidoux, Jan. - Feb. 1999

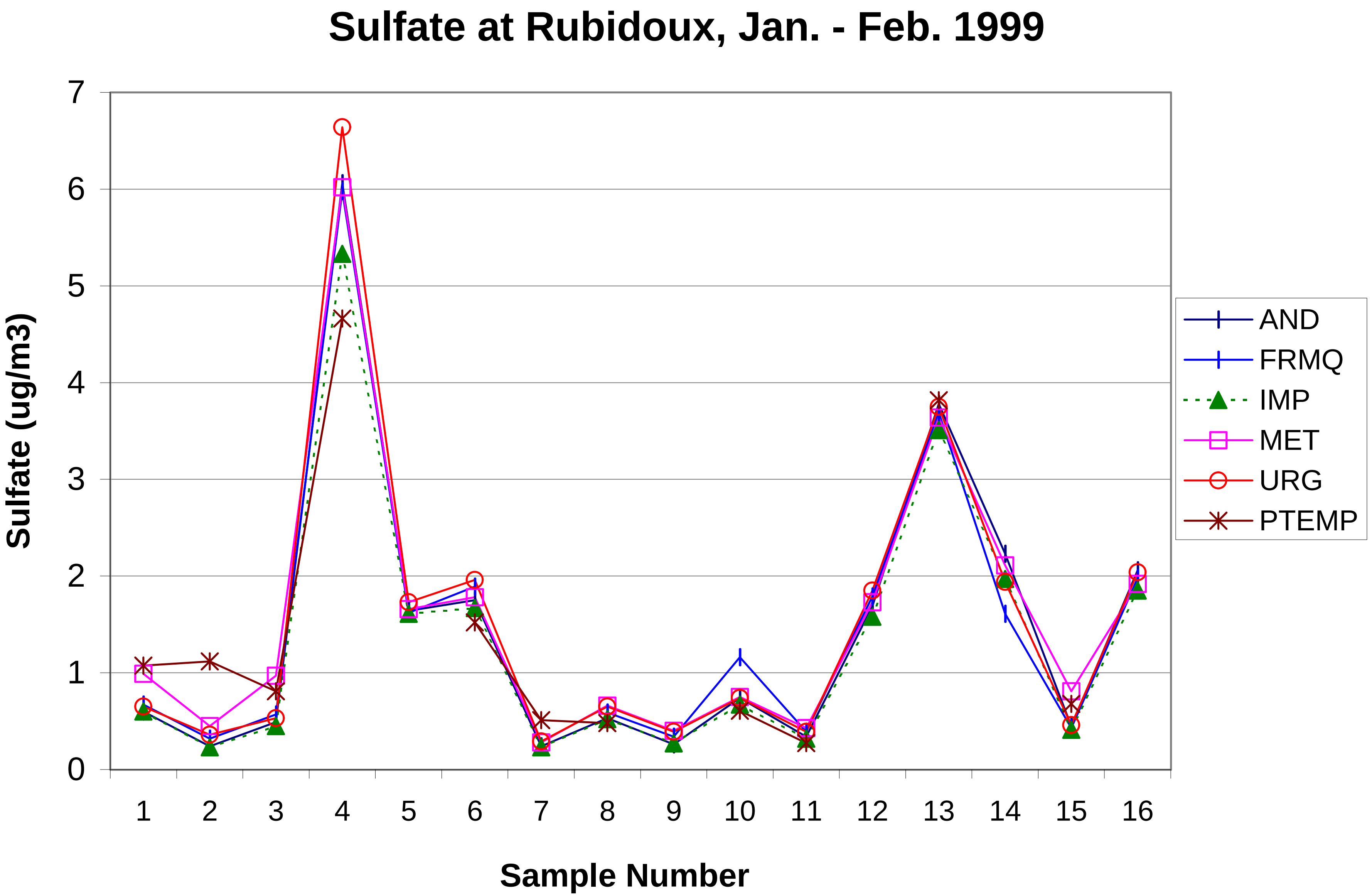

PM2.5 Mass at Phoenix, Jan. - Feb. 1999
PM2.5 (ug/m3)
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Sample Number
AND
FRM-T
IMP
MET
URG
VAPS

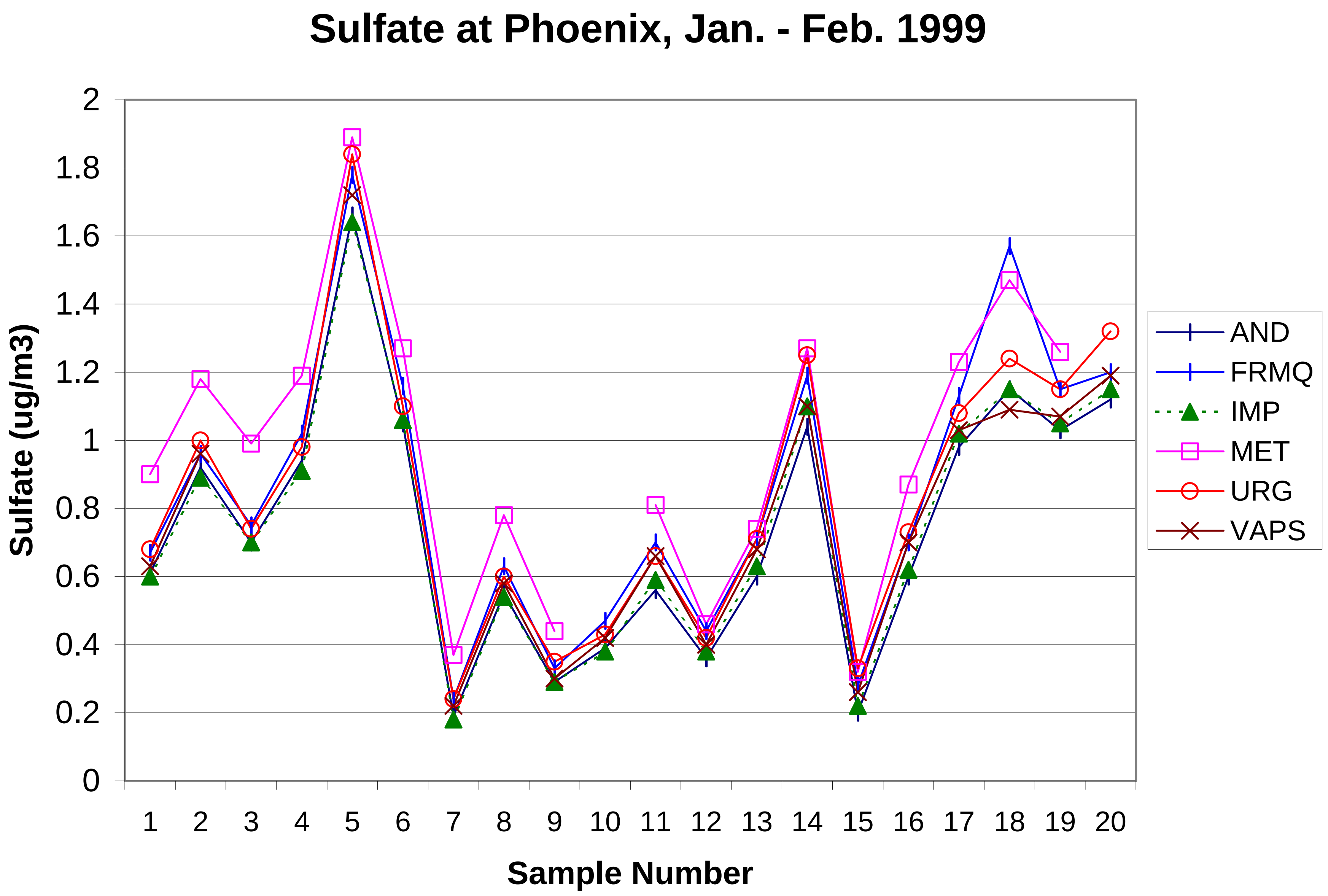
PM2.5 Mass at Philadelphia, Jan. - Feb. 1999



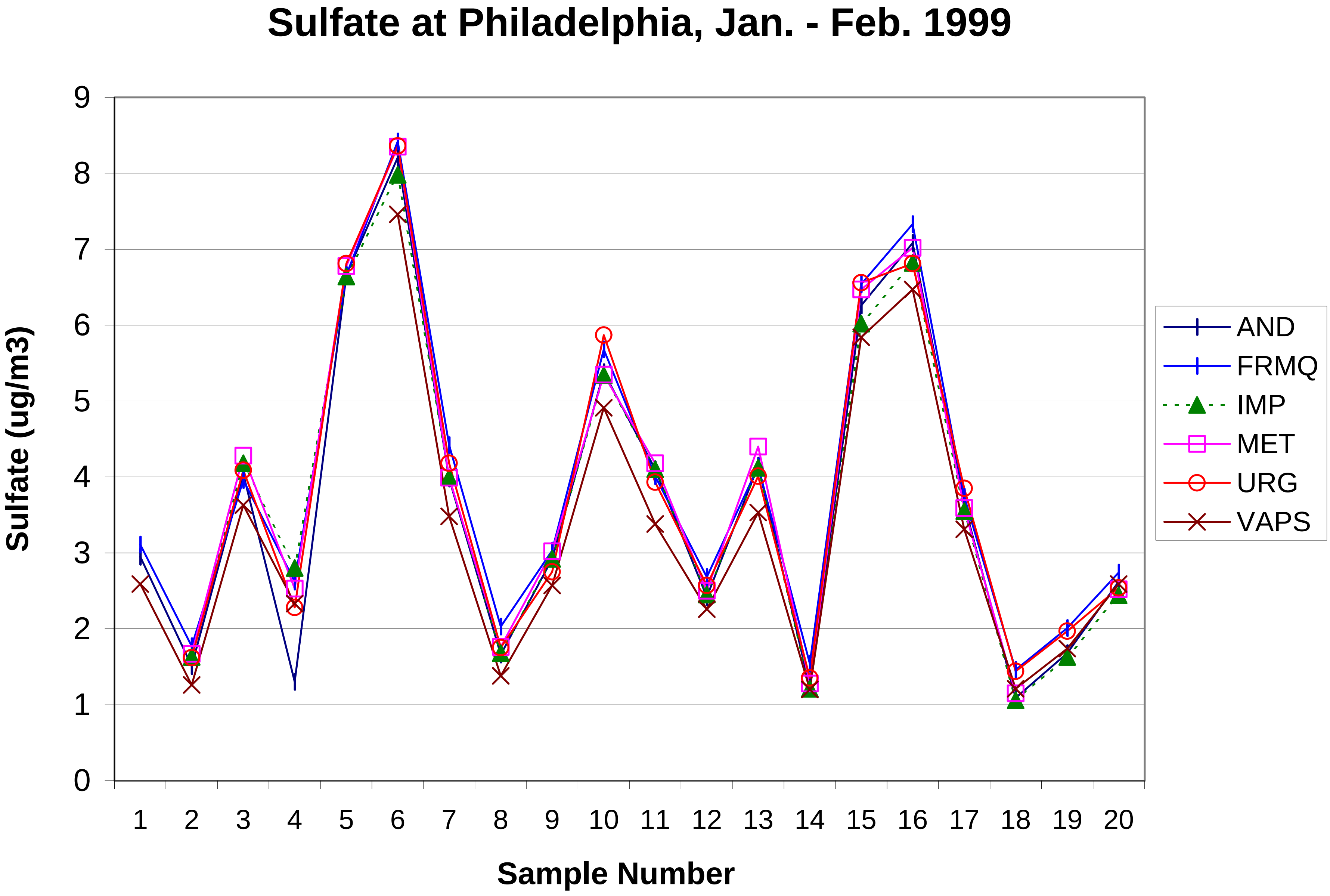


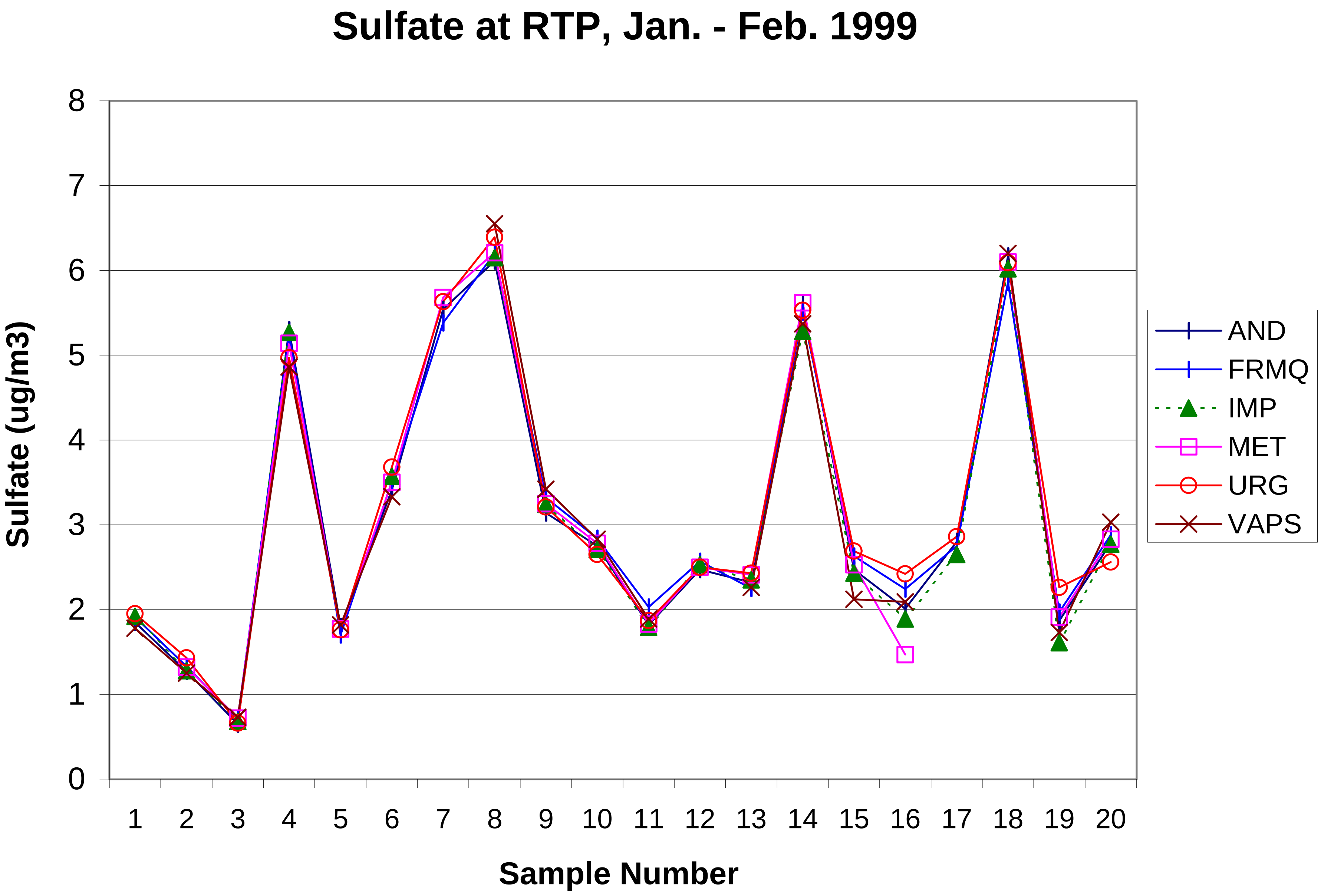
05 Appendix E1 TS-Mass & SO4.xls/Mass@RTP (11/8/2000)


Sulfate at Rubidoux, Jan. - Feb. 1999
Sulfate (ug/m3)
0
1
2
3
4
5
6
7
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Sample Number
AND
FRMQ
IMP
MET
URG
PTEMP



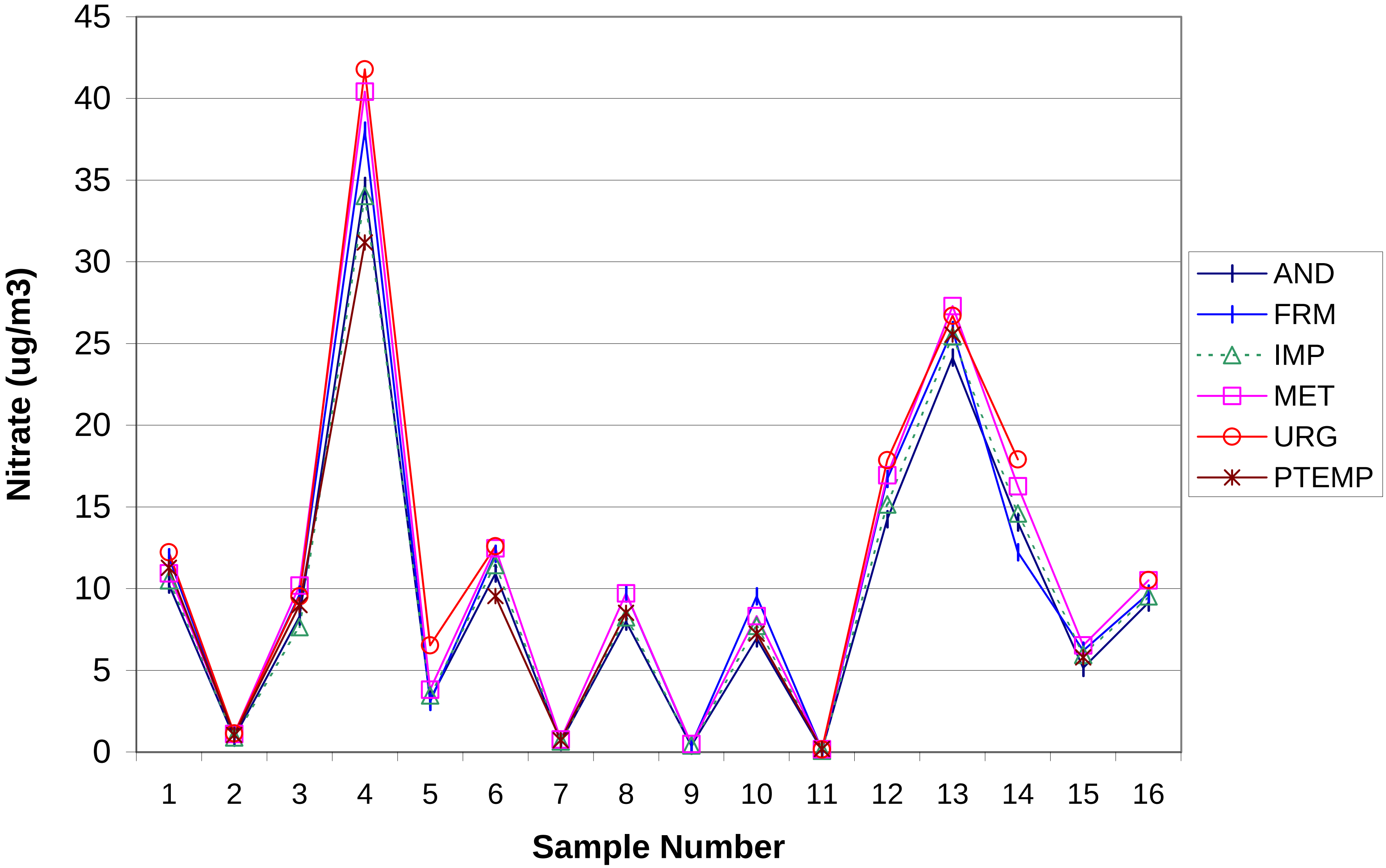
05 Appendix E1 TS-Mass & SO4.xls/Sulfate@Phoenix (11/8/2000)


Sulfate at Philadelphia, Jan. - Feb. 1999
Sulfate (ug/m3)
0
1
2
3
4
5
6
7
8
9
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Sample Number
AND
FRMQ
IMP
MET
URG
VAPS



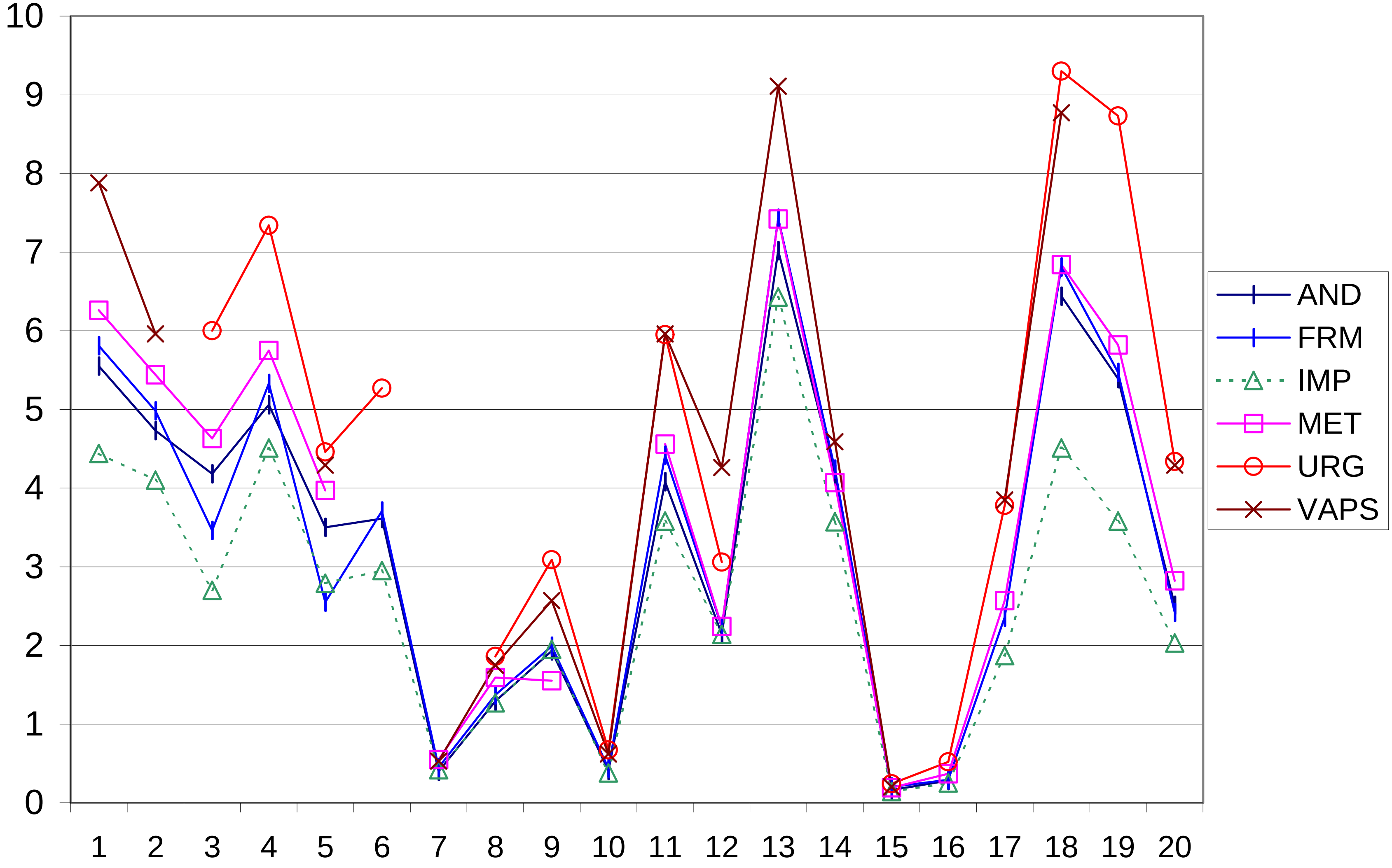
05 Appendix E1 TS-Mass & SO4.xls/Sulfate at RTP (11/8/2000)

Nitrate at Rubidoux, Jan.-Feb. 1999

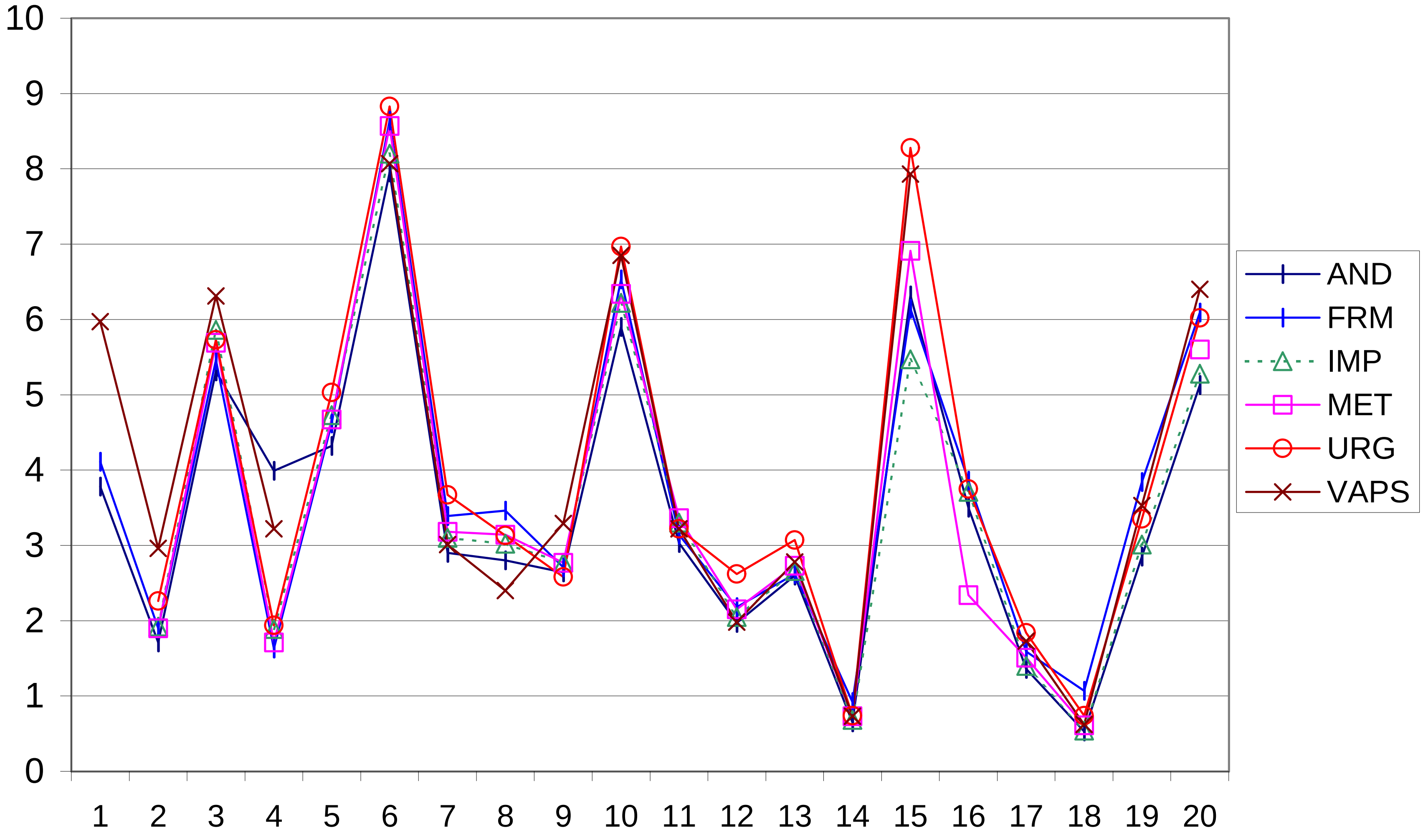


05 Appendix E2 TS-NO3 & NH4.xls/Nitrate@RUB (11/8/2000)

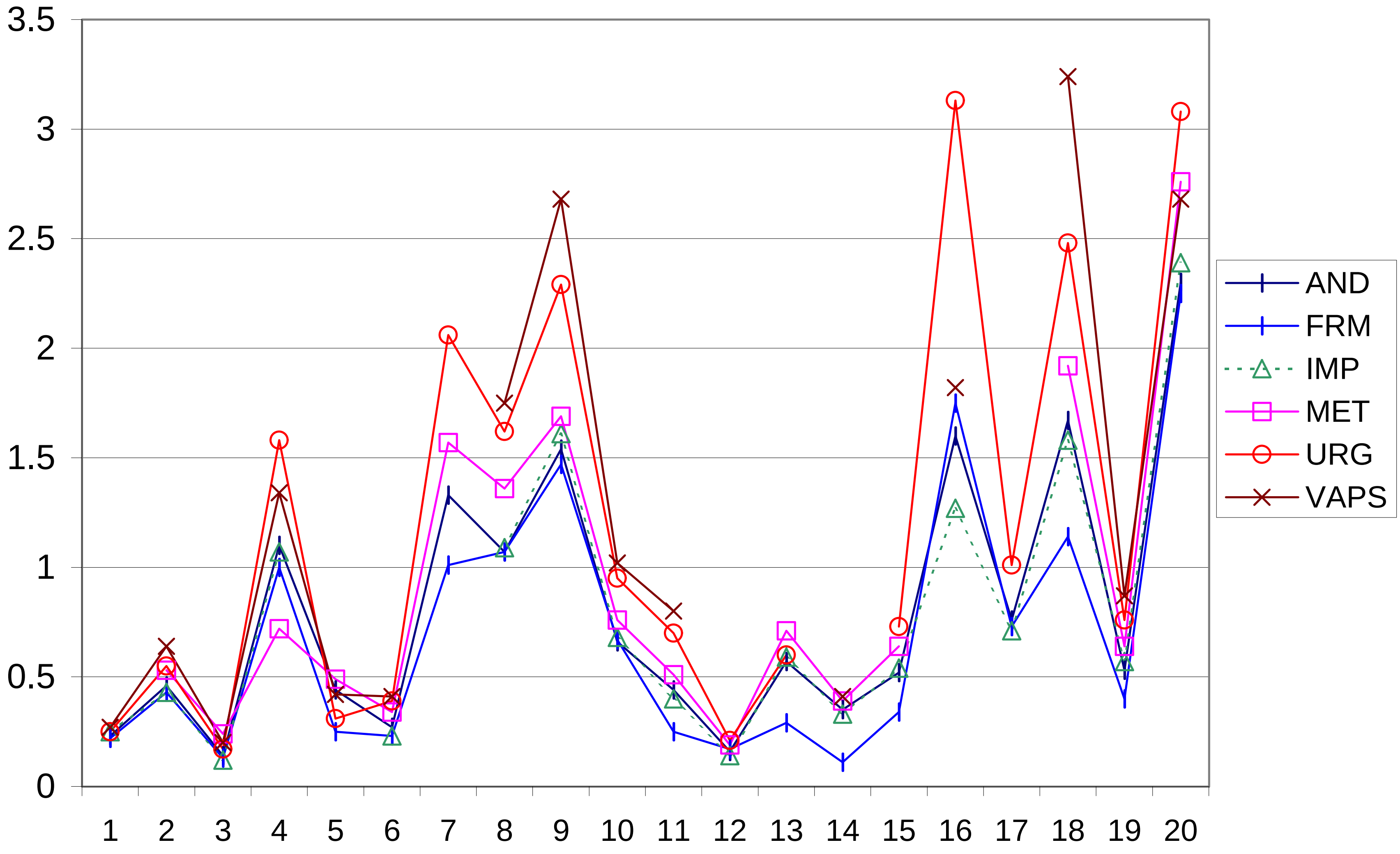
Nitrate at Phoenix, Jan - Feb 1999



Nitrate at Philadelphia, Jan.-Feb. 1999

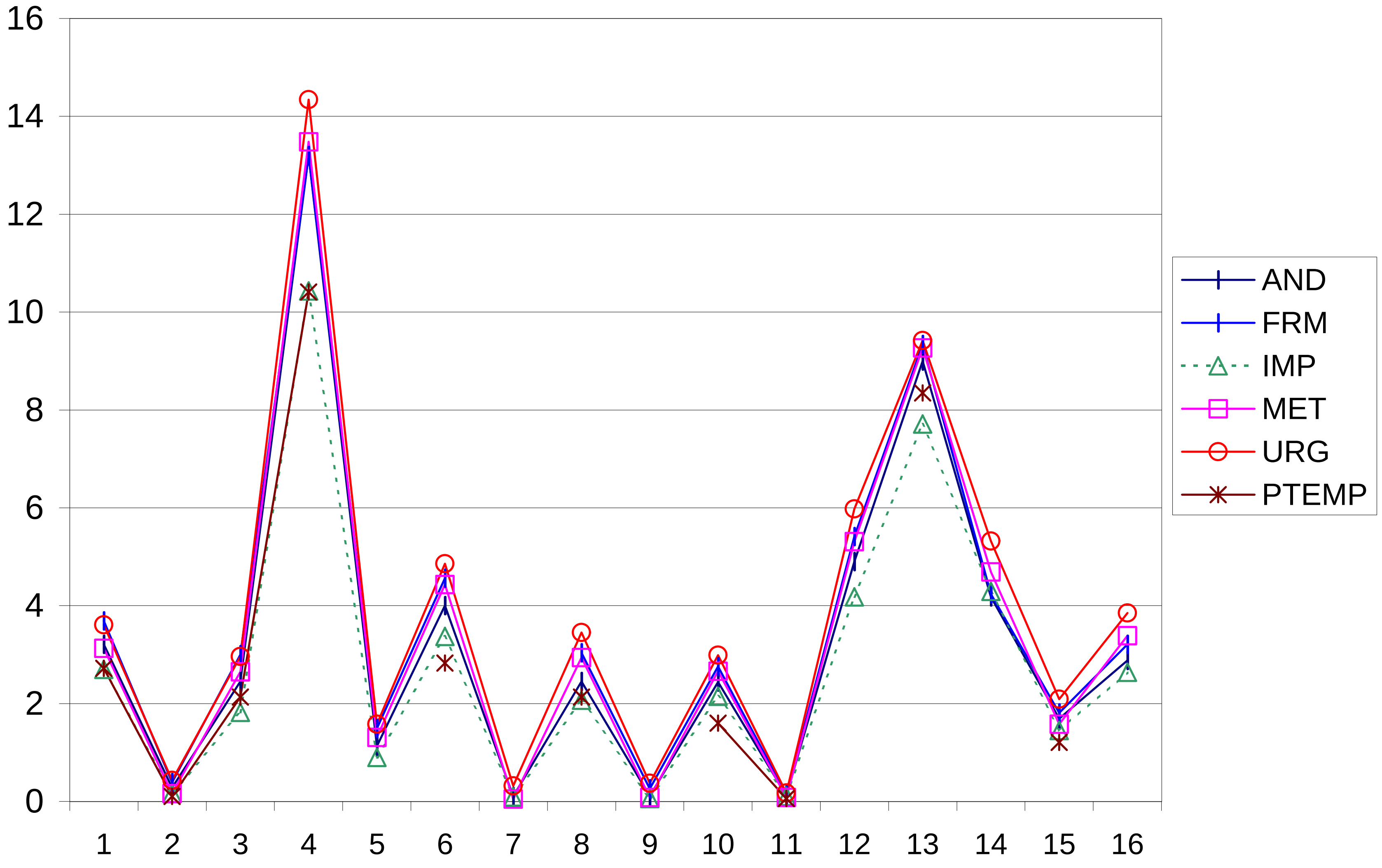


Nitrate at Research Triangle Park, Jan.-Feb. 1999

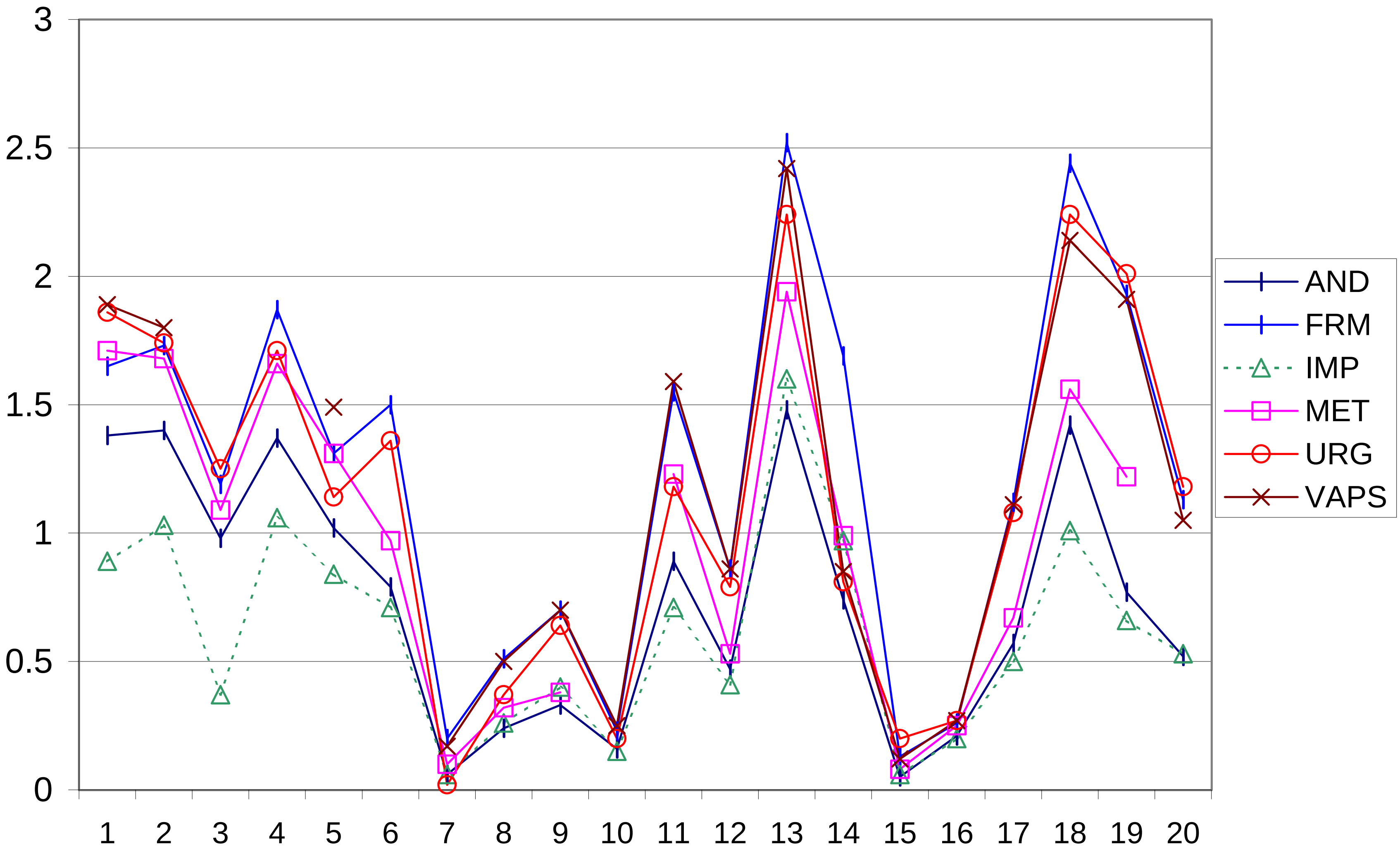


05 Appendix E2 TS-NO3 & NH4.xls/Nitrate@RTP (11/8/2000)

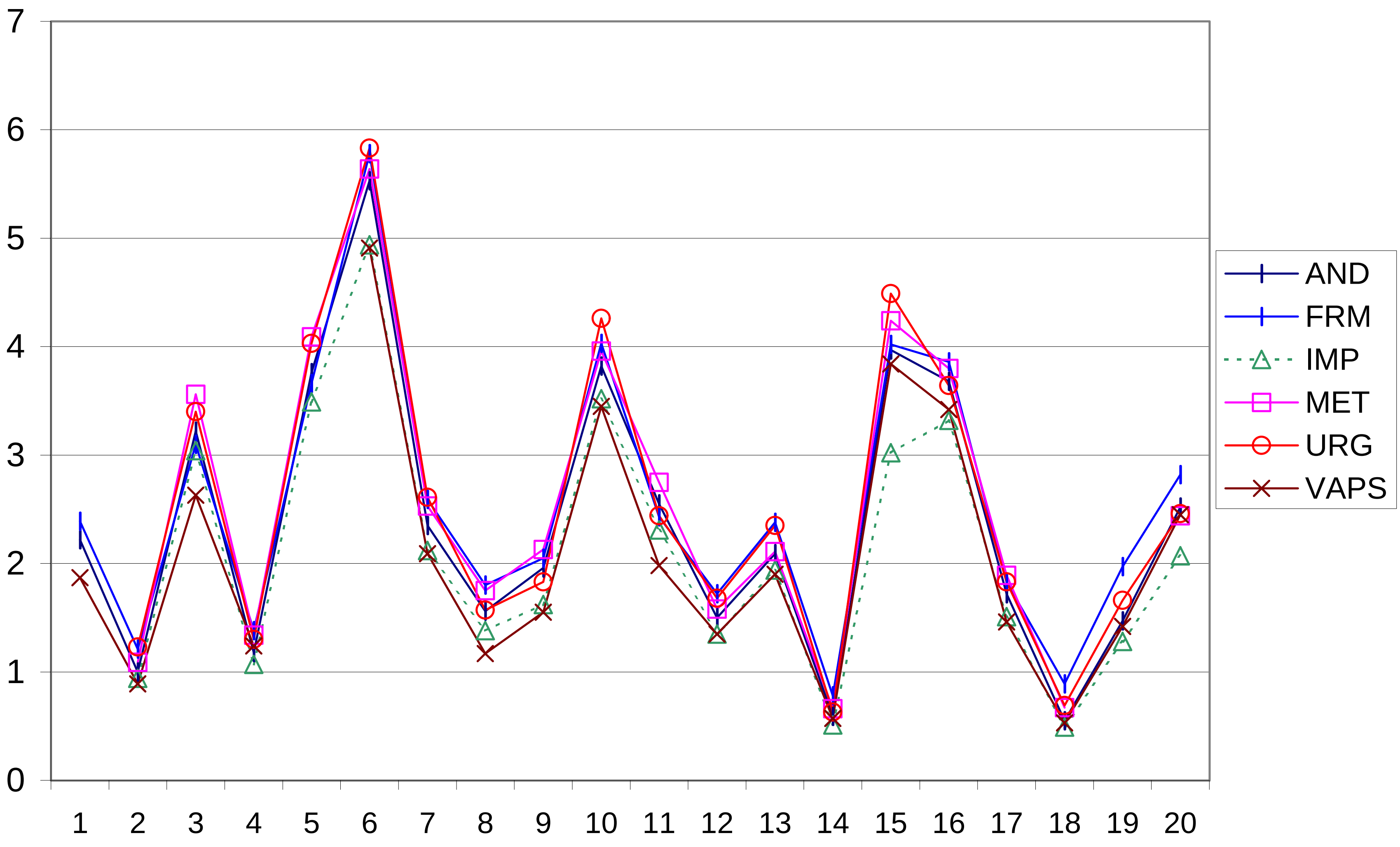
Ammonium at Rubidoux, Jan.-Feb. 1999

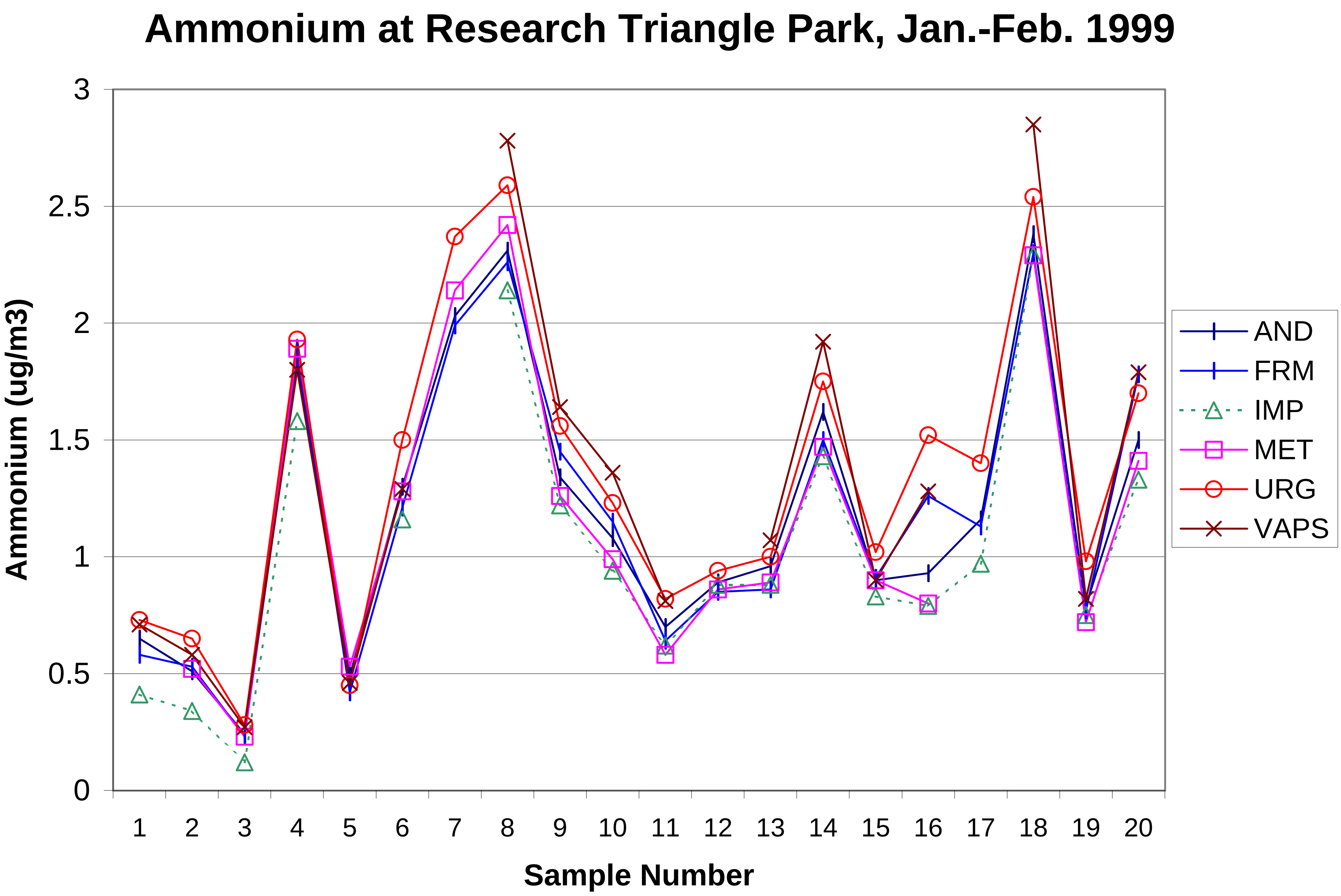


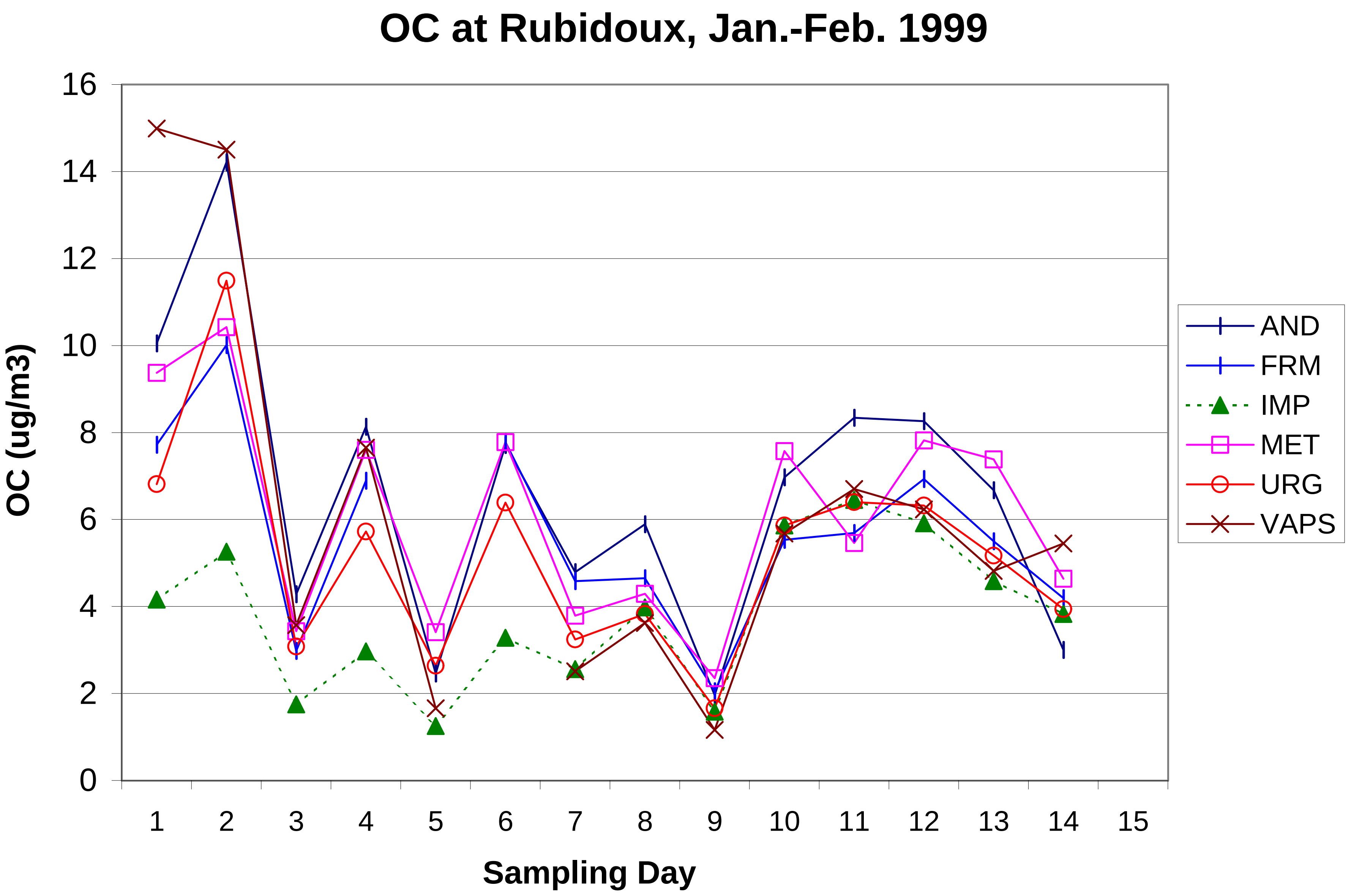
Ammonium at Phoenix, Jan.-Feb. 1999

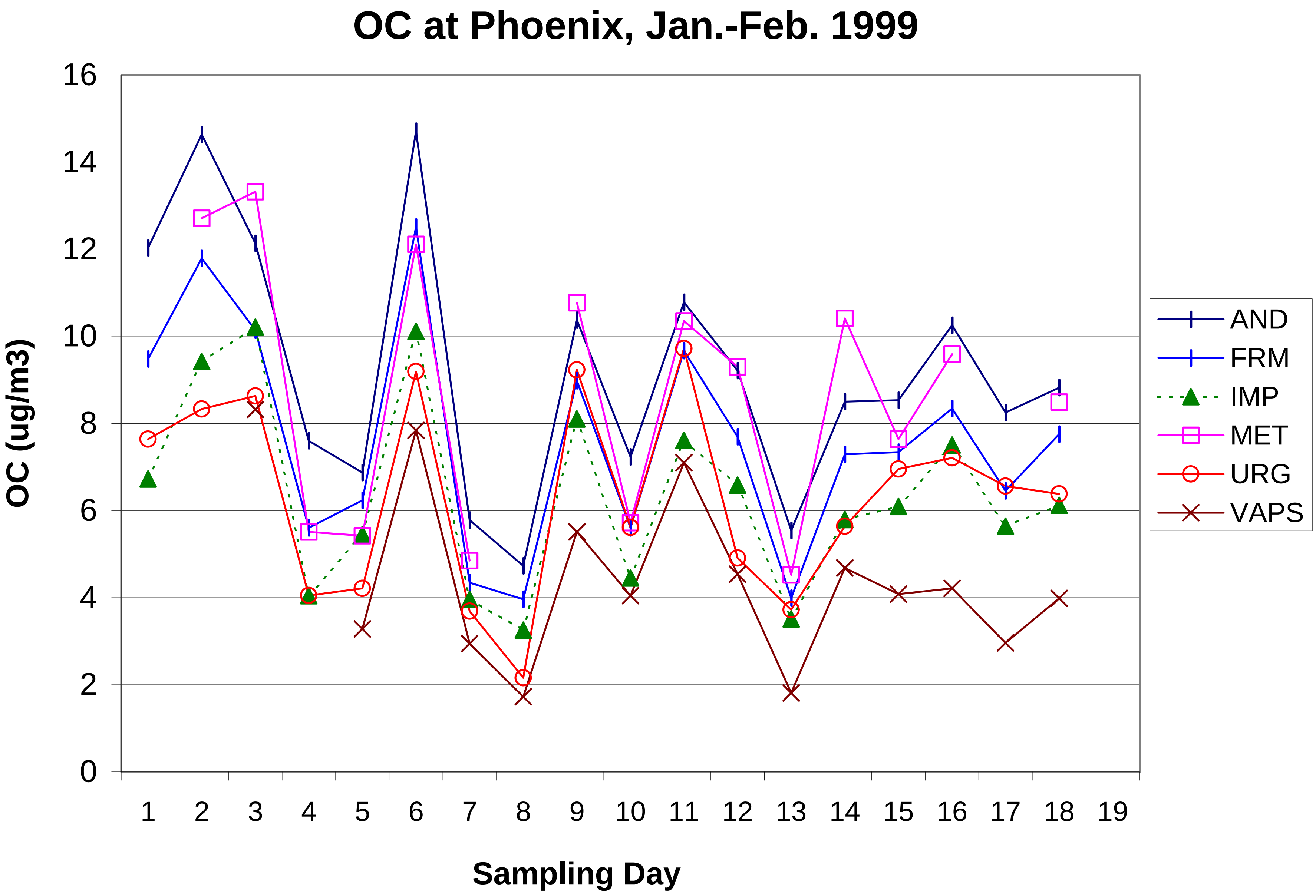


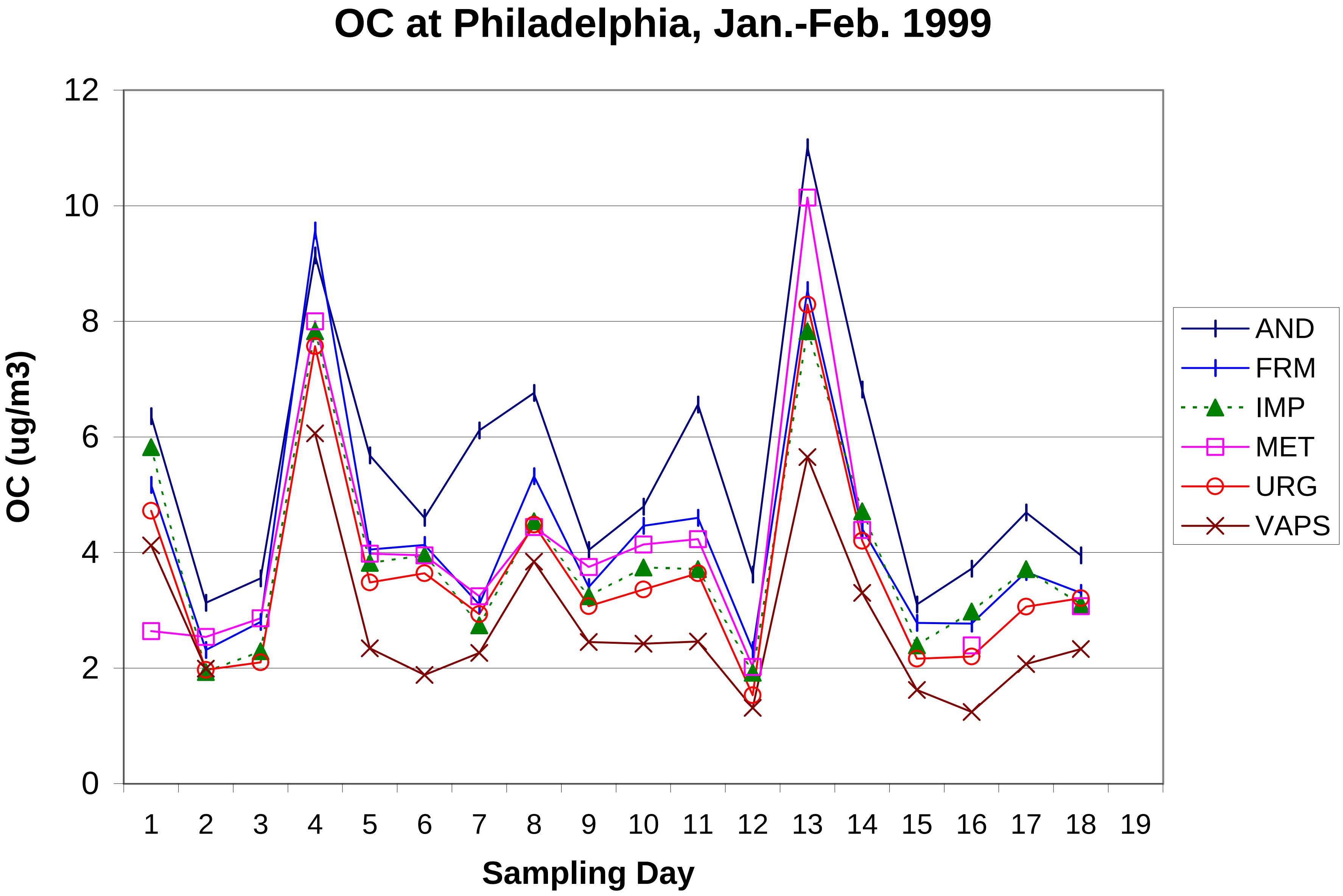
Ammonium at Philadelphia, Jan.-Feb. 1999

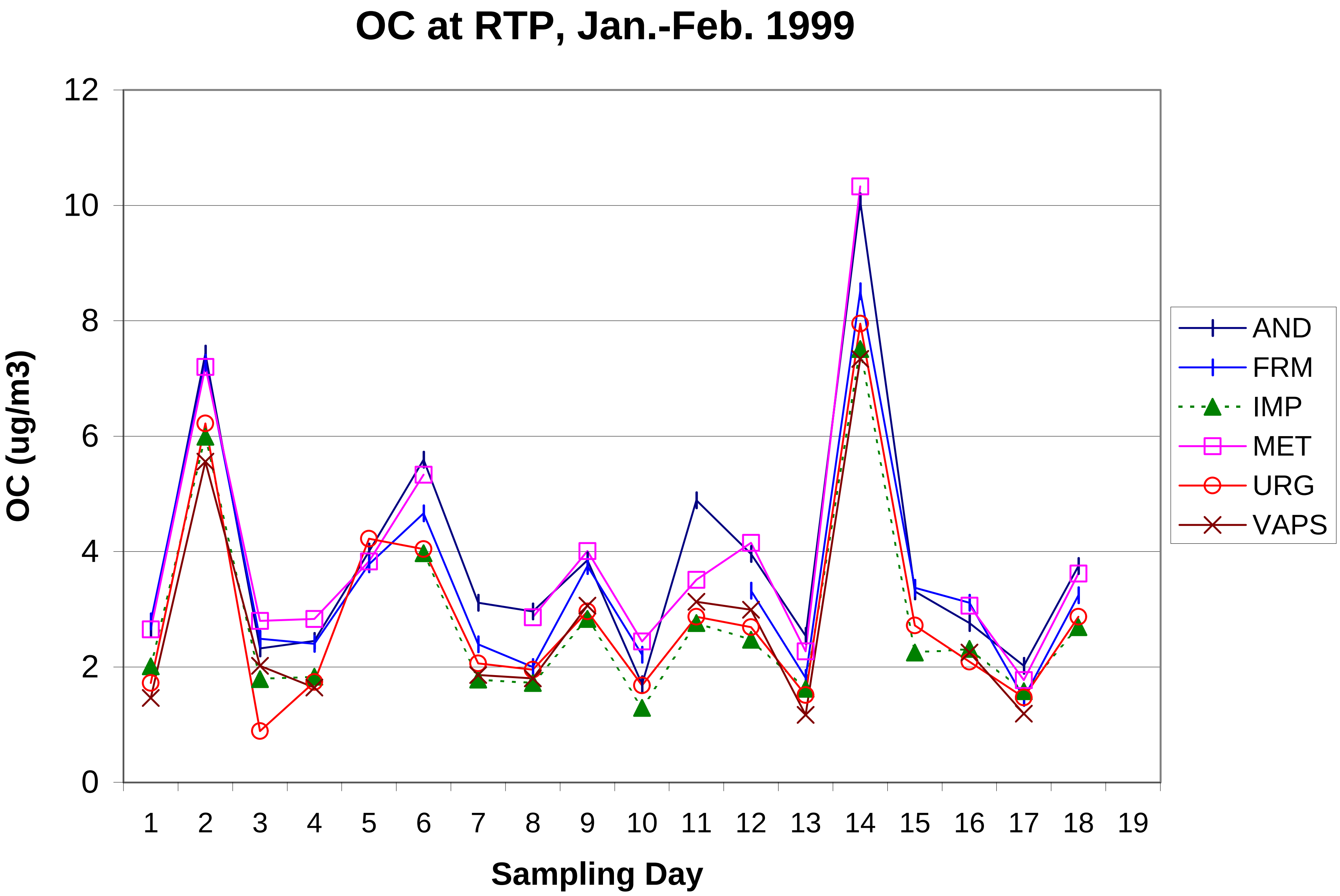


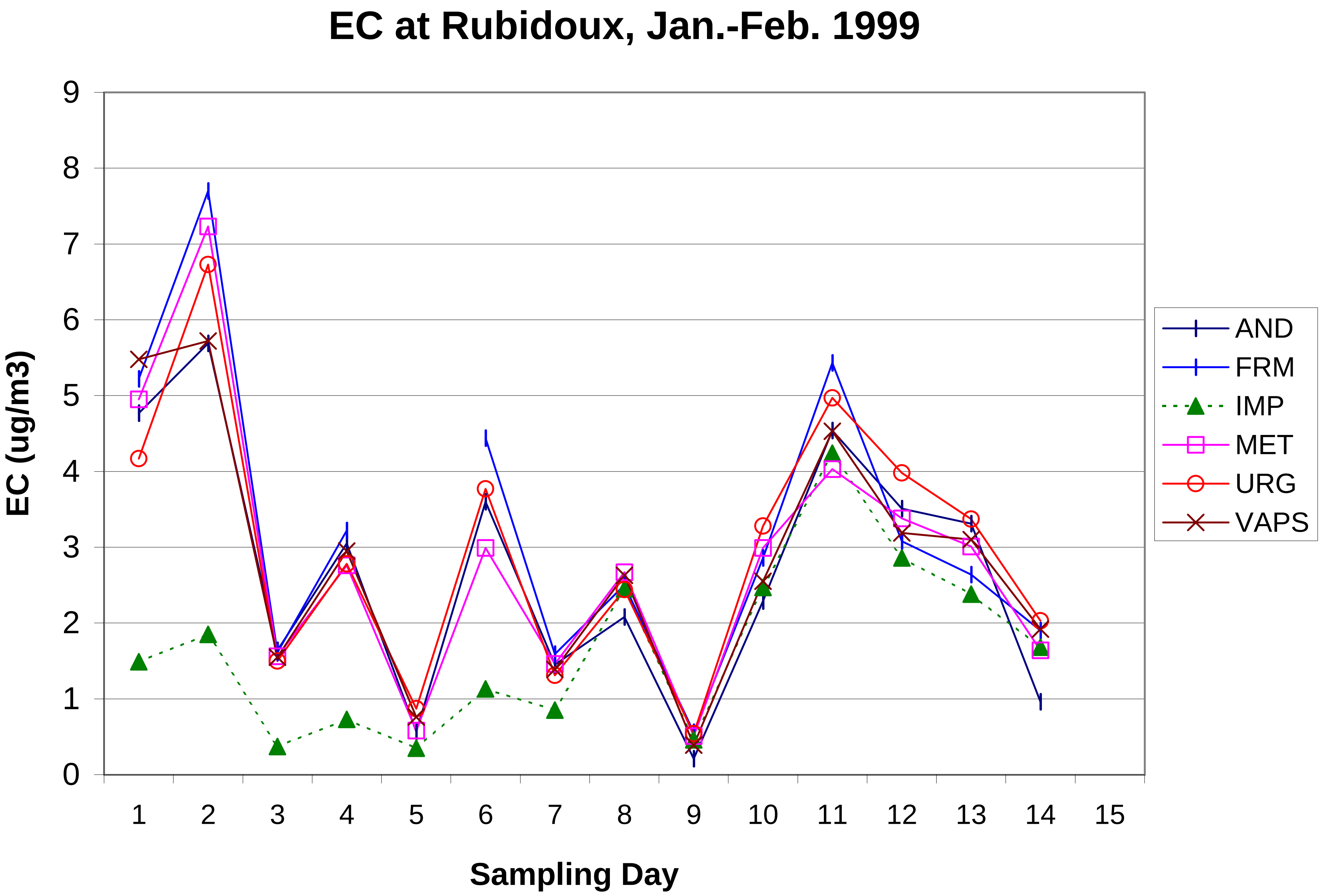

Ammonium at Research Triangle Park, Jan.-Feb. 1999
Ammonium (ug/m3)
3
2.5
2
1.5
1
0.5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Sample Number
AND
FRM
IMP
MET
URG
VAPS

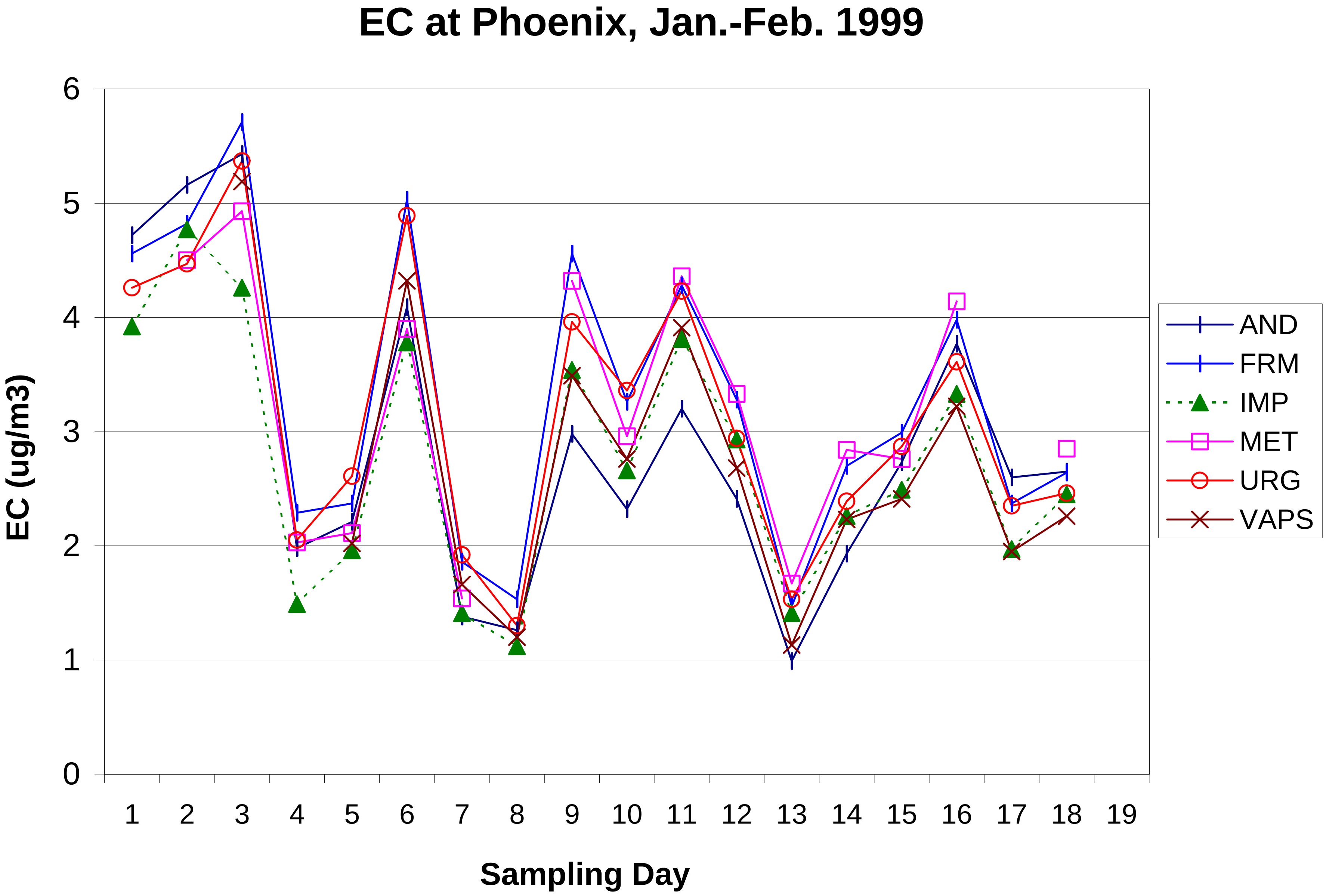

OC at Rubidoux, Jan.-Feb. 1999
OC (ug/m3)
0
2
4
6
8
10
12
14
16
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Sampling Day
AND
FRM
IMP
MET
URG
VAPS

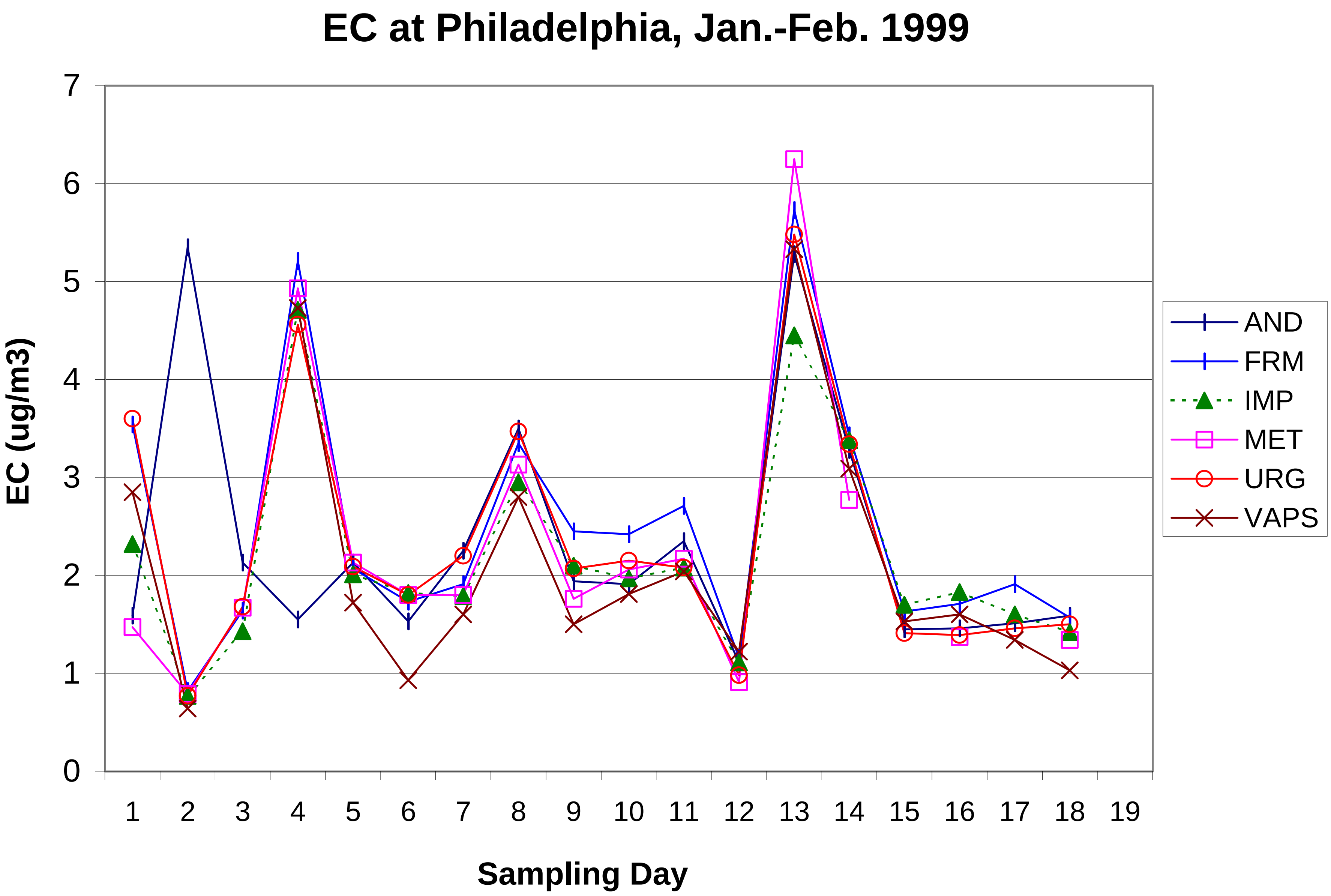

OC at Phoenix, Jan.-Feb. 1999
OC (ug/m3)
0
2
4
6
8
10
12
14
16
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Sampling Day
AND
FRM
IMP
MET
URG
VAPS

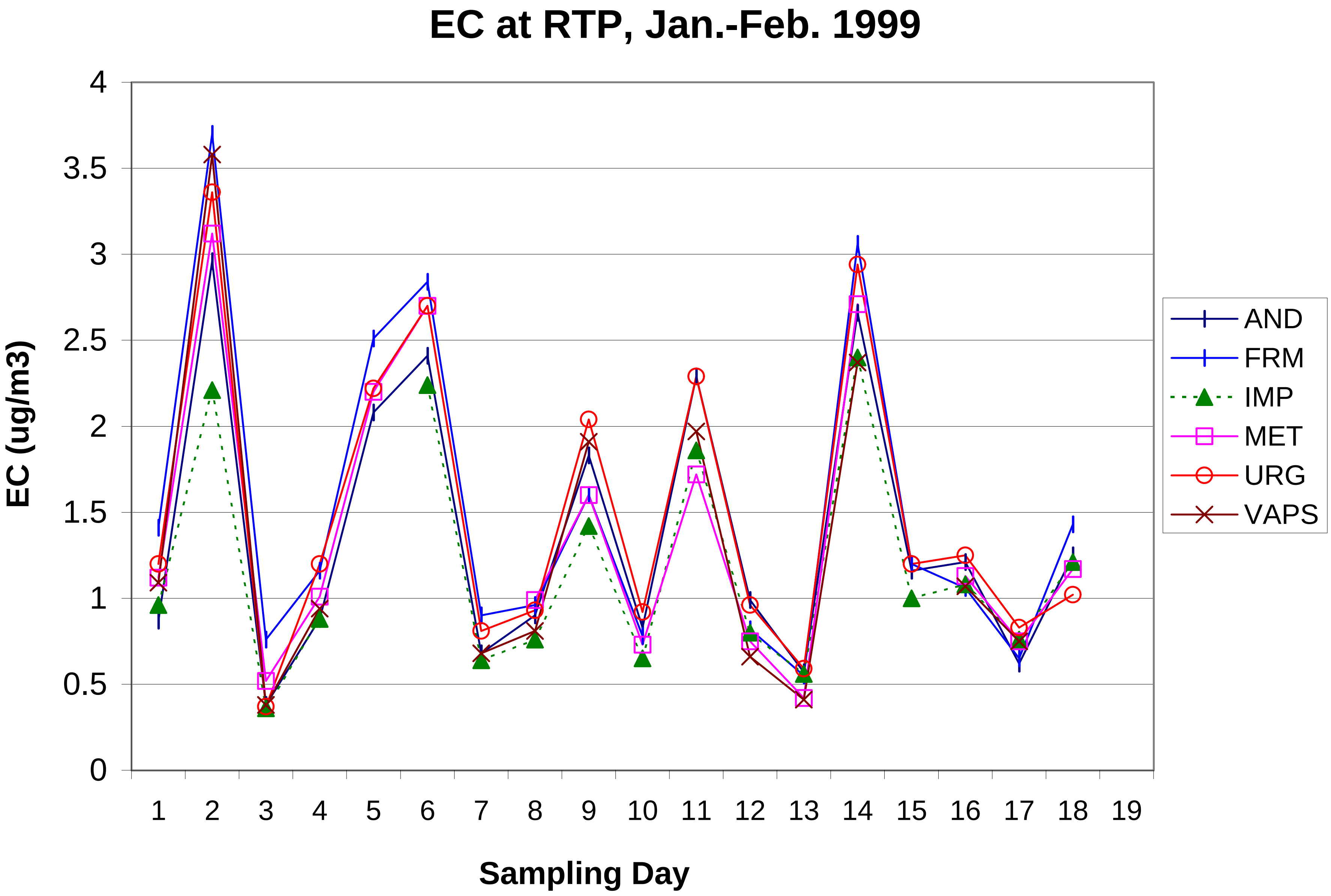


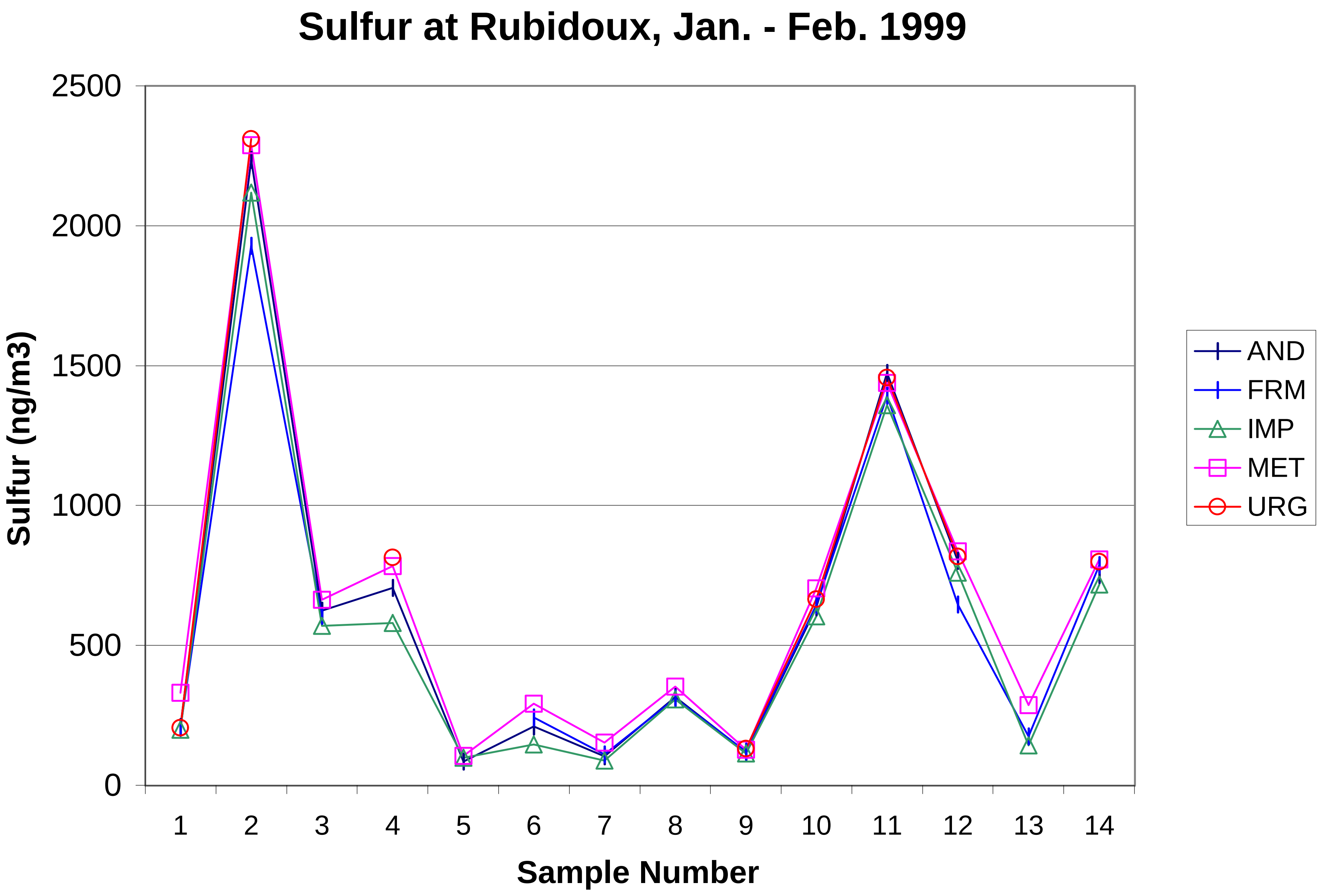

OC at RTP, Jan.-Feb. 1999
OC (ug/m3)
0
2
4
6
8
10
12
Sampling Day
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
AND
FRM
IMP
MET
URG
VAPS

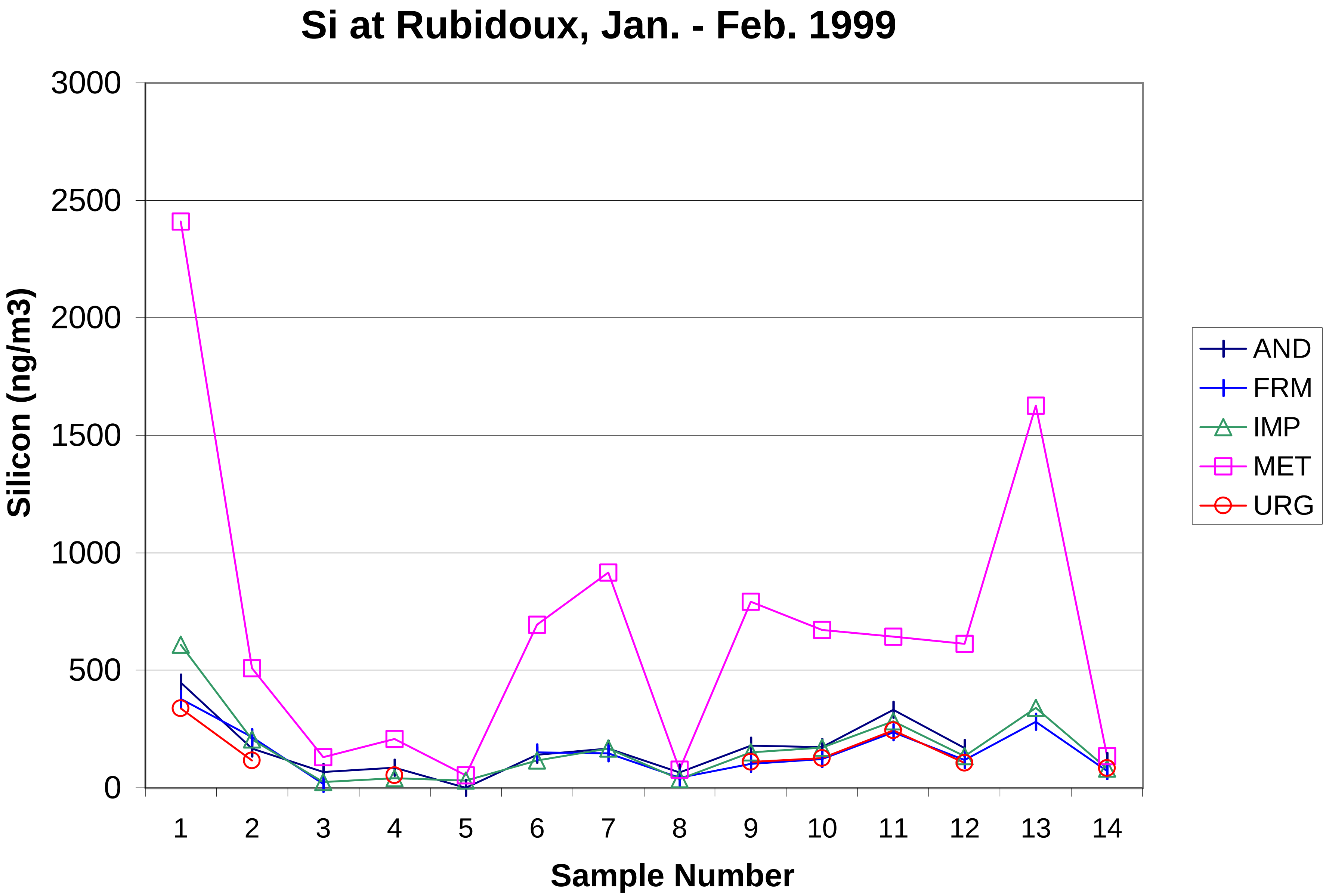
EC at Rubidoux, Jan.-Feb. 1999
EC (ug/m3)
0
1
2
3
4
5
6
7
8
9
Sampling Day
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
AND
FRM
IMP
MET
URG
VAPS

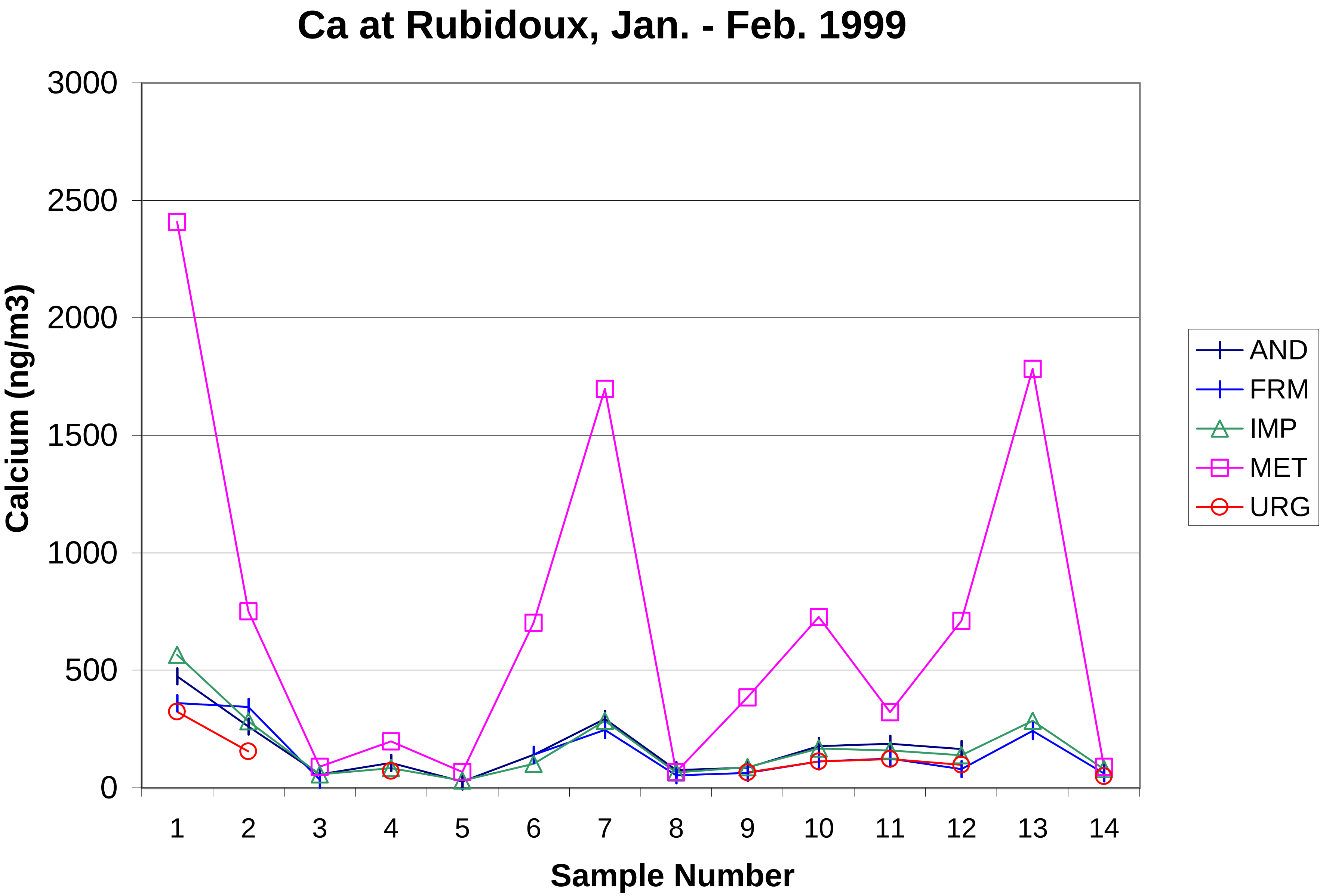

EC at Phoenix, Jan.-Feb. 1999
EC (ug/m3)
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Sampling Day
AND
FRM
IMP
MET
URG
VAPS

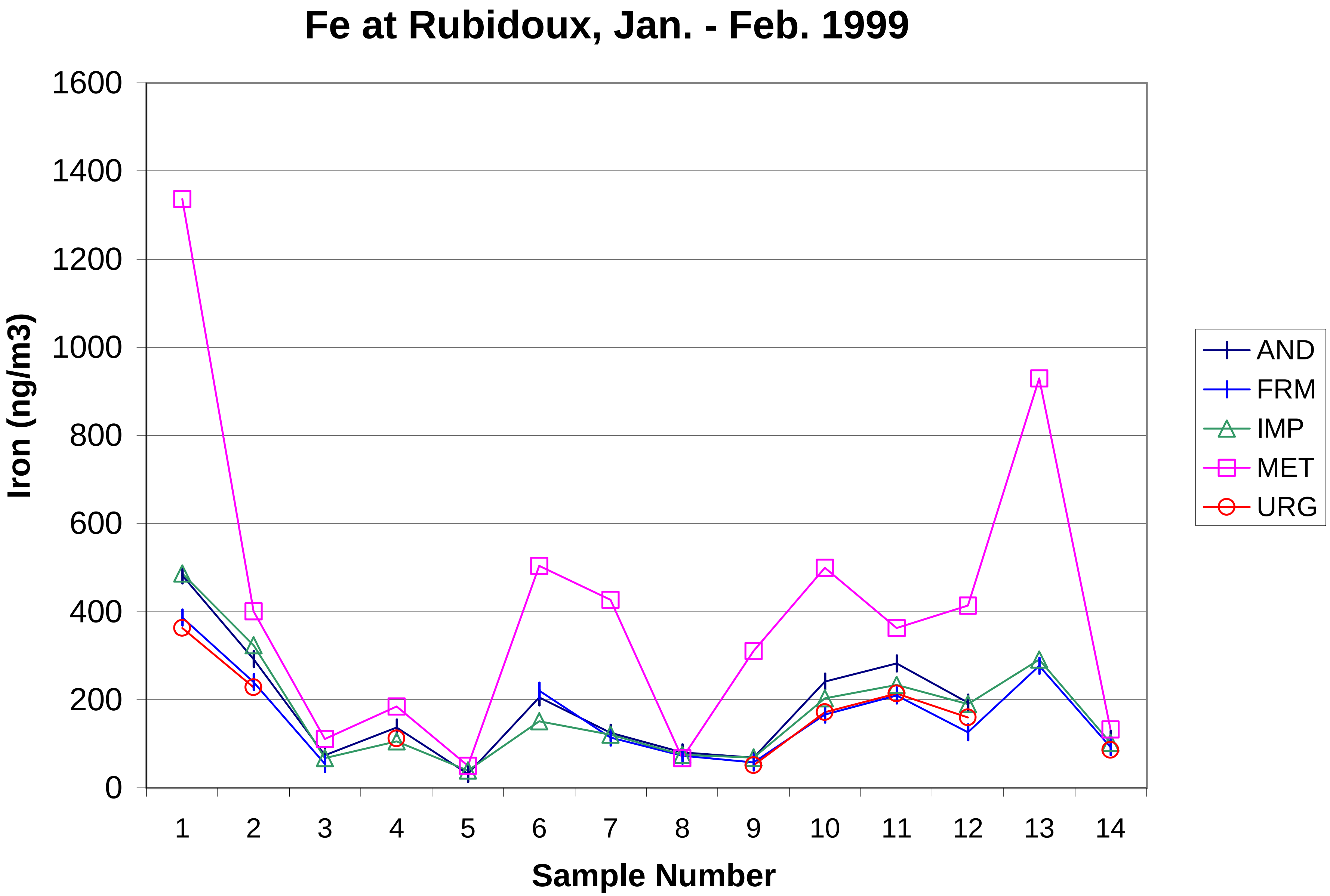

EC at Philadelphia, Jan.-Feb. 1999
EC (ug/m3)
0
1
2
3
4
5
6
7
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Sampling Day
AND
FRM
IMP
MET
URG
VAPS

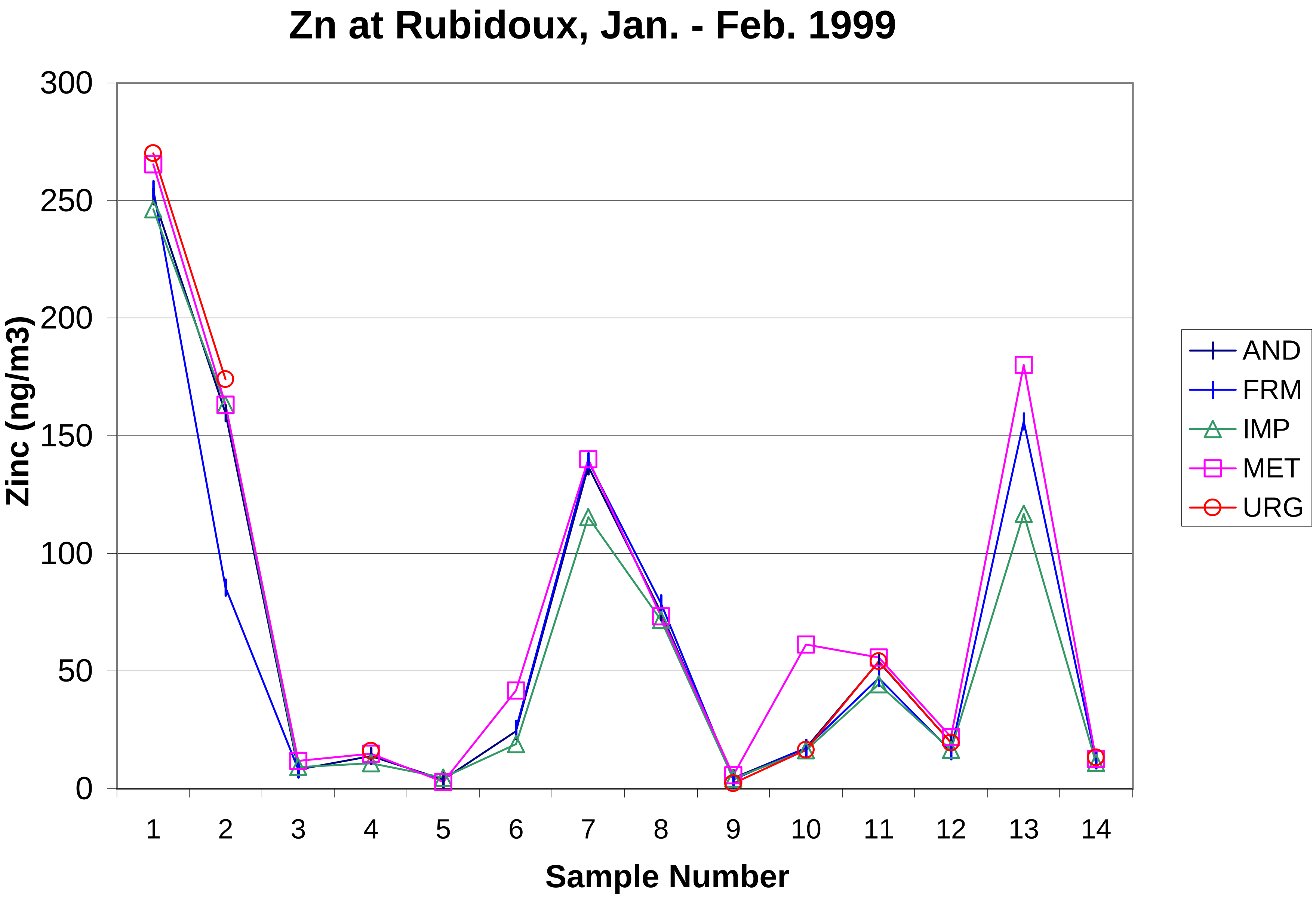

EC at RTP, Jan.-Feb. 1999
EC (ug/m3)
0
0.5
1
1.5
2
2.5
3
3.5
4
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Sampling Day
AND
FRM
IMP
MET
URG
VAPS

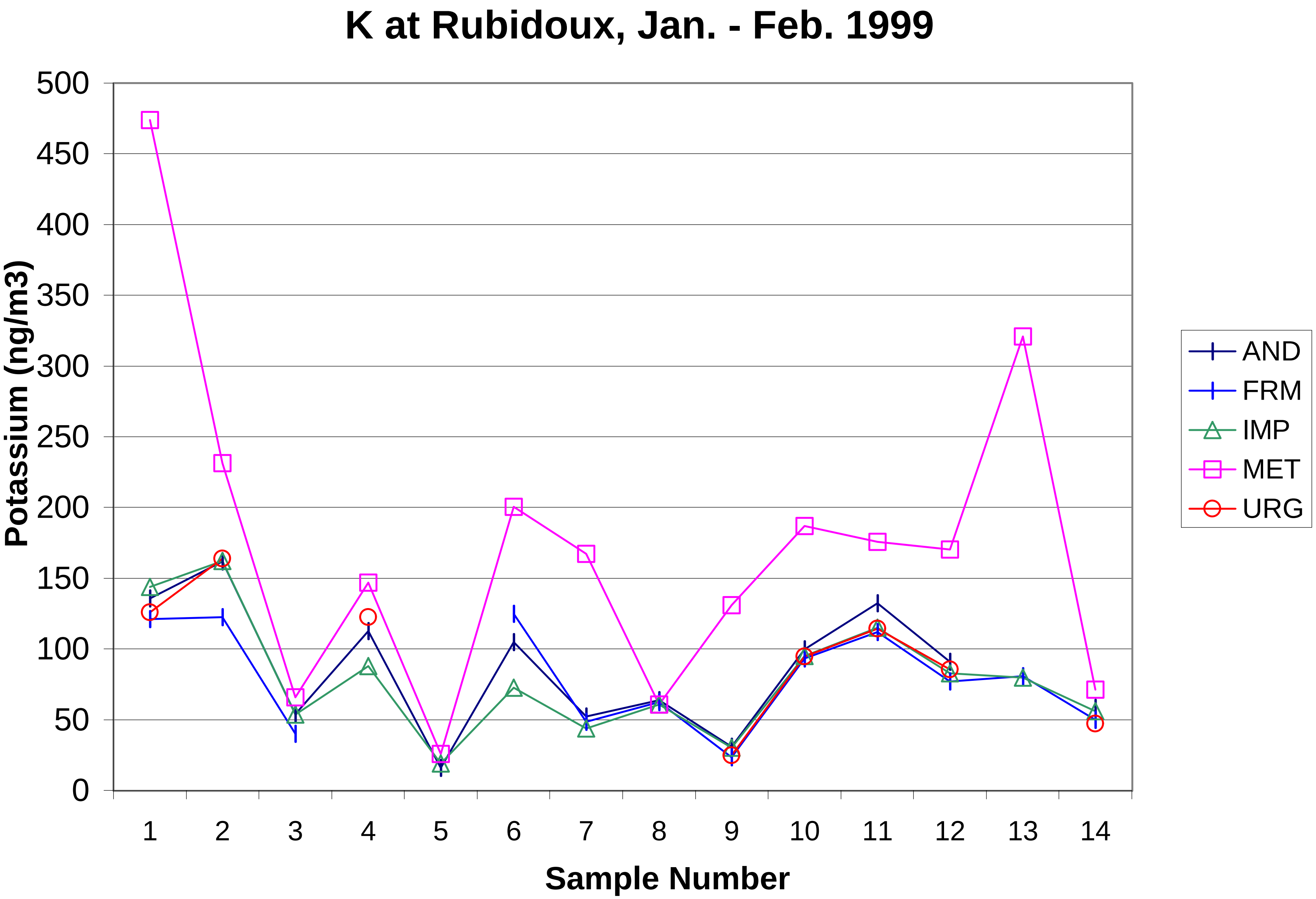

Sulfur at Rubidoux, Jan. - Feb. 1999
Sulfur (ng/m3)
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG


Si at Rubidoux, Jan. - Feb. 1999
Silicon (ng/m3)
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

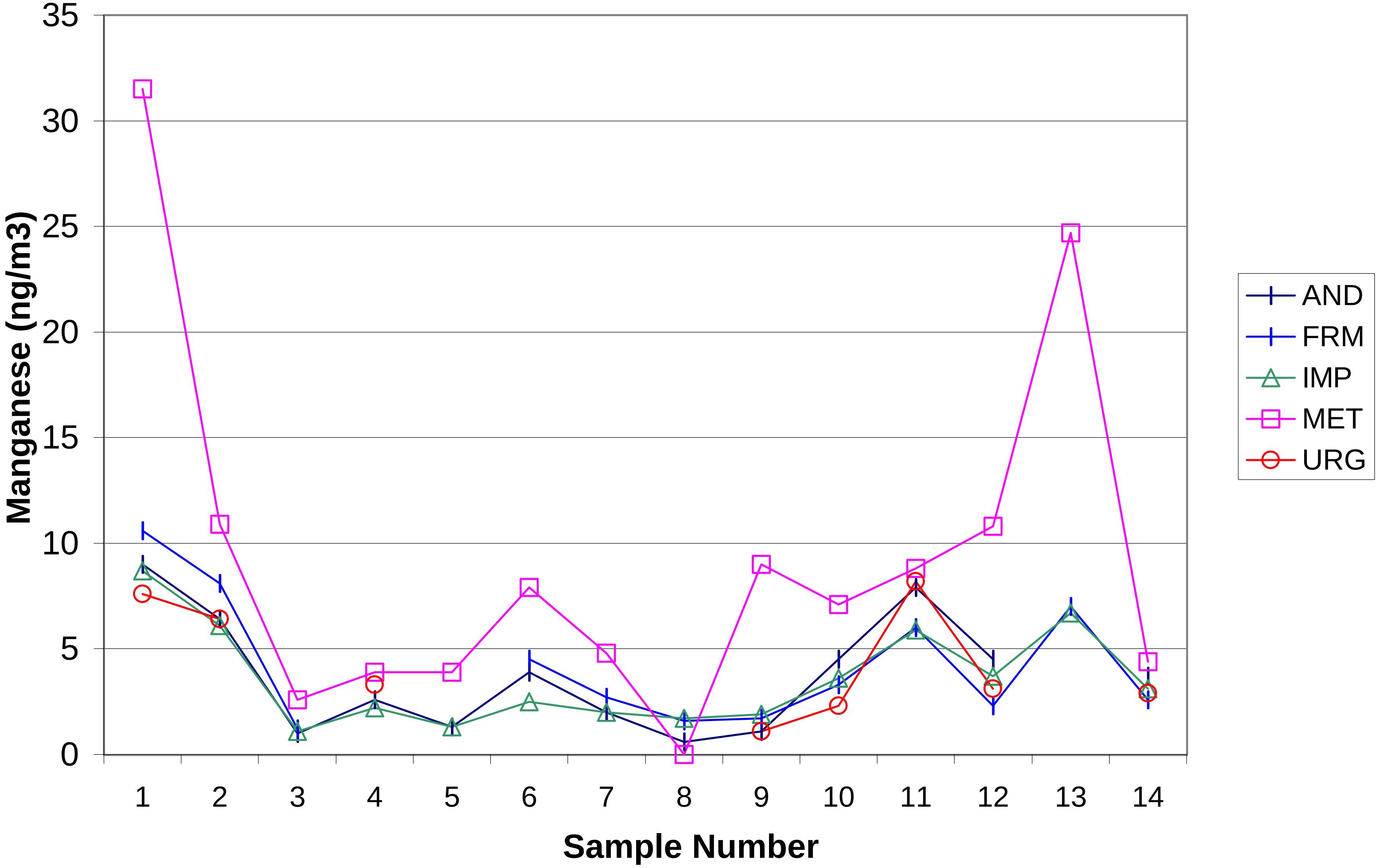

Ca at Rubidoux, Jan. - Feb. 1999
Calcium (ng/m3)
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

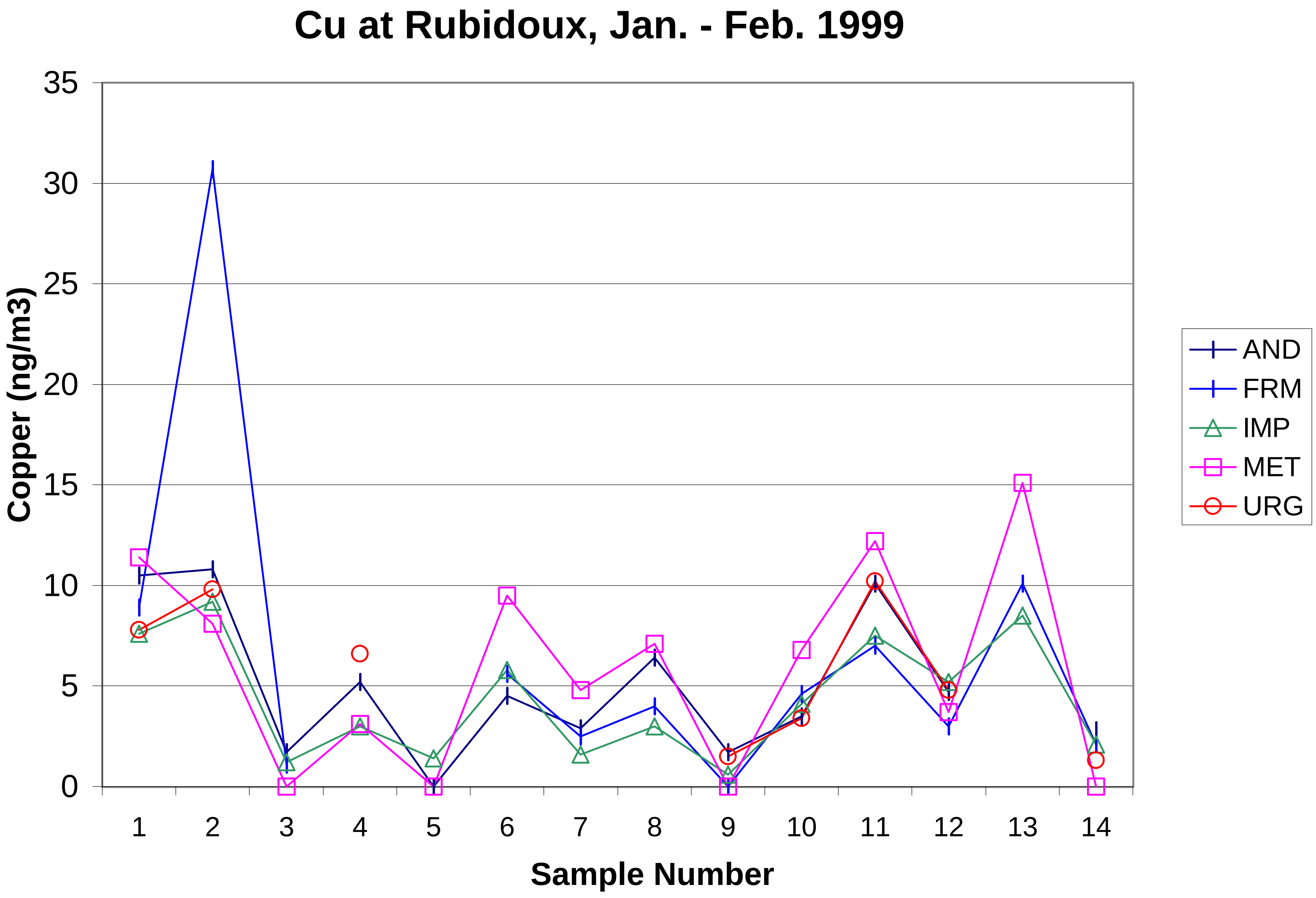

Fe at Rubidoux, Jan. - Feb. 1999
Iron (ng/m3)
1600
1400
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

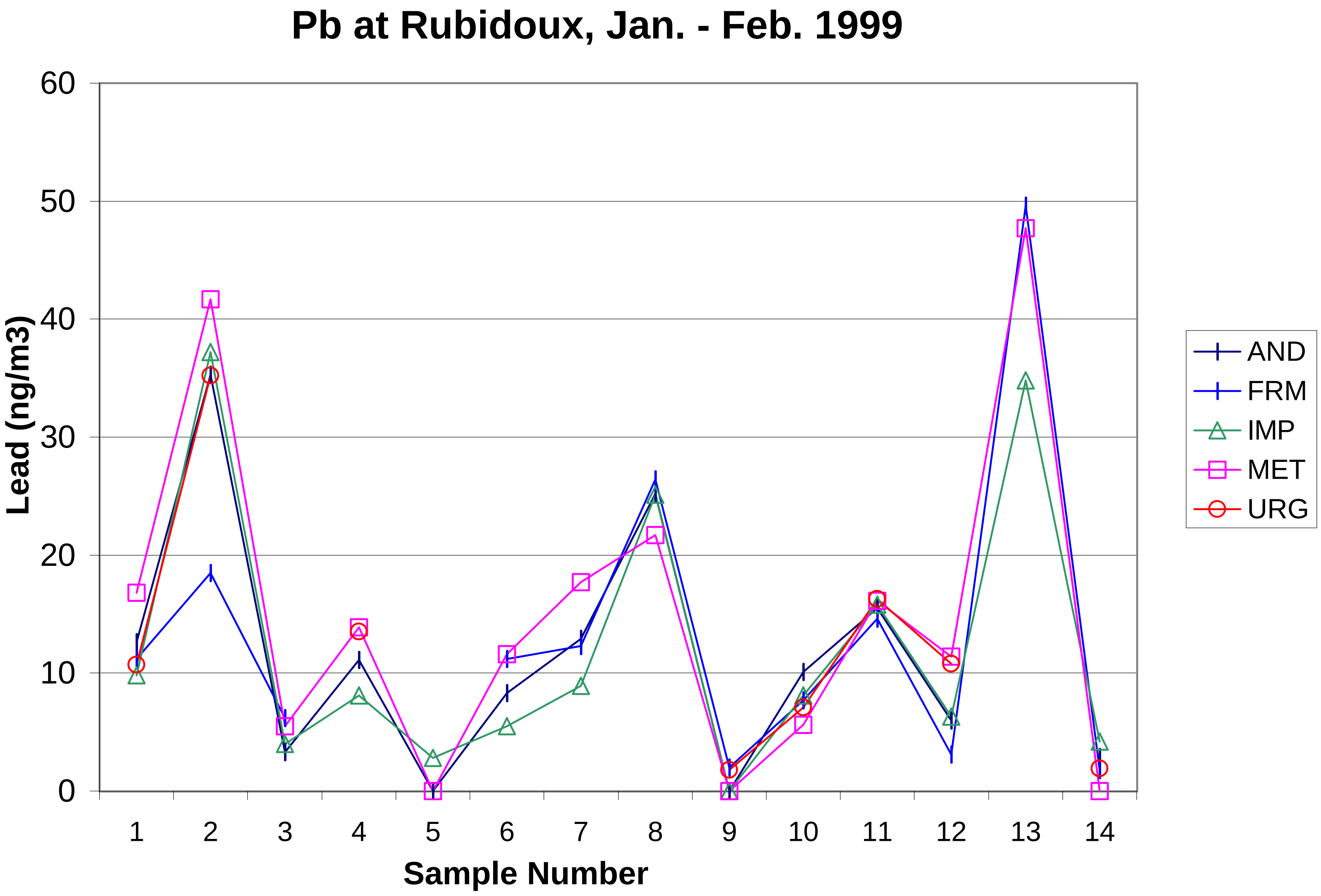

Zn at Rubidoux, Jan. - Feb. 1999
Zinc (ng/m3)
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

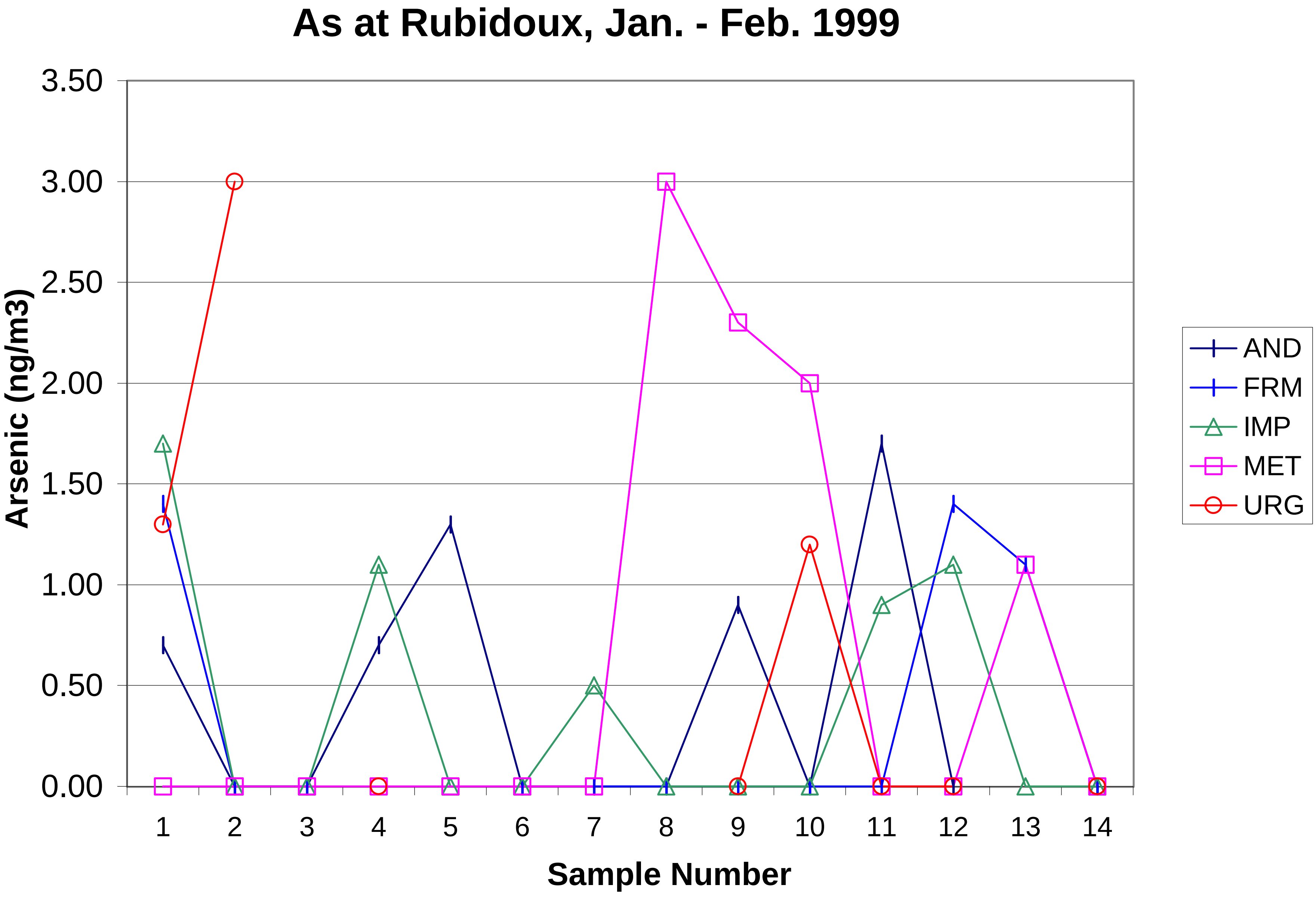

K at Rubidoux, Jan. - Feb. 1999
Potassium (ng/m3)
500
450
400
350
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

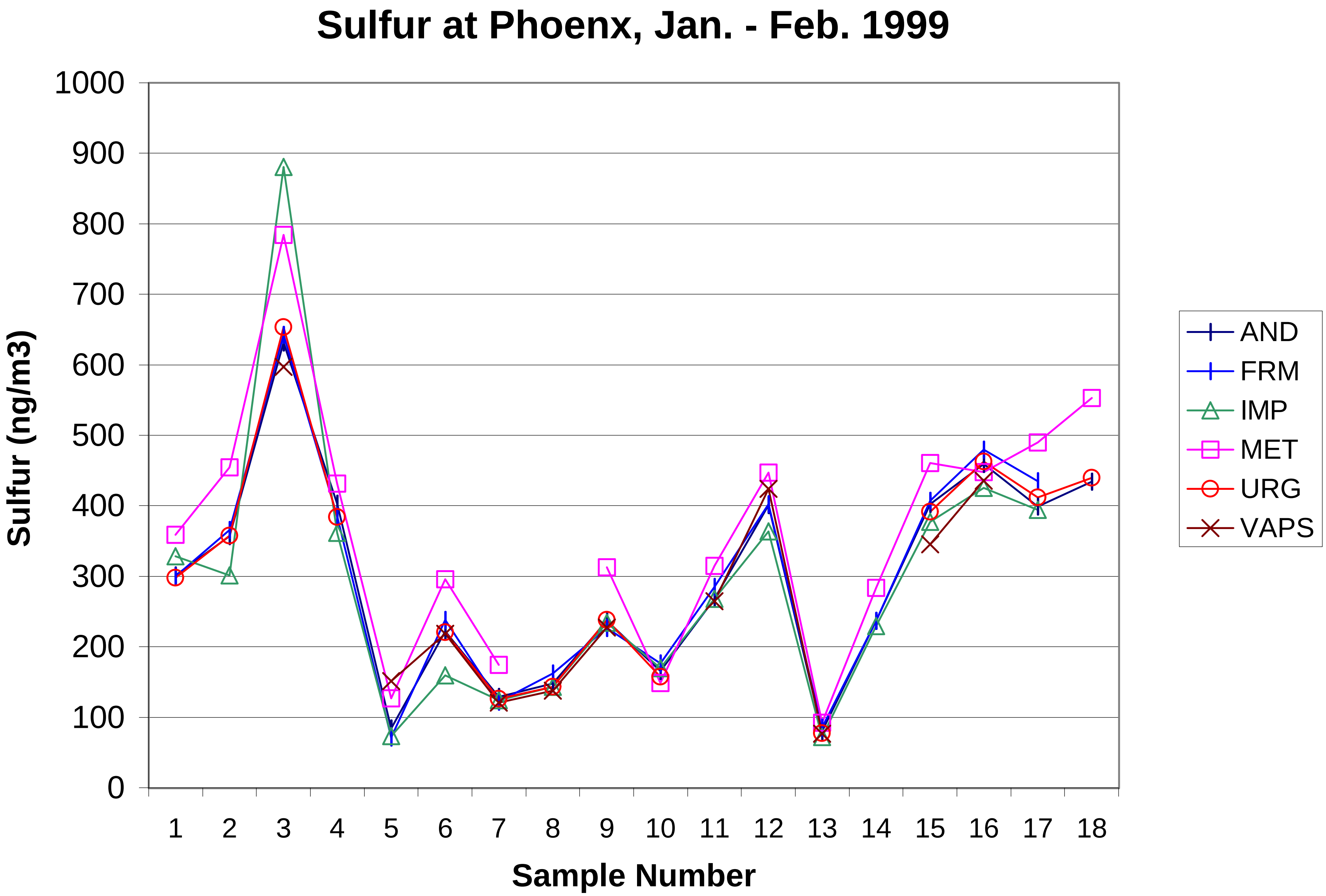
Mn at Rubidoux, Jan. - Feb. 1999

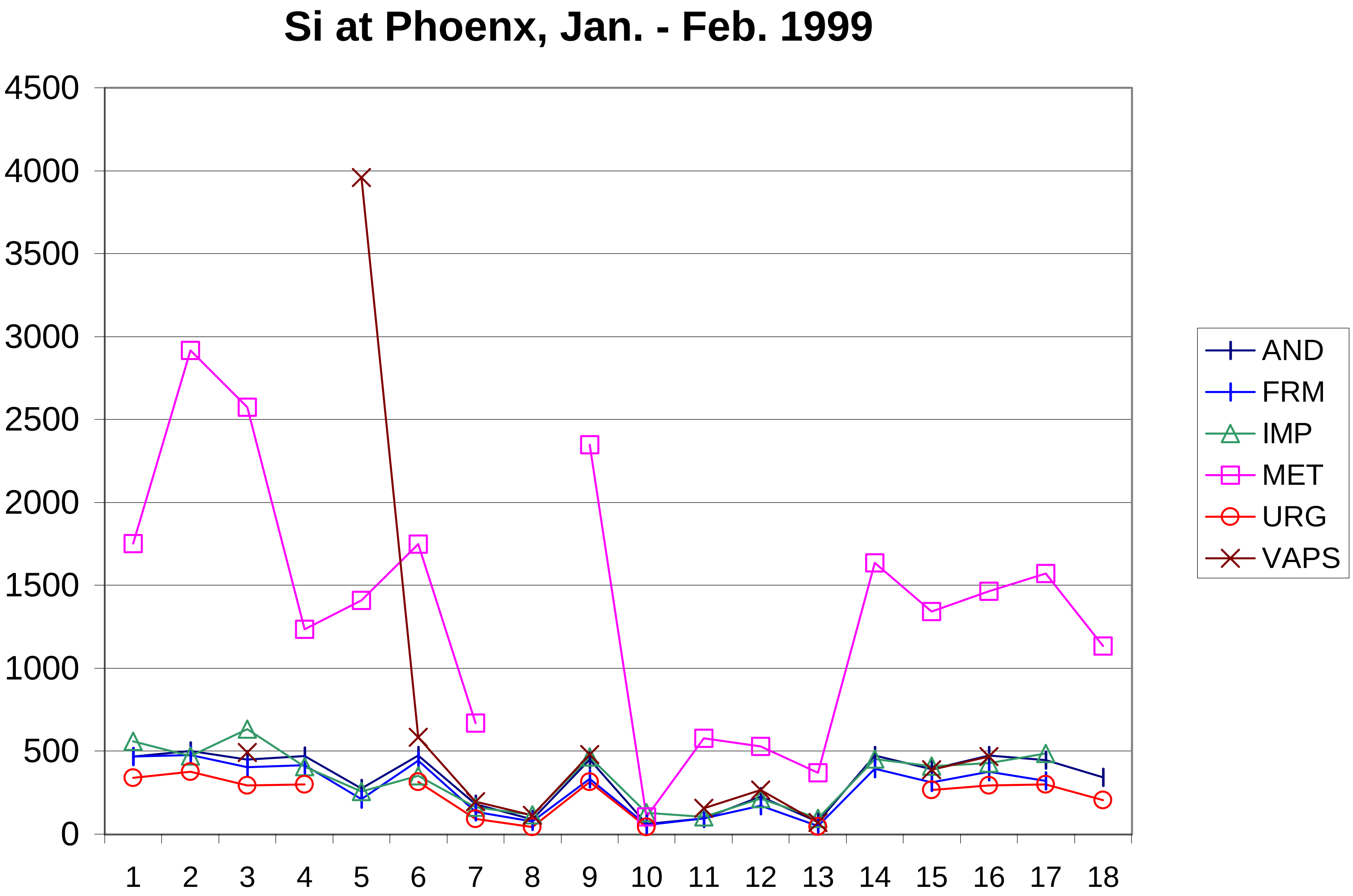


Cu at Rubidoux, Jan. - Feb. 1999
Copper (ng/m3)
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

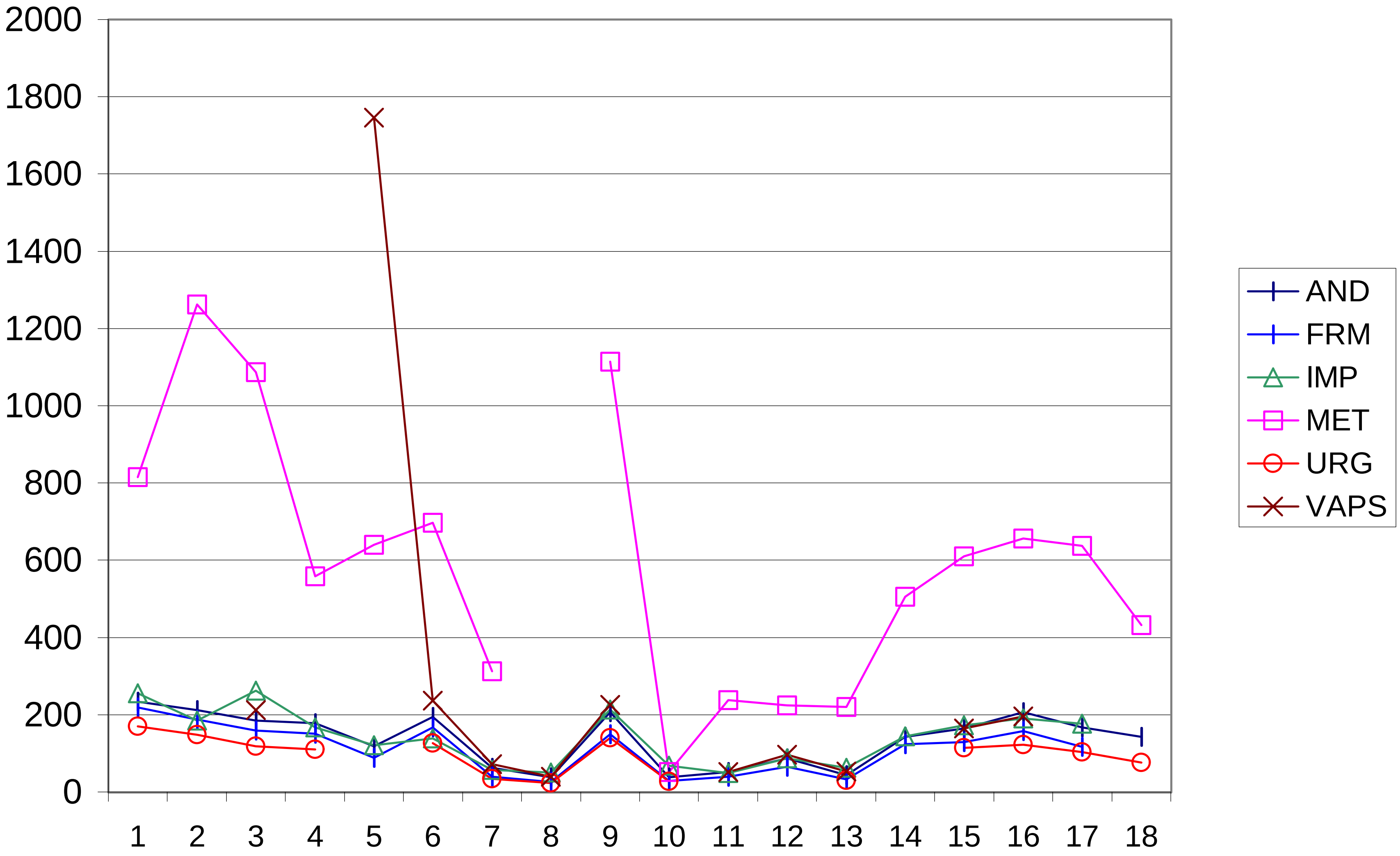

Pb at Rubidoux, Jan. - Feb. 1999
Lead (ng/m3)
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

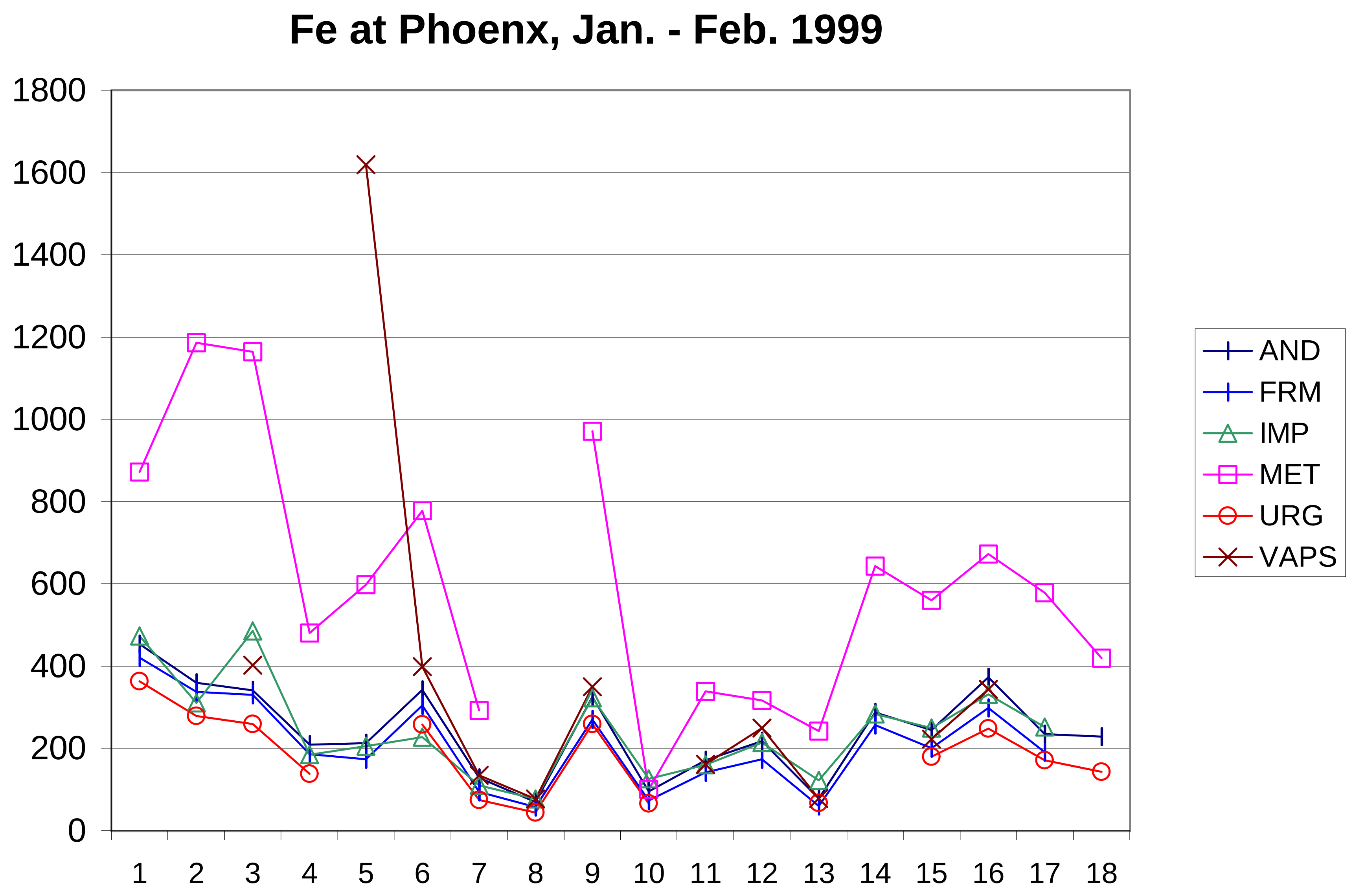

As at Rubidoux, Jan. - Feb. 1999
Arsenic (ng/m3)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Sample Number
AND
FRM
IMP
MET
URG

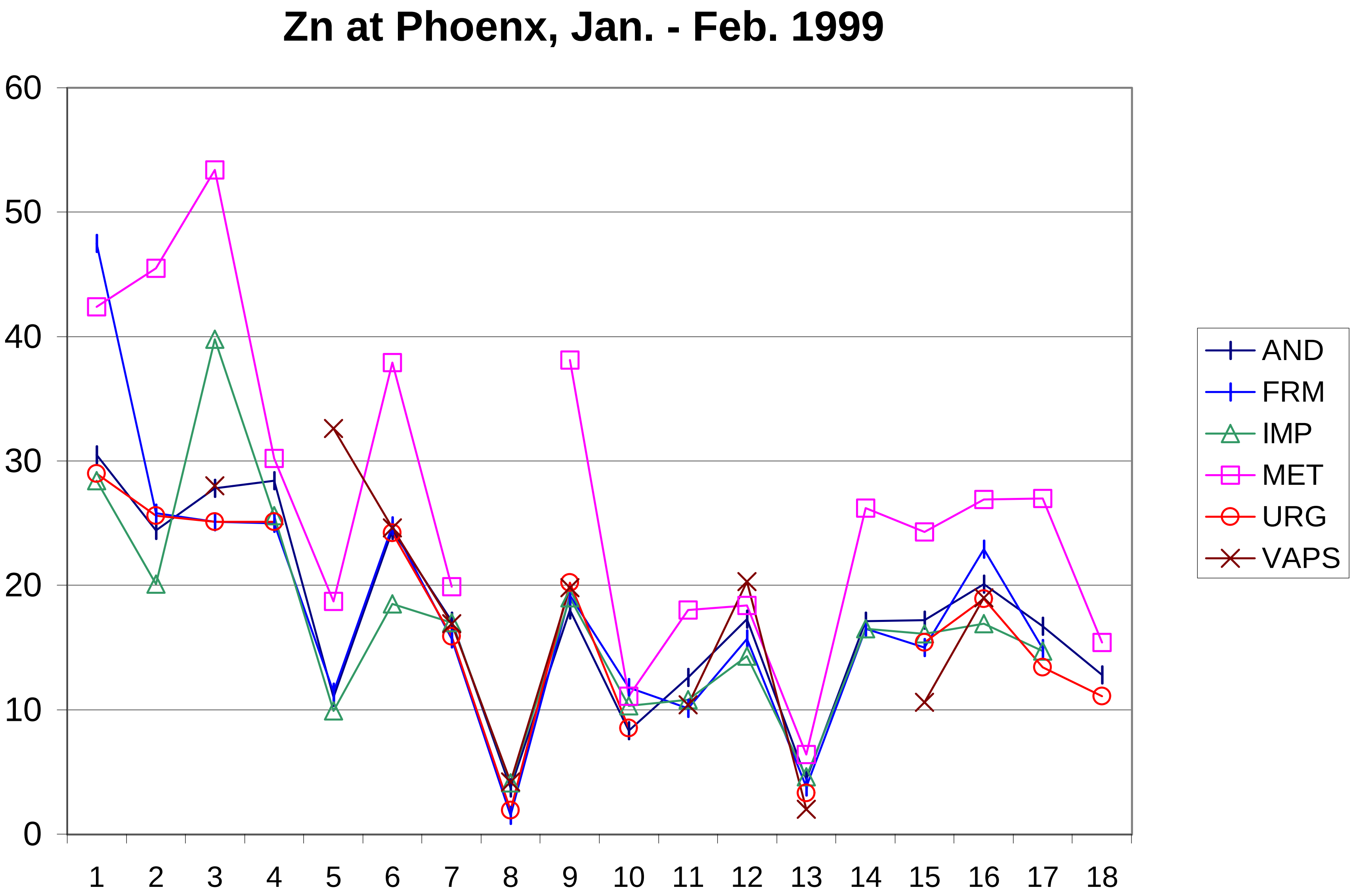

Sulfur at Phoenix, Jan. - Feb. 1999
Sulfur (ng/m3)
1000
900
800
700
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

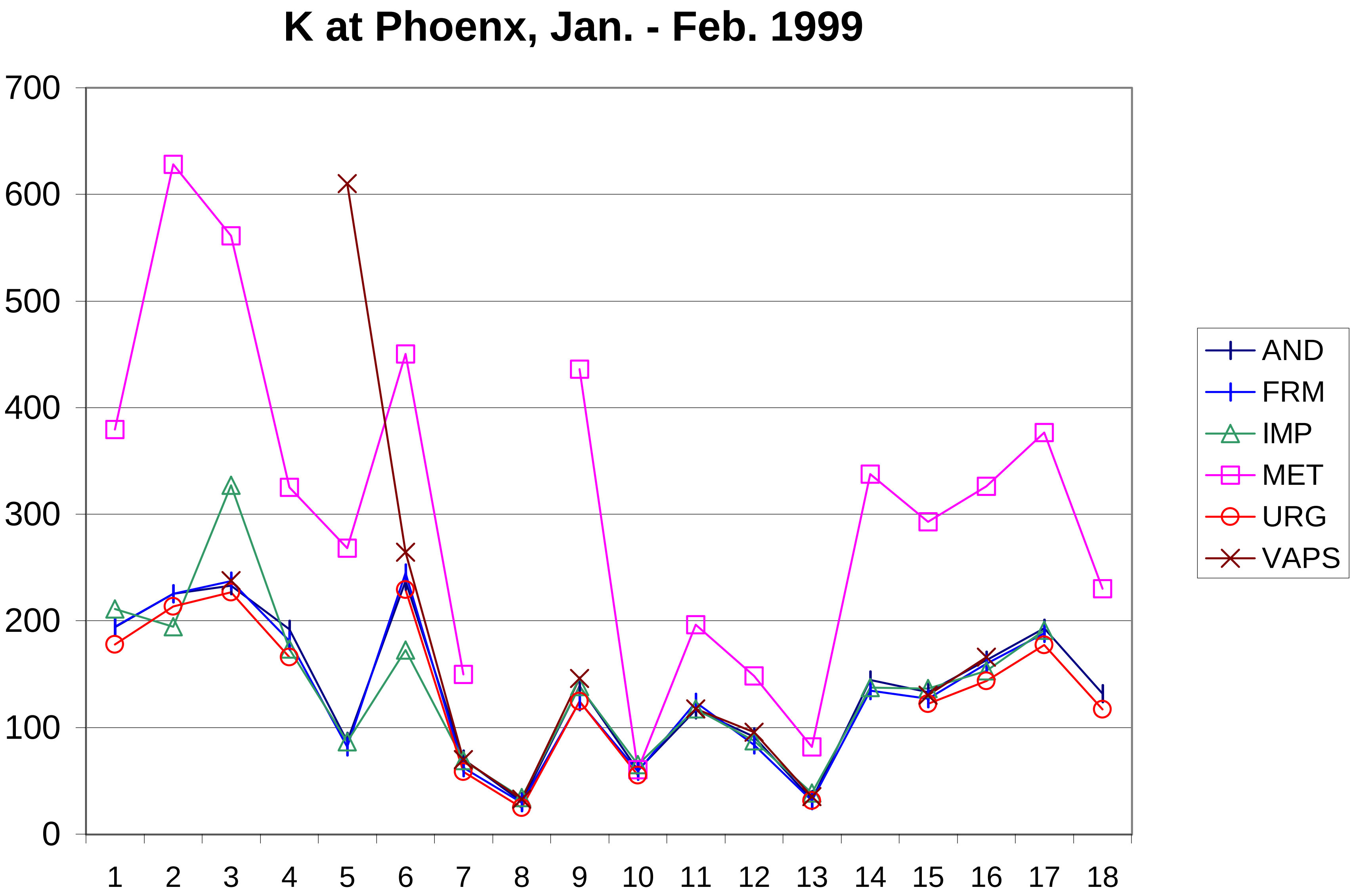

Si at Phoenx, Jan. - Feb. 1999
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

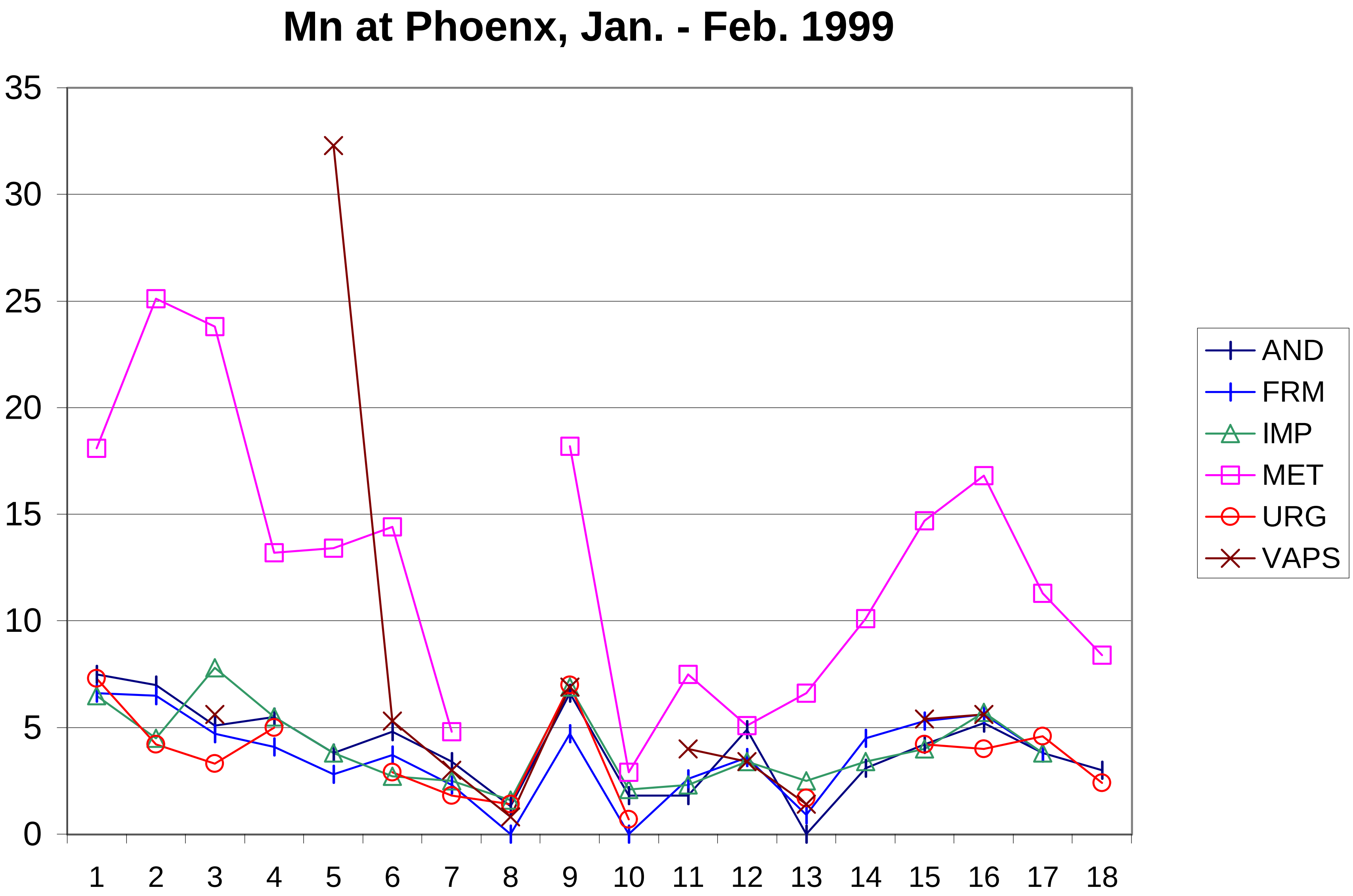
Ca at Phoenx, Jan. - Feb. 1999



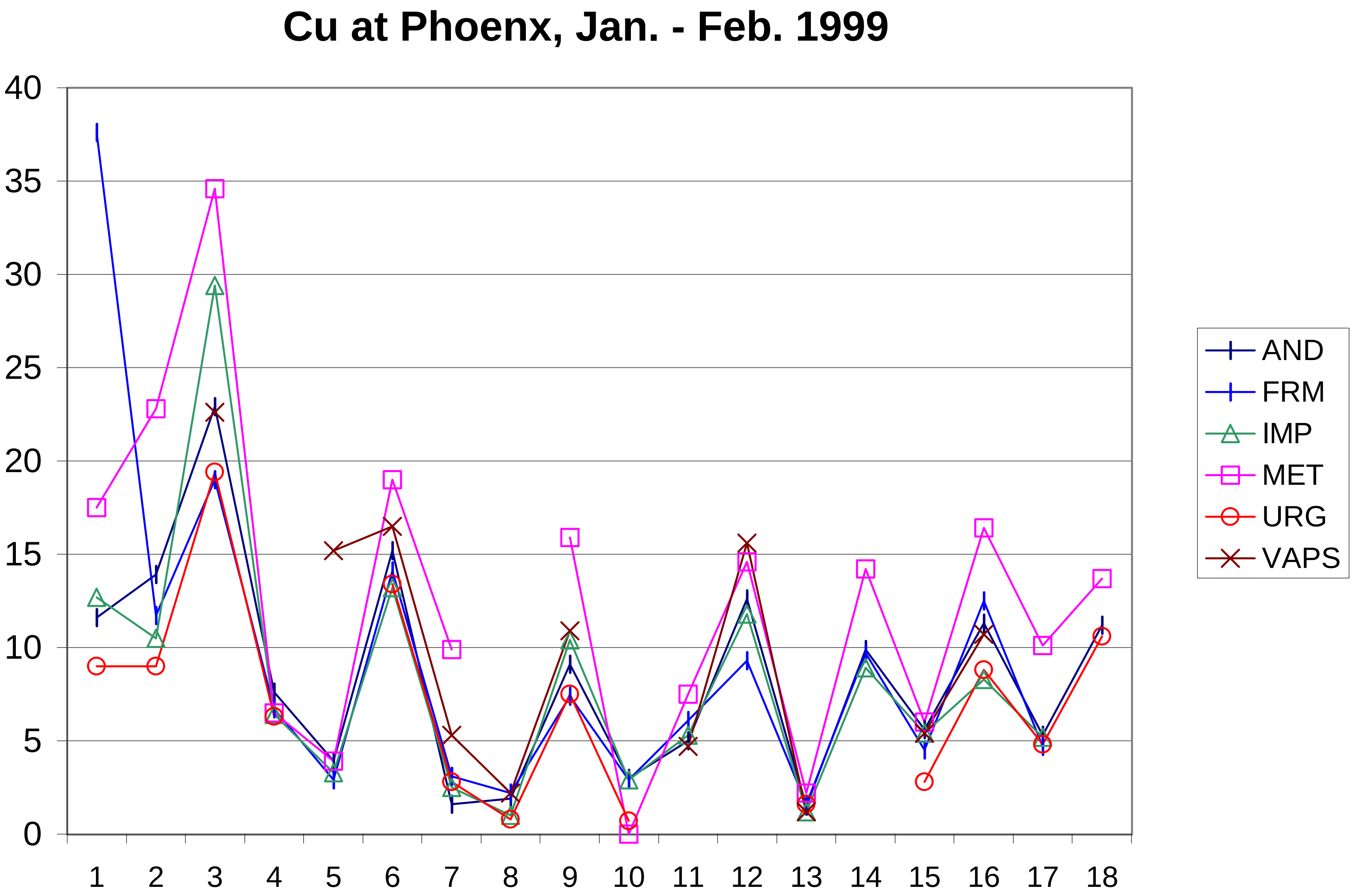

Fe at Phoenx, Jan. - Feb. 1999
1800
1600
1400
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

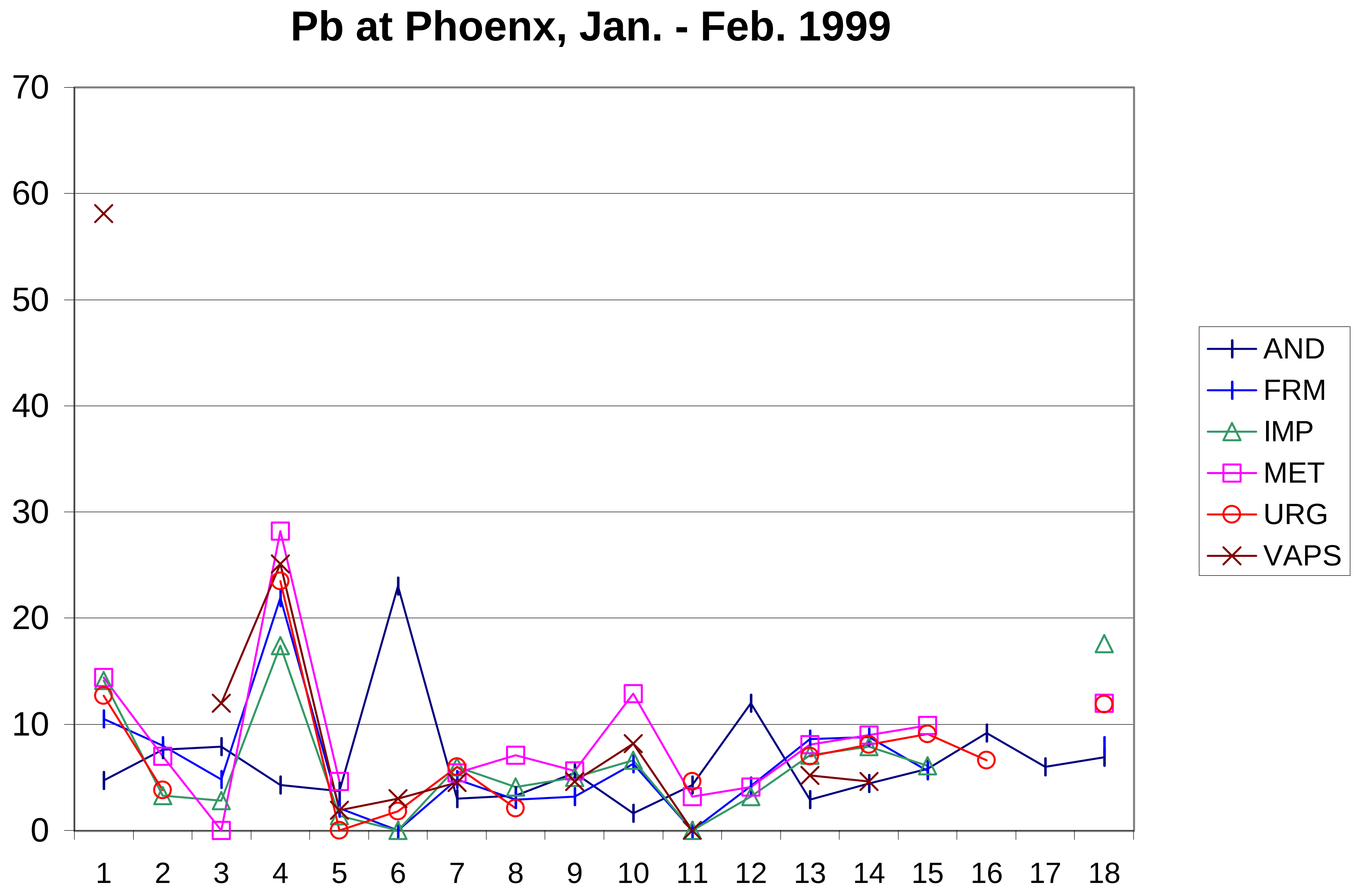

Zn at Phoenx, Jan. - Feb. 1999
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

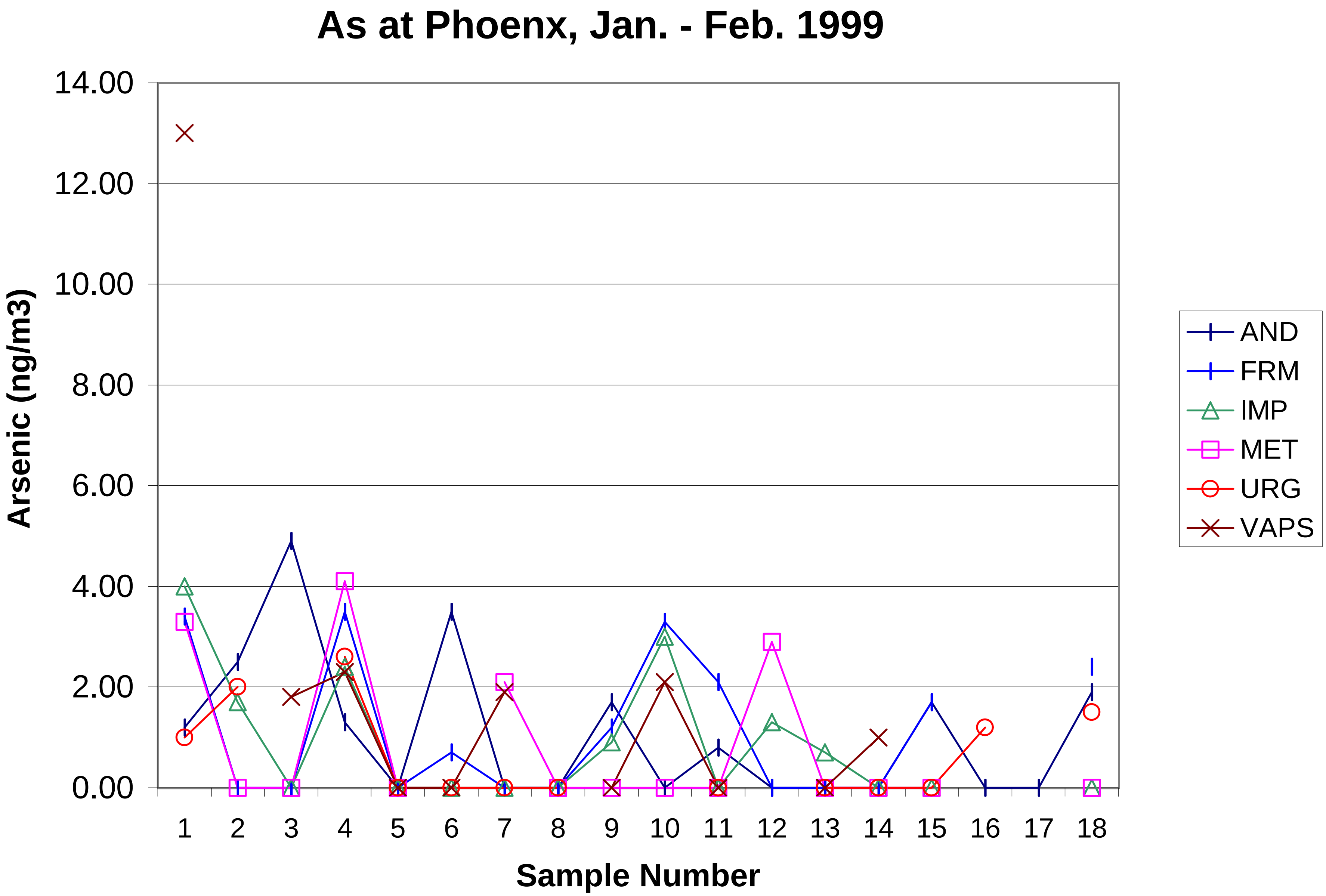

K at Phoenx, Jan. - Feb. 1999
700
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

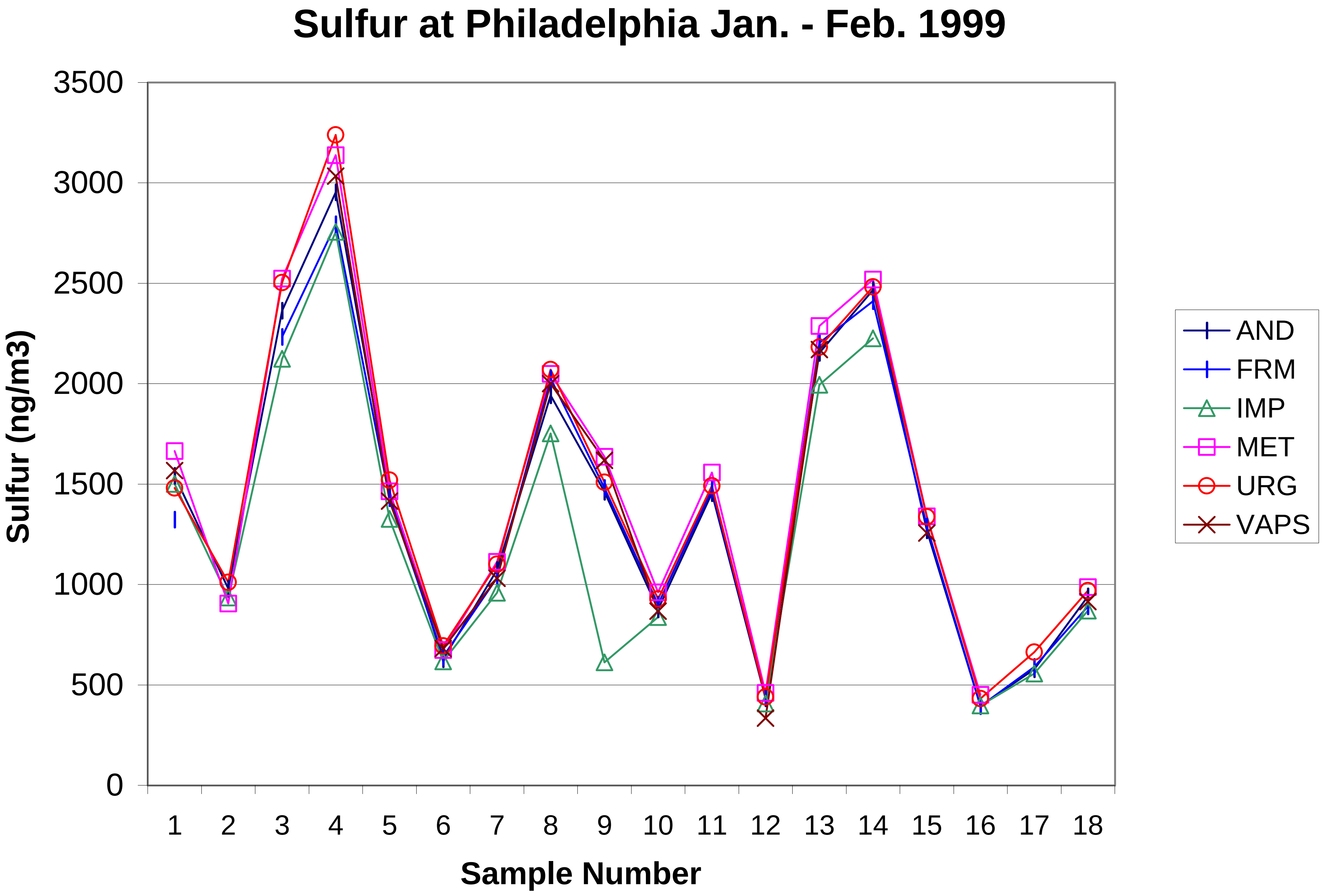


Mn at Phoenx, Jan. - Feb. 1999
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

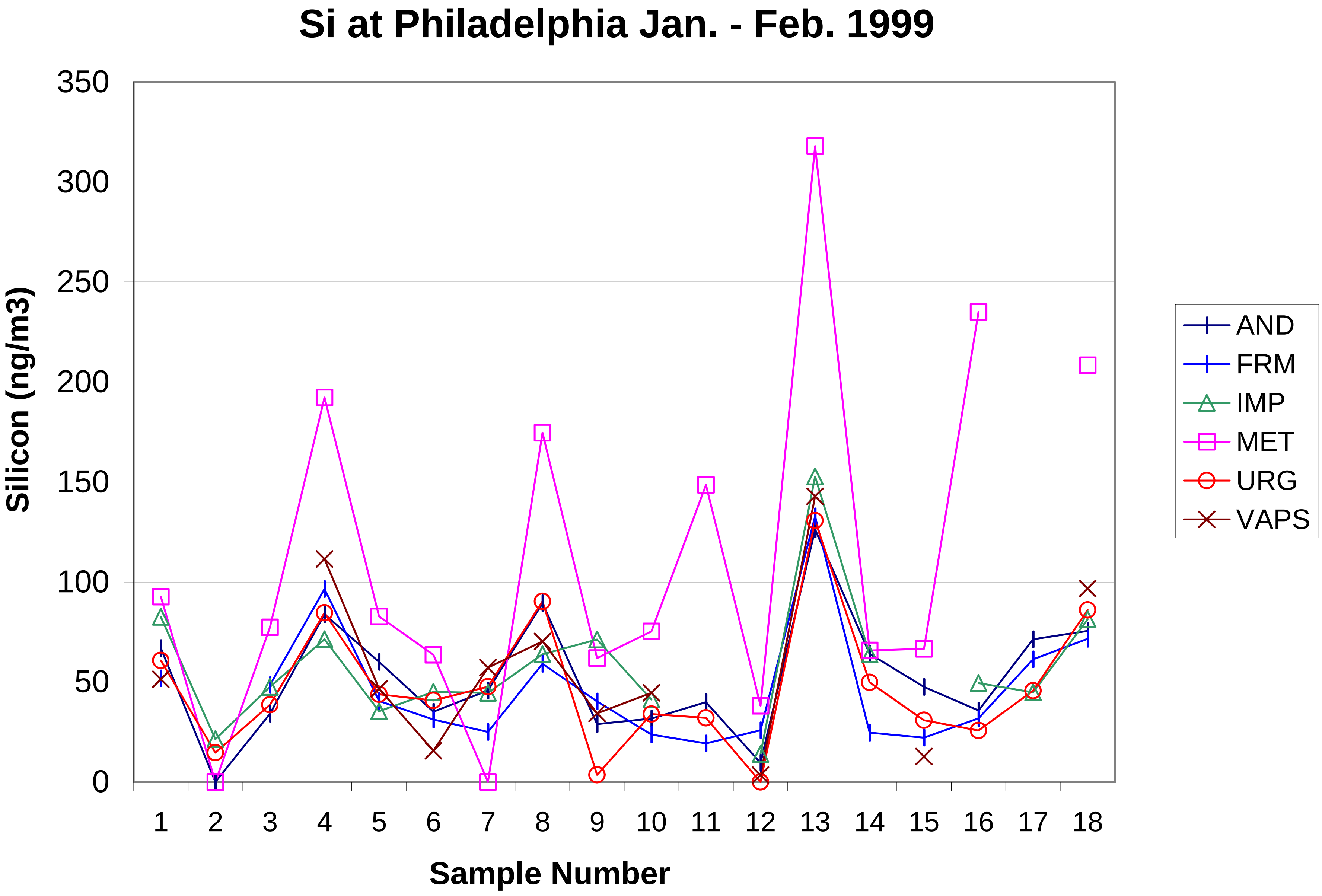

Cu at Phoenx, Jan. - Feb. 1999
0
5
10
15
20
25
30
35
40
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

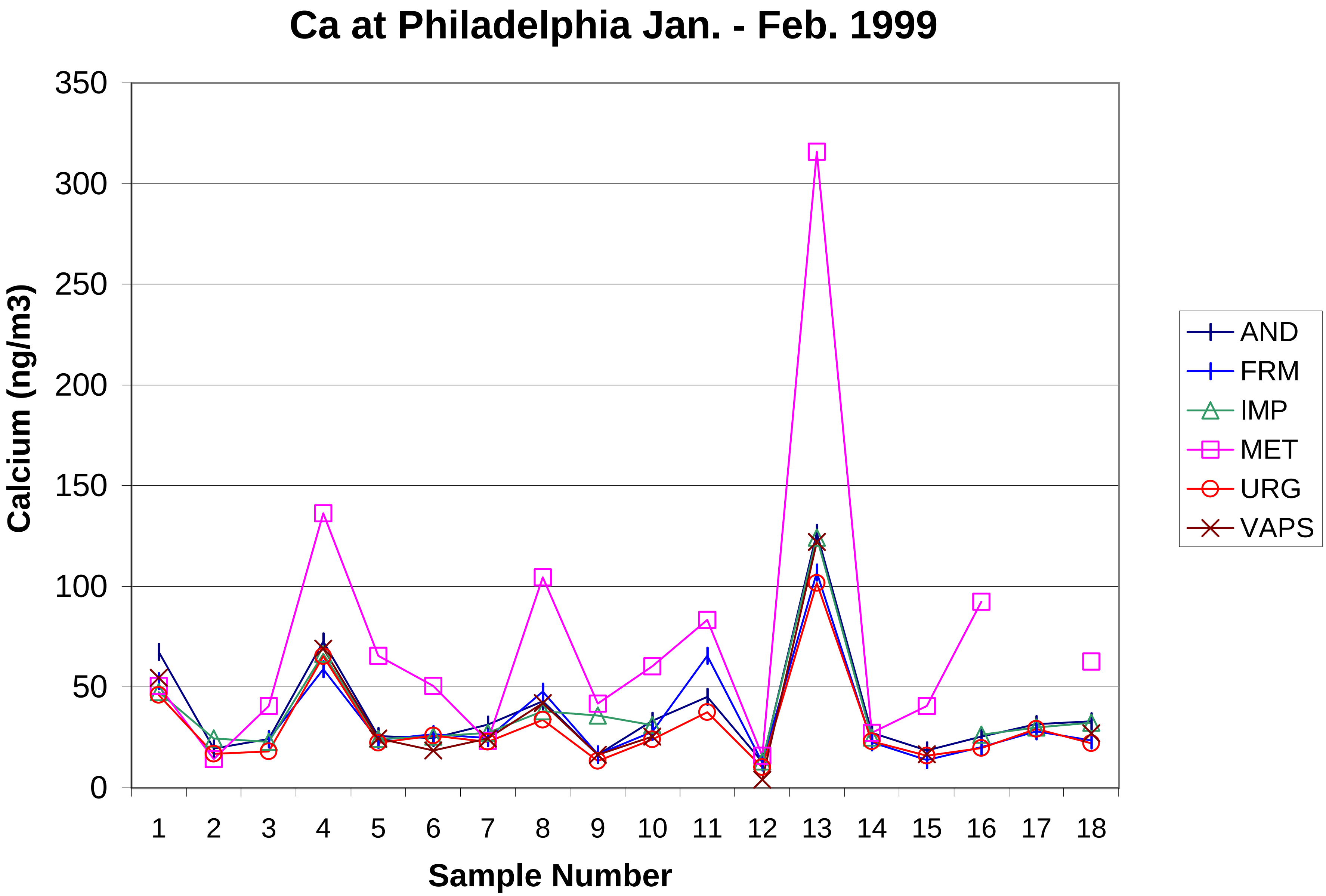
Pb at Phoenx, Jan. - Feb. 1999
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS


As at Phoenx, Jan. - Feb. 1999
Arsenic (ng/m3)
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

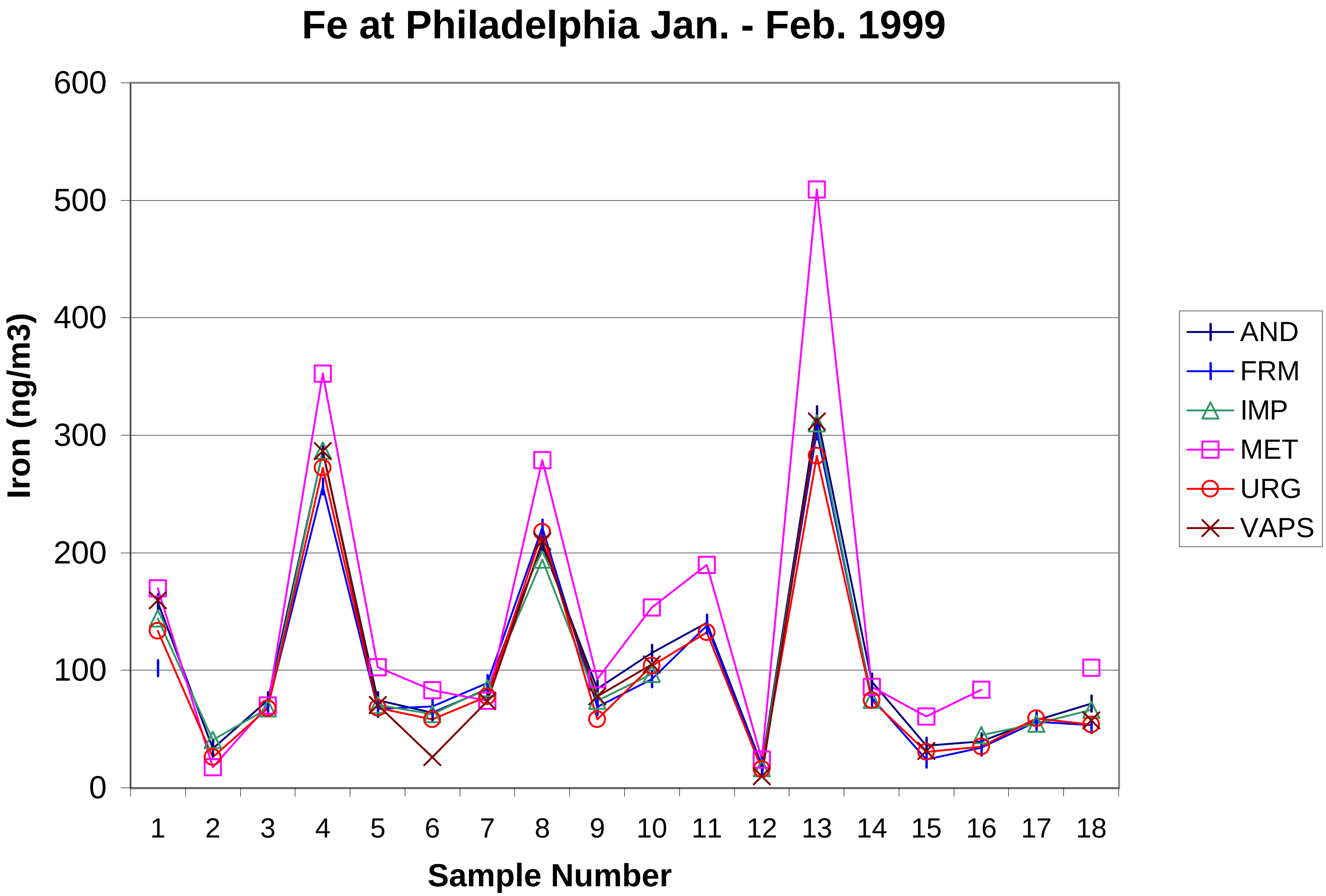


Sulfur at Philadelphia Jan. - Feb. 1999
Sulfur (ng/m3)
3500
3000
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

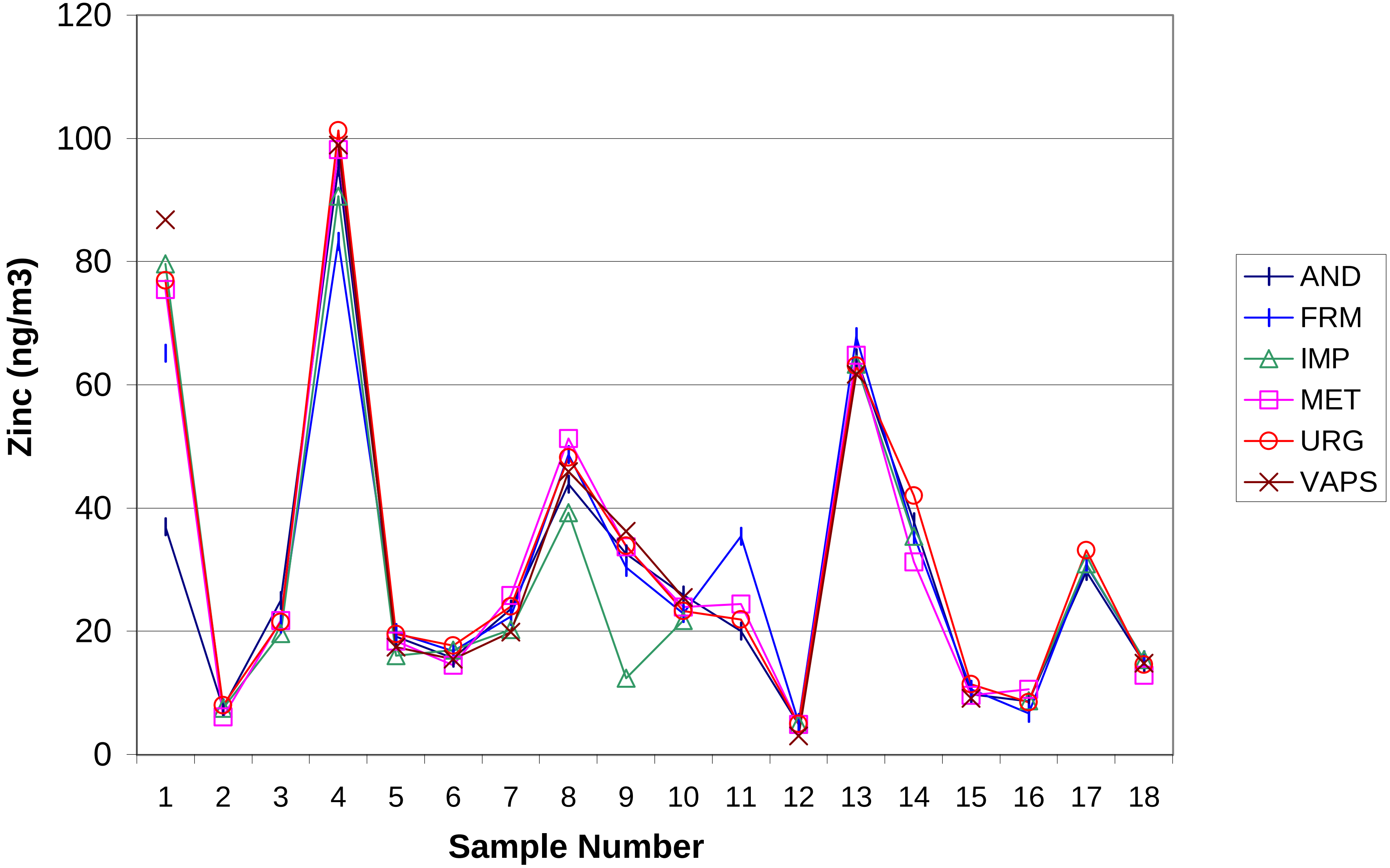

Si at Philadelphia Jan. - Feb. 1999
Silicon (ng/m3)
350
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

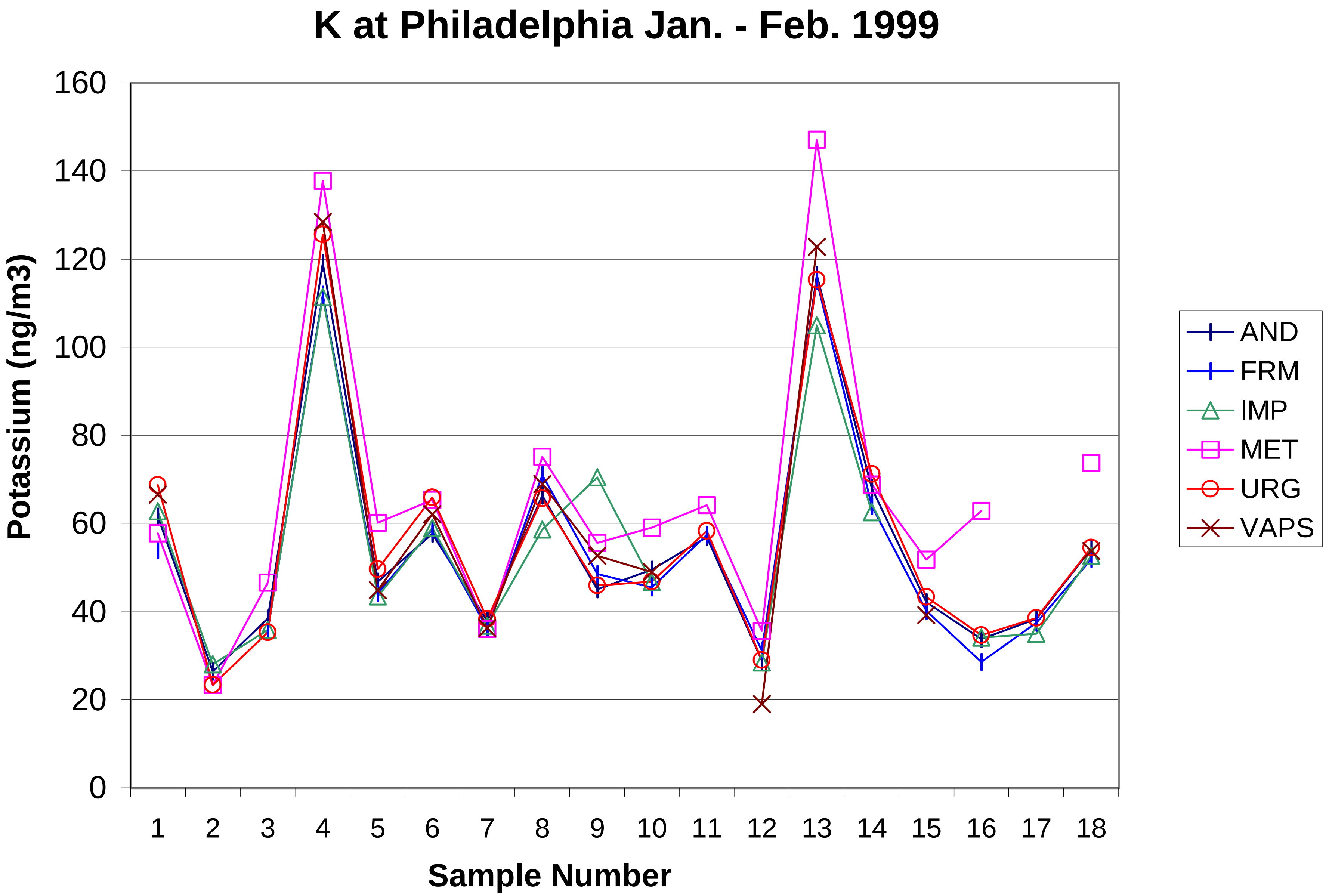


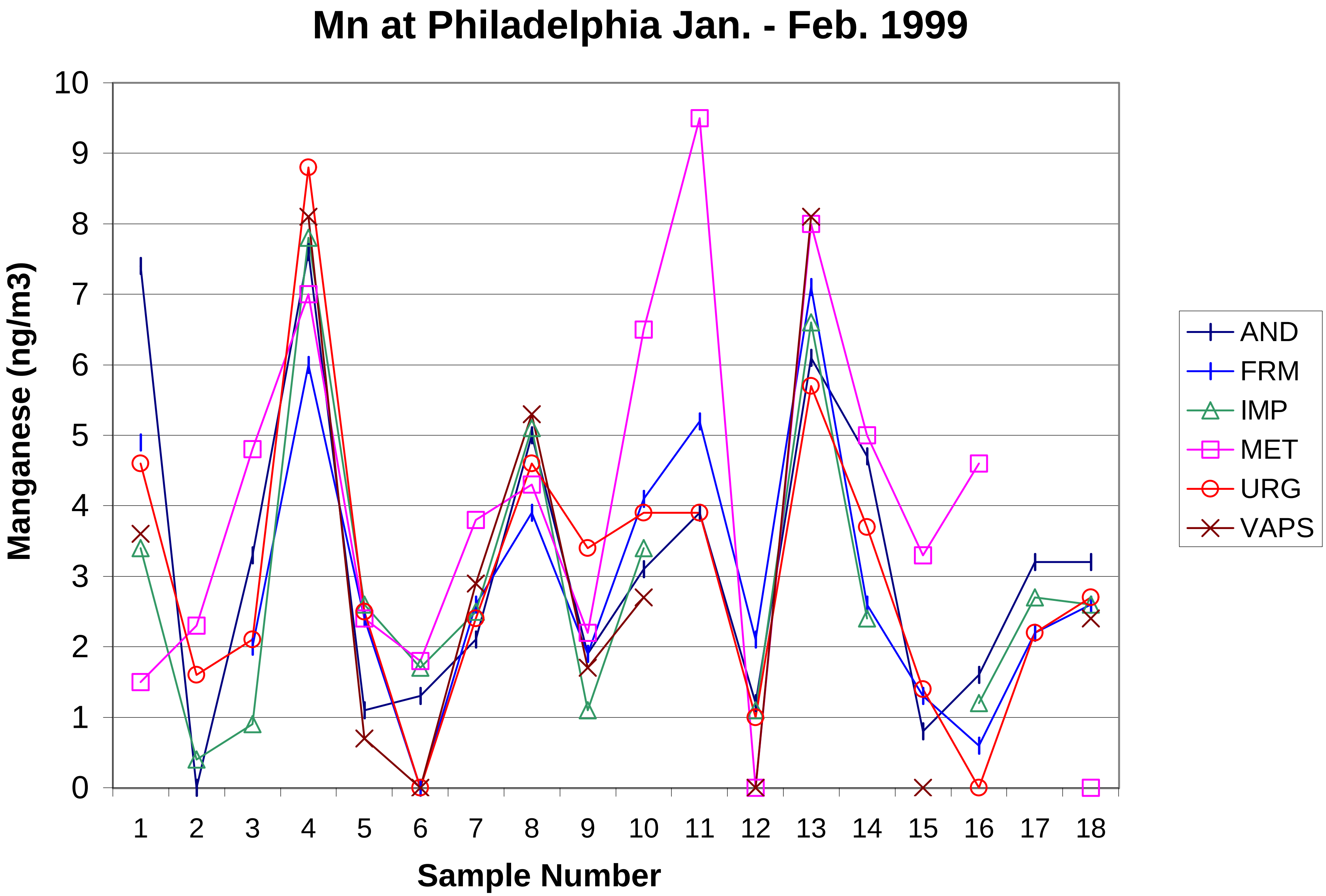
Ca at Philadelphia Jan. - Feb. 1999
Calcium (ng/m3)
0
50
100
150
200
250
300
350
Sample Number
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

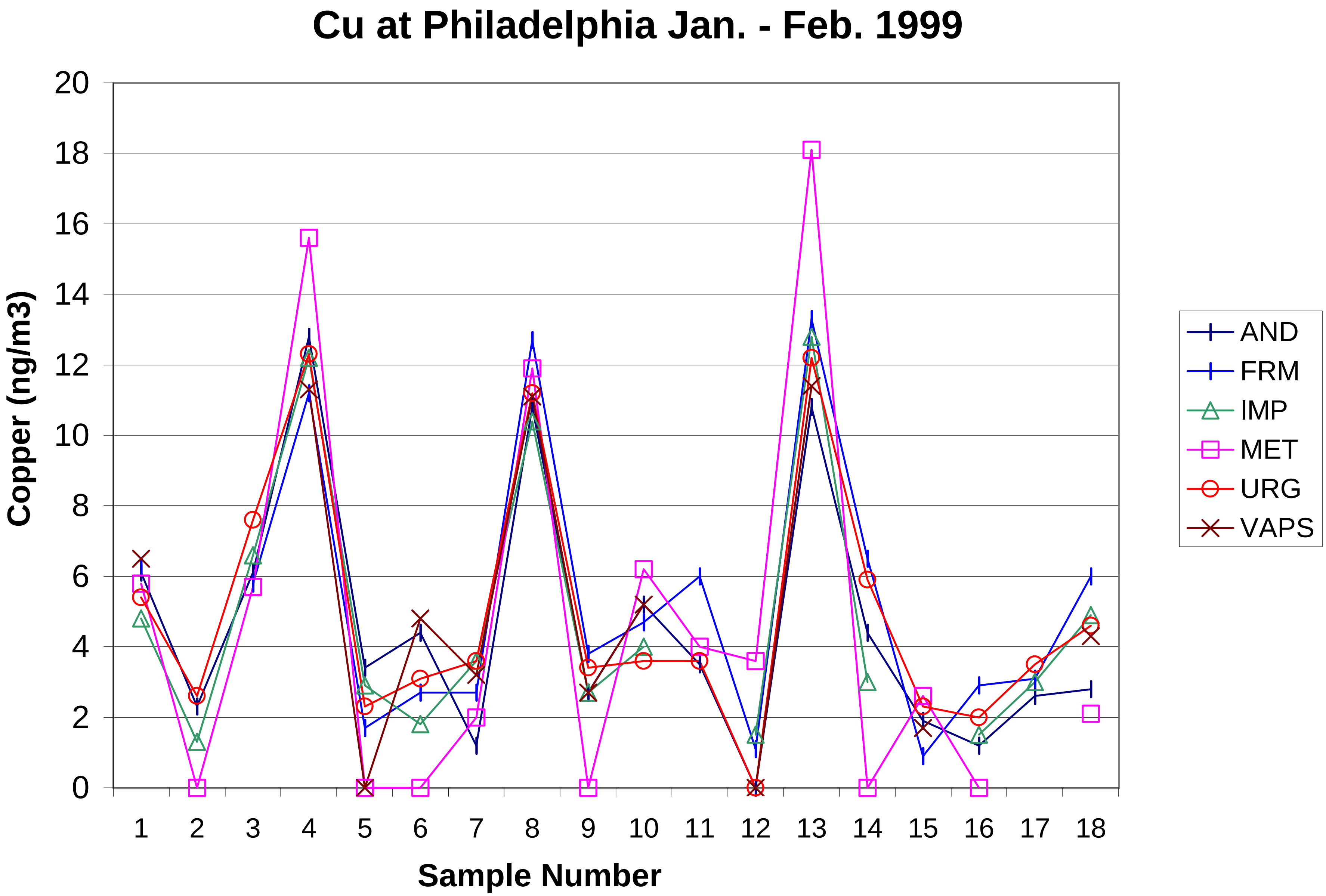

Fe at Philadelphia Jan. - Feb. 1999
Iron (ng/m3)
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

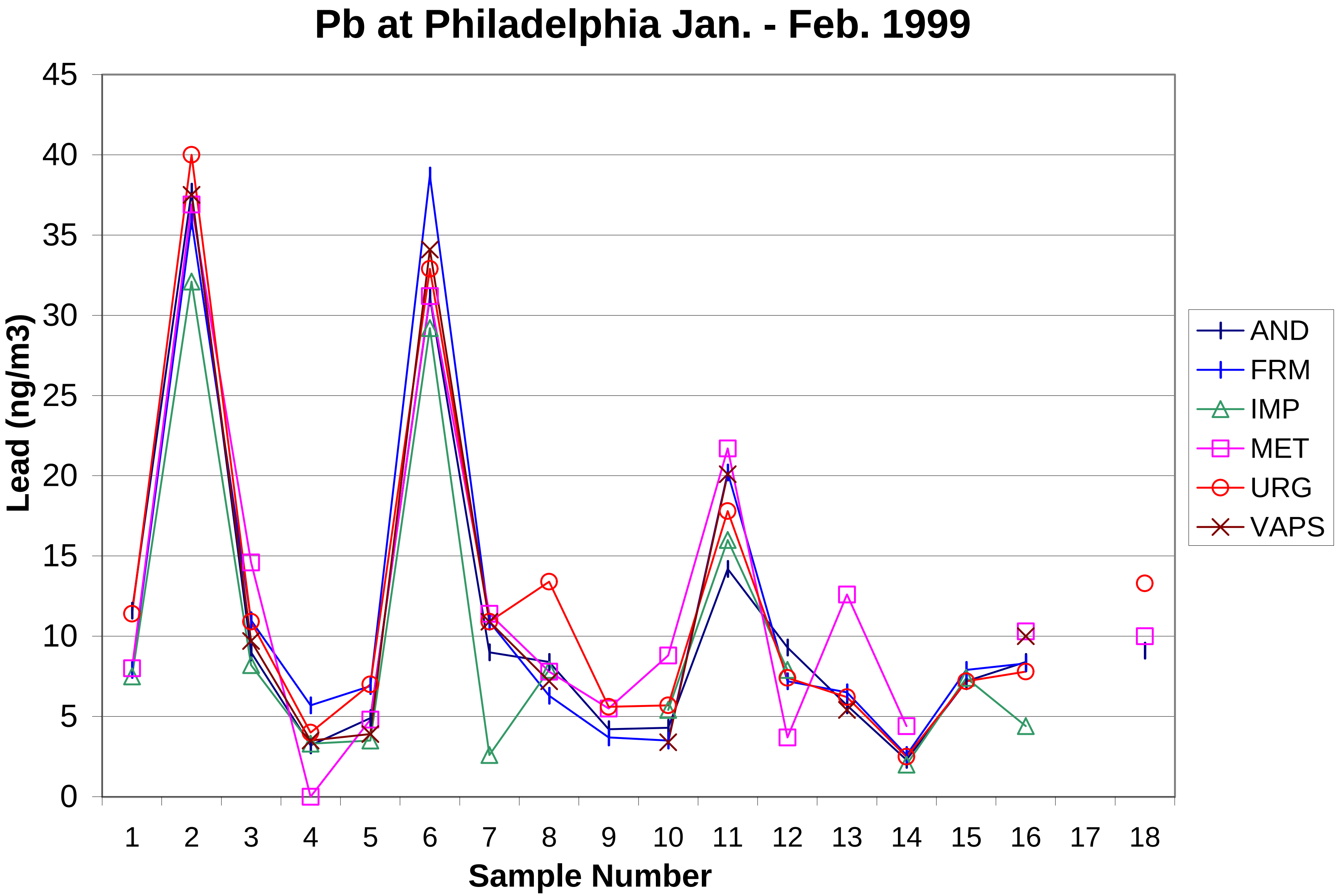
Zn at Philadelphia Jan. - Feb. 1999

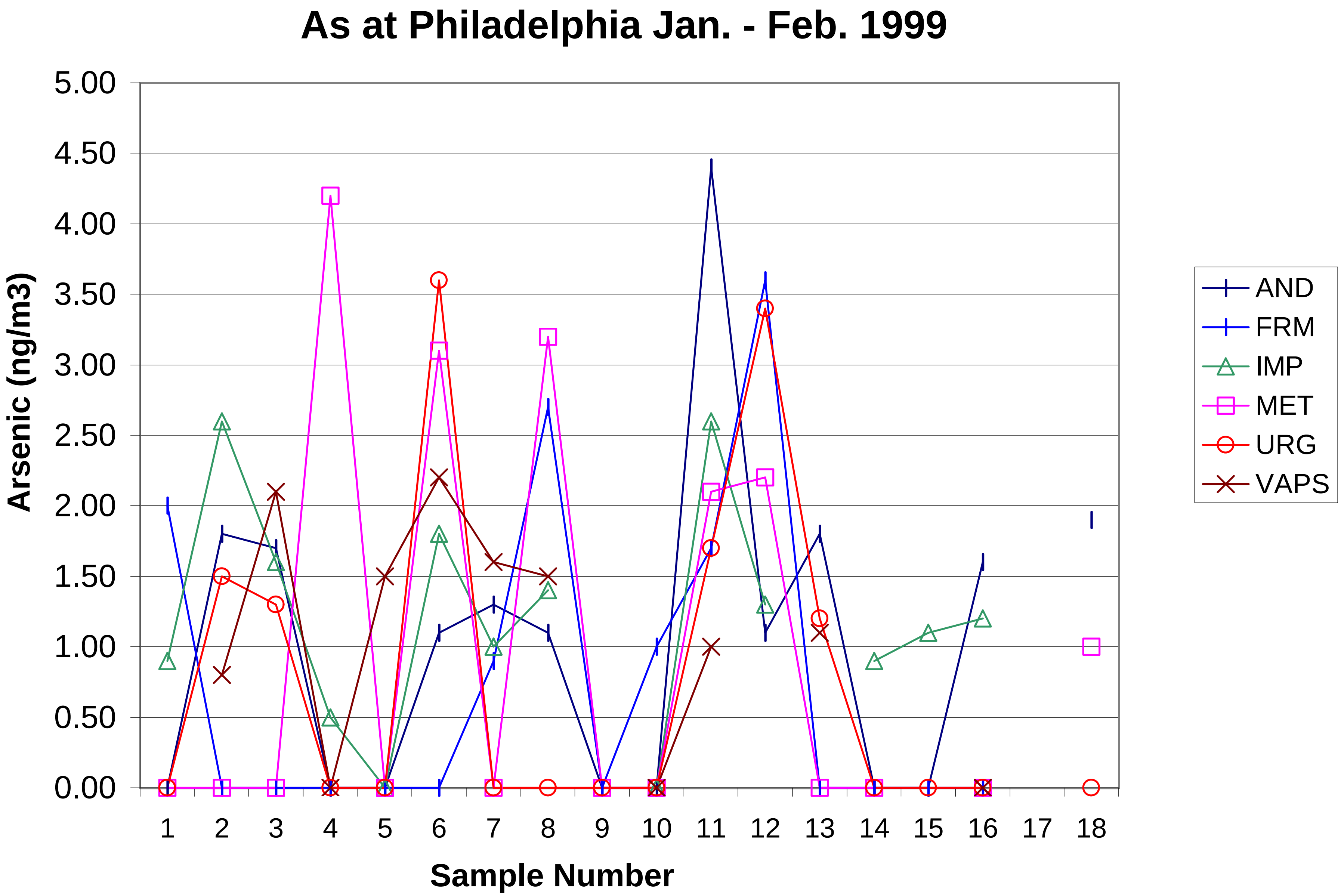


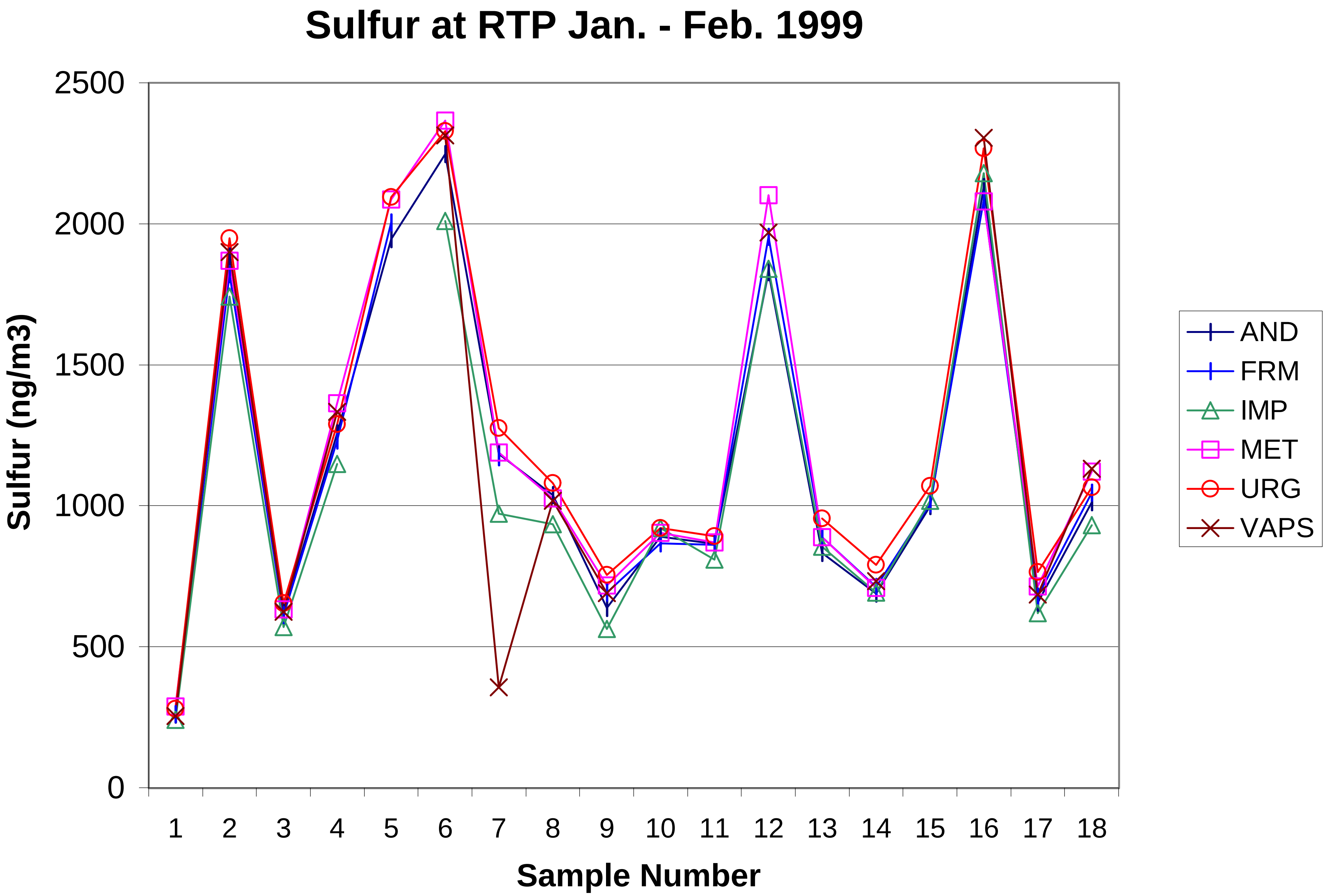

K at Philadelphia Jan. - Feb. 1999
Potassium (ng/m3)
0
20
40
60
80
100
120
140
160
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

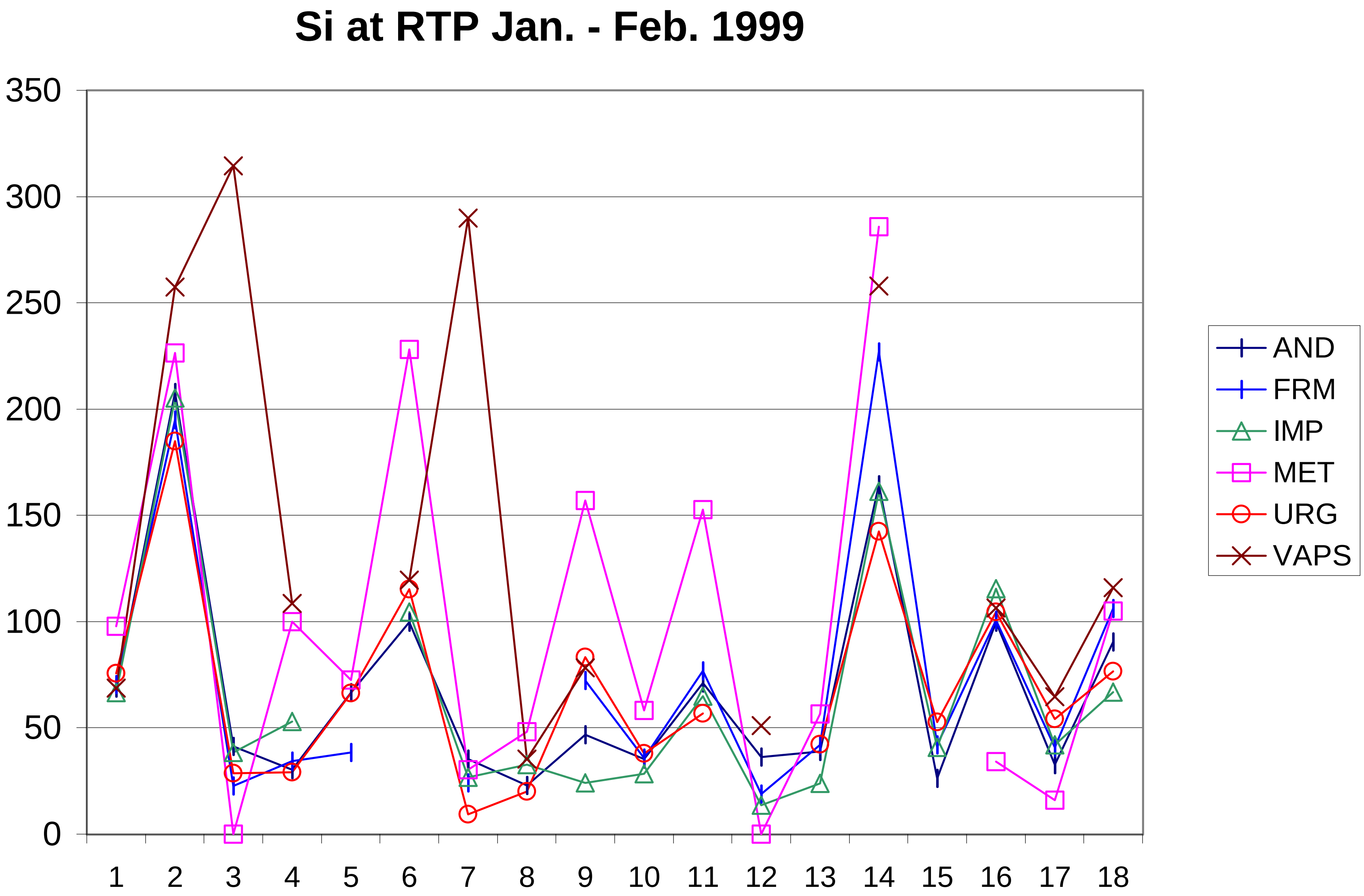

Mn at Philadelphia Jan. - Feb. 1999
Manganese (ng/m3)
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS


Cu at Philadelphia Jan. - Feb. 1999
Copper (ng/m3)
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

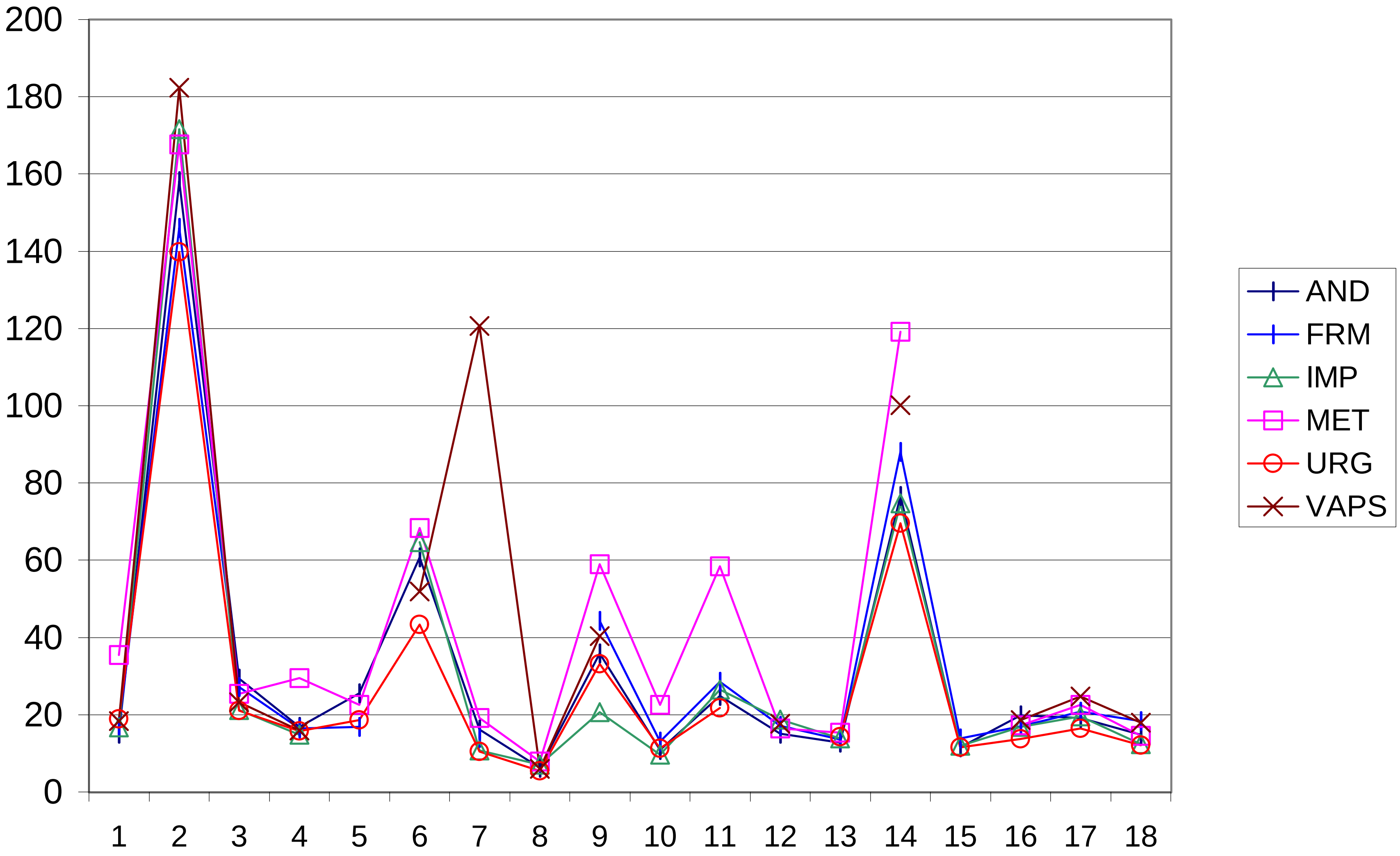

Pb at Philadelphia Jan. - Feb. 1999
Lead (ng/m3)
45
40
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS


As at Philadelphia Jan. - Feb. 1999
Arsenic (ng/m3)
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

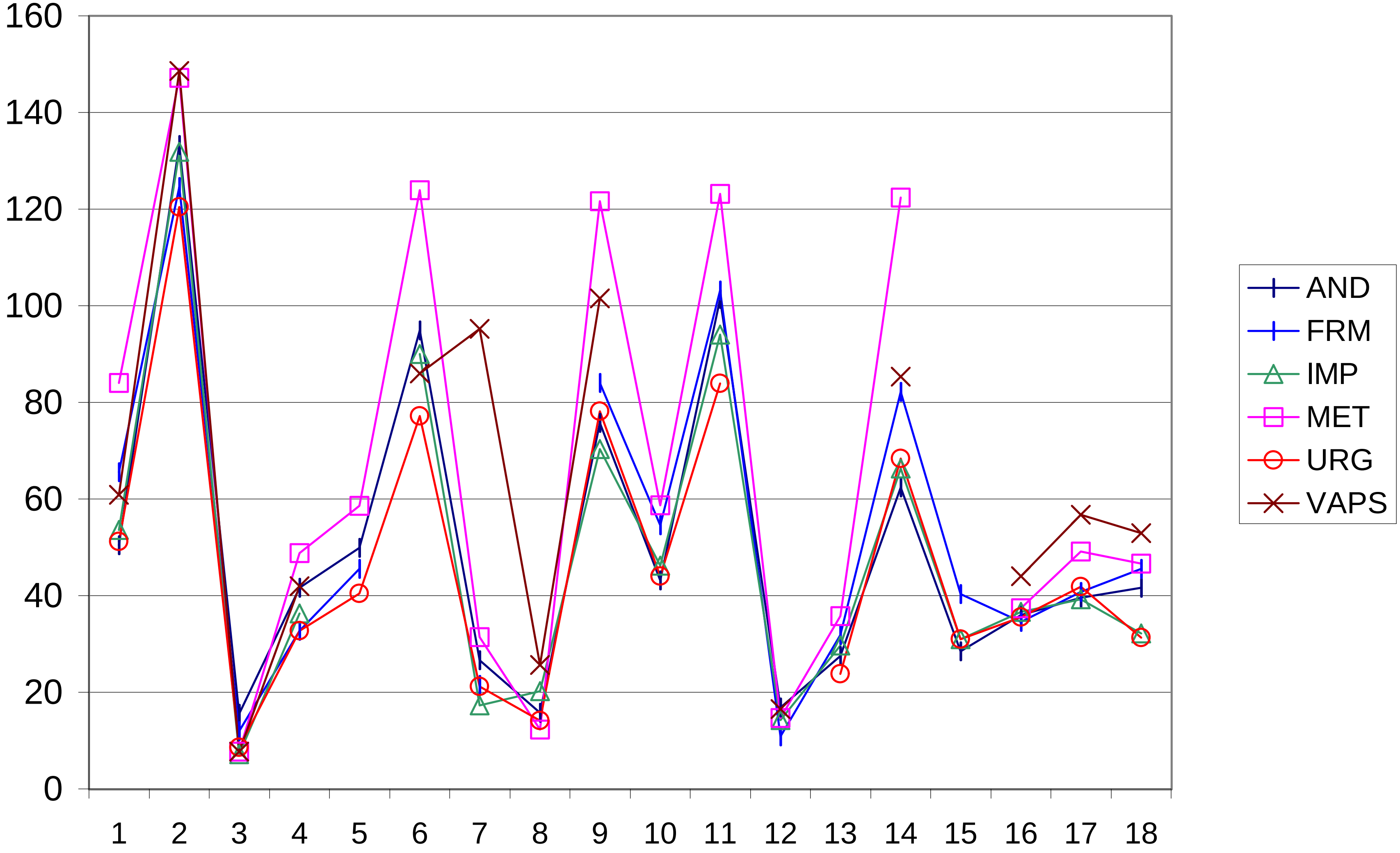

Sulfur at RTP Jan. - Feb. 1999
Sulfur (ng/m3)
2500
2000
1500
1000
500
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

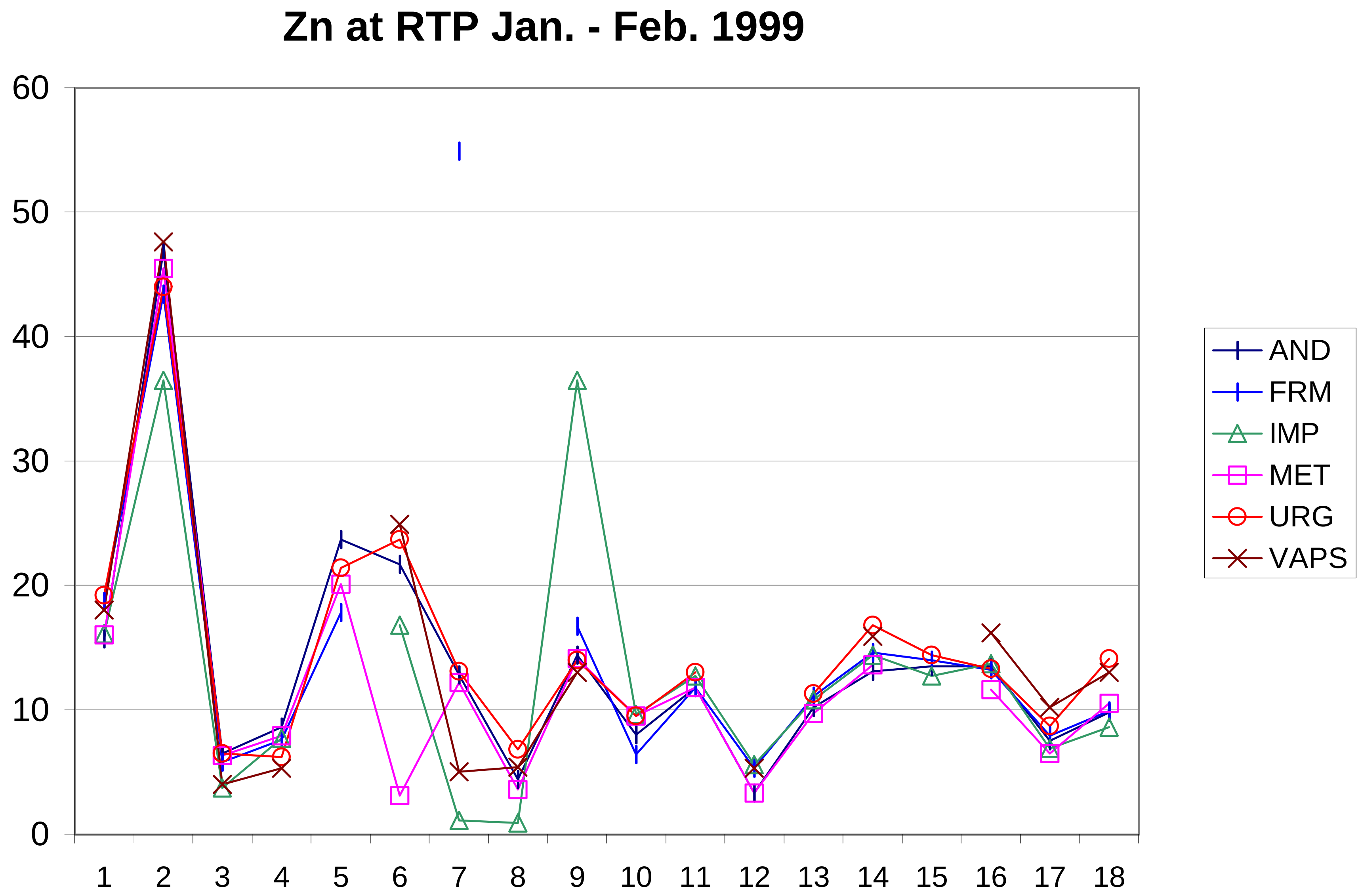

Si at RTP Jan. - Feb. 1999
350
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

Ca at RTP Jan. - Feb. 1999

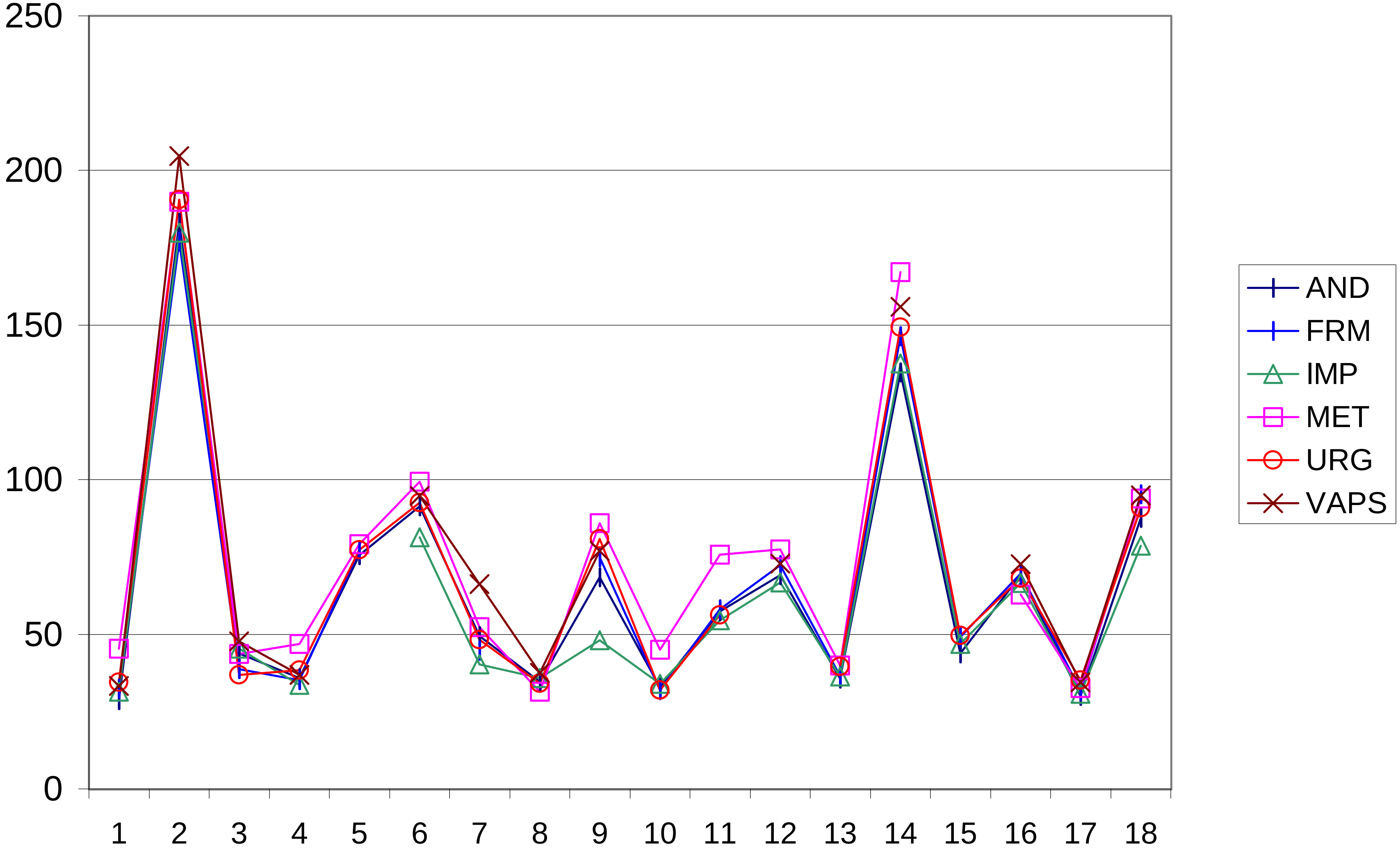


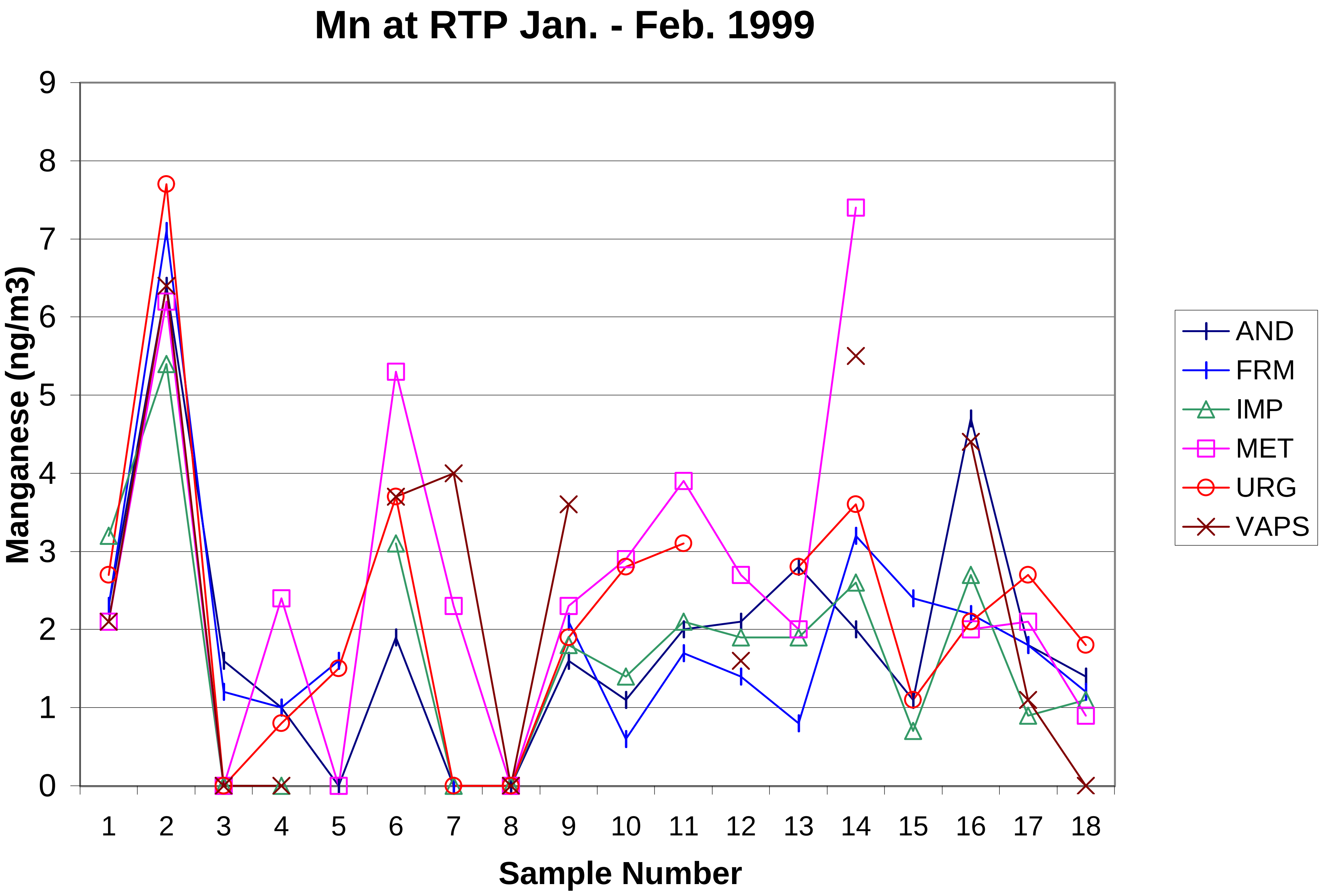
Fe at RTP Jan. - Feb. 1999



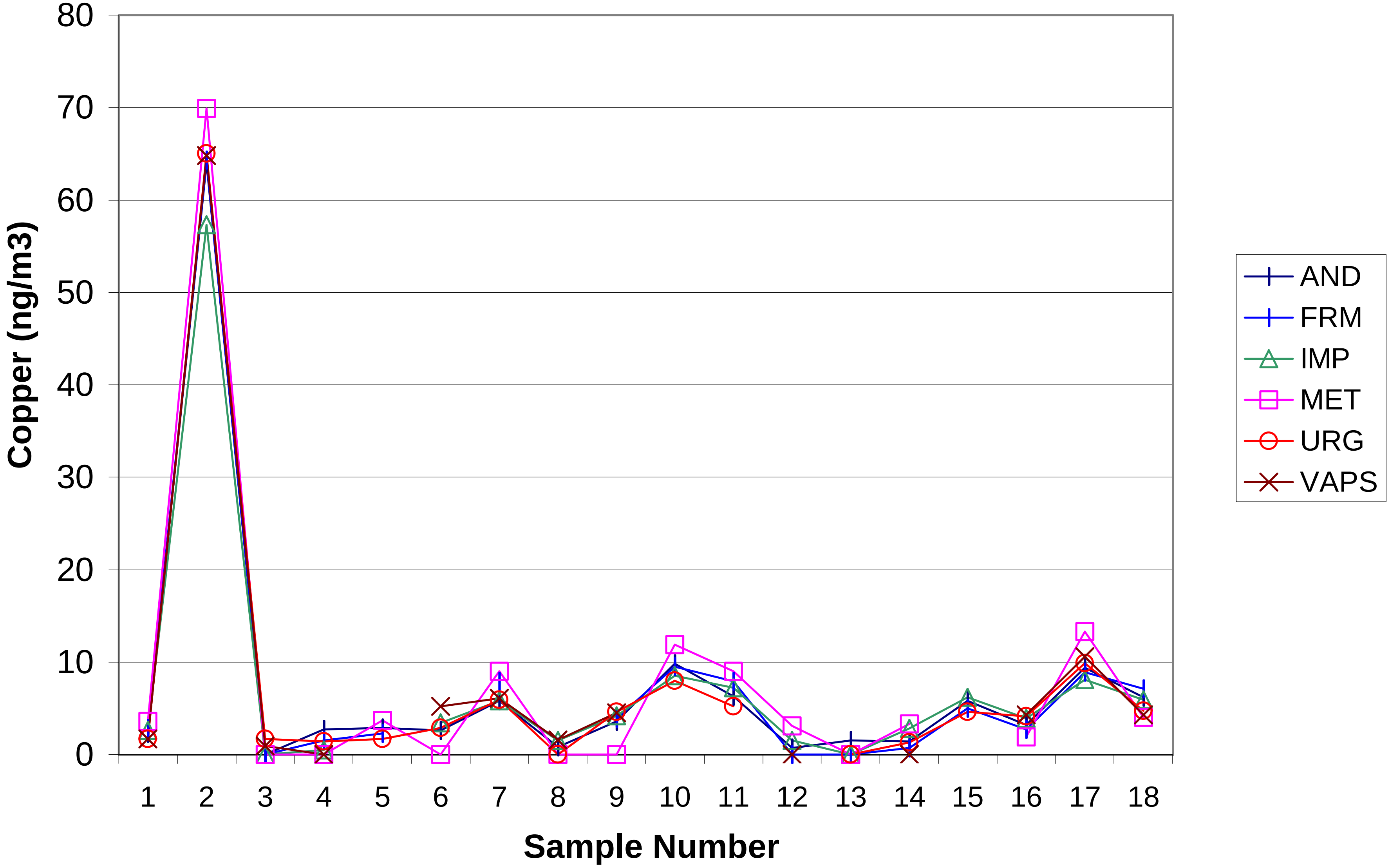

Zn at RTP Jan. - Feb. 1999
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

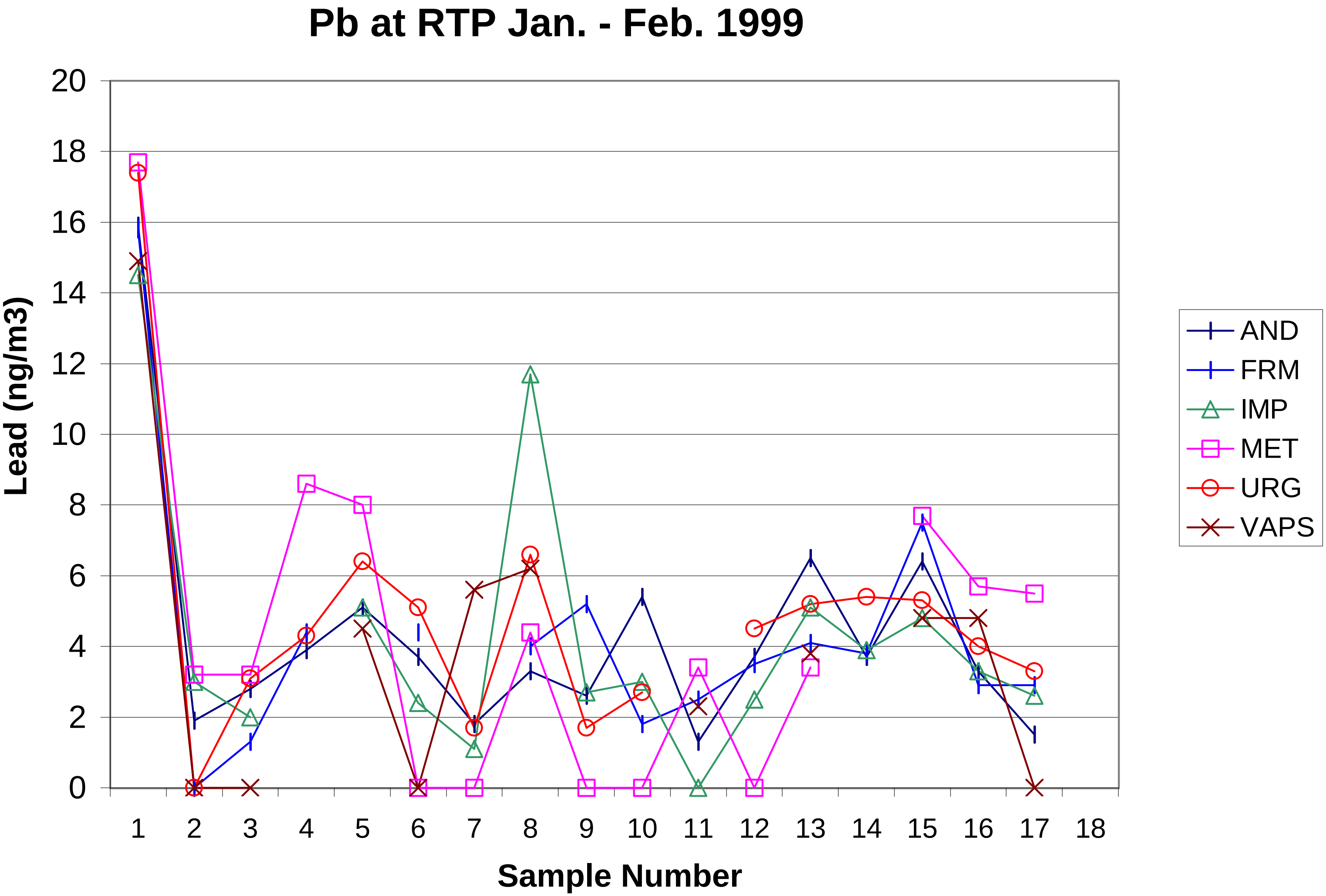
K at RTP Jan. - Feb. 1999



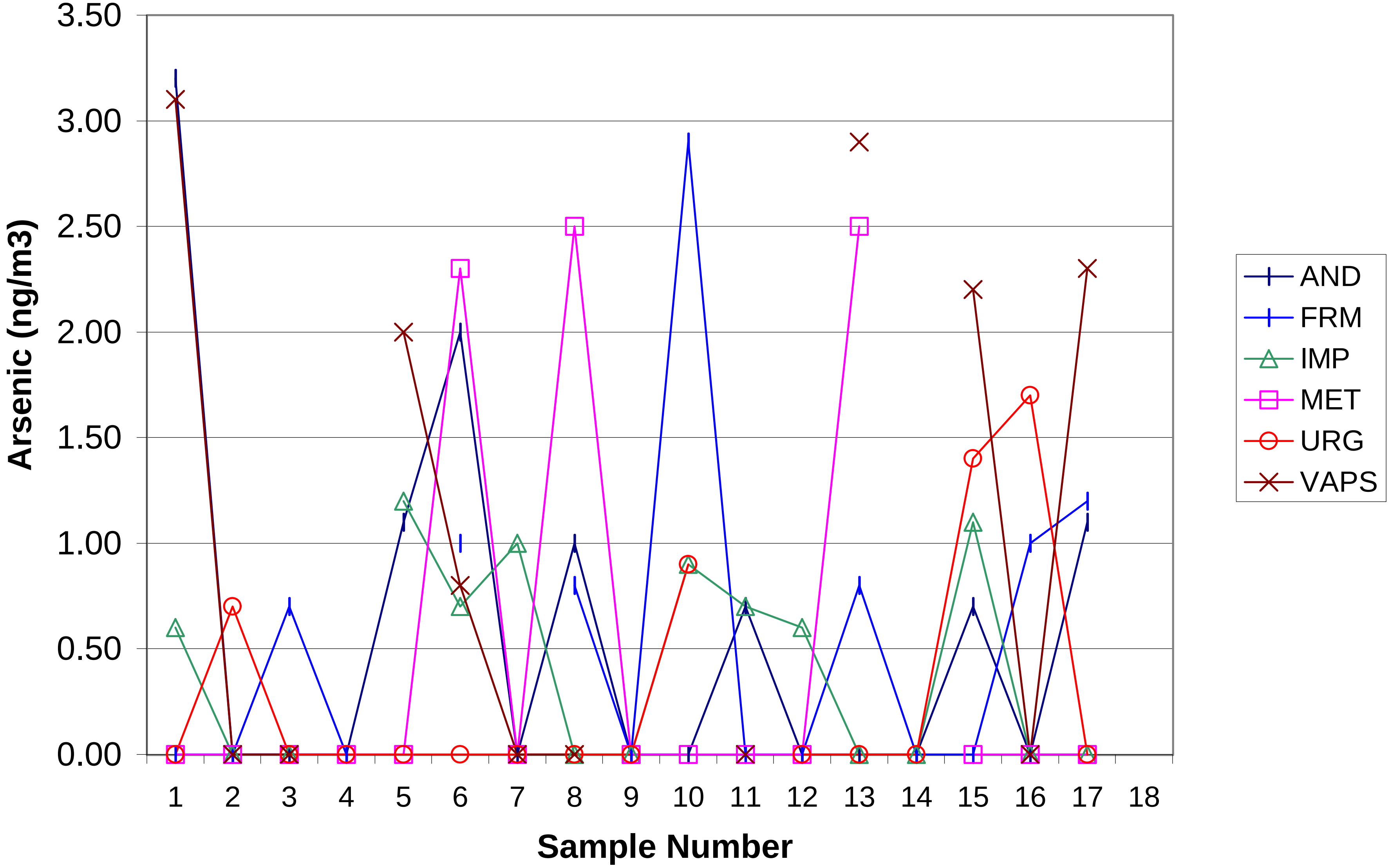

Mn at RTP Jan. - Feb. 1999
Manganese (ng/m3)
0
1
2
3
4
5
6
7
8
9
Sample Number
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
AND
FRM
IMP
MET
URG
VAPS

Cu at RTP Jan. - Feb. 1999



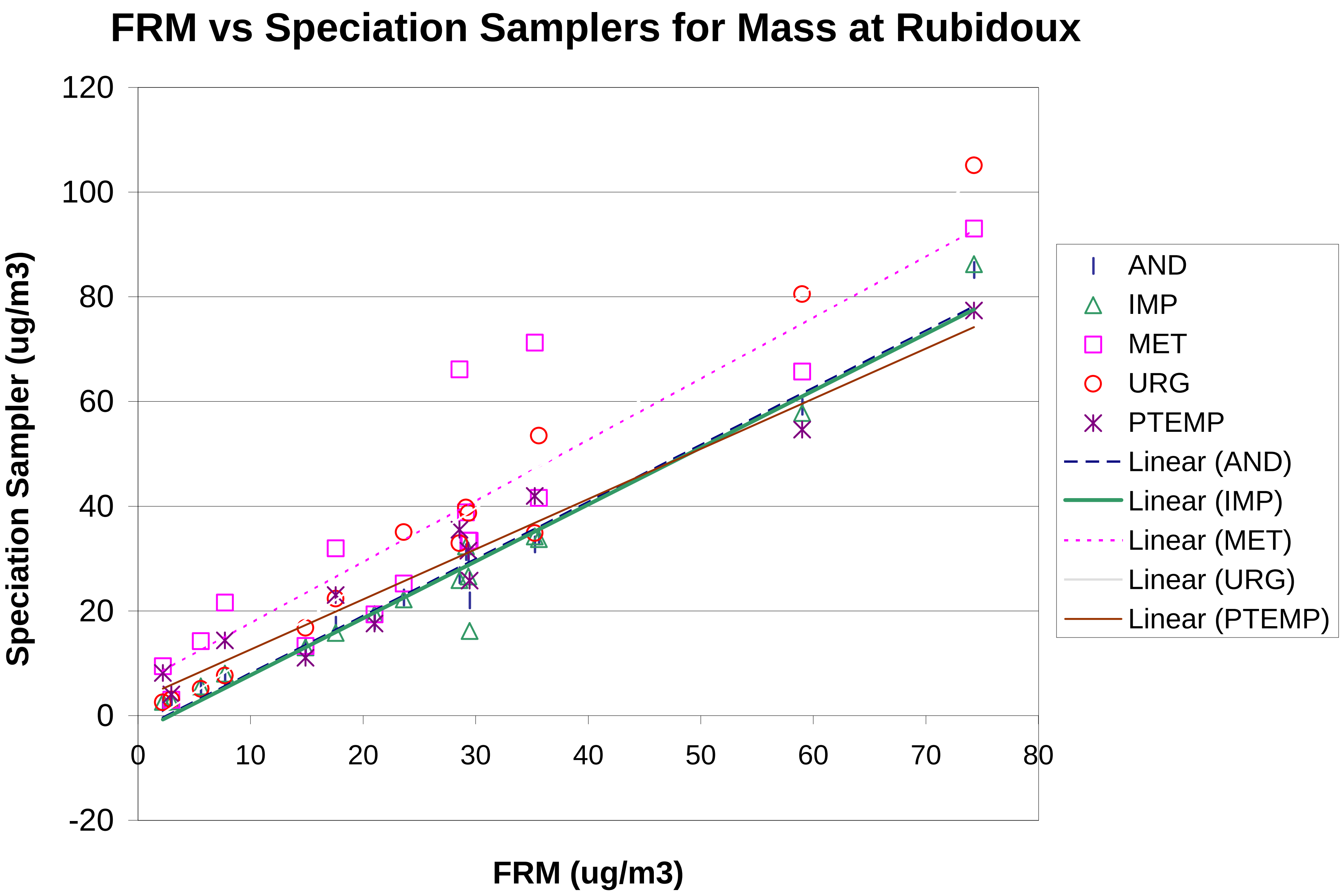

Pb at RTP Jan. - Feb. 1999
Lead (ng/m3)
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Sample Number
AND
FRM
IMP
MET
URG
VAPS

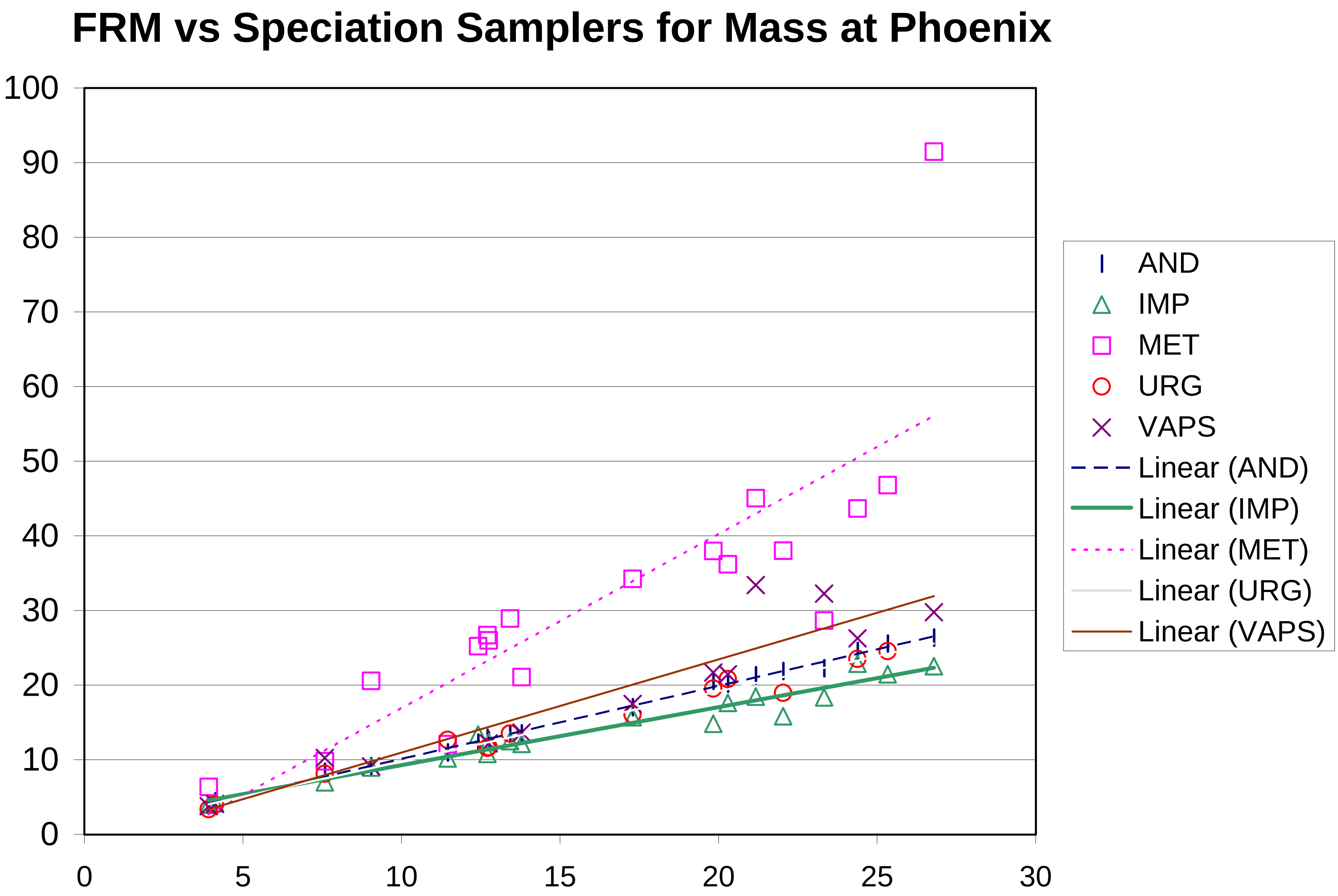
As at RTP Jan. - Feb. 1999



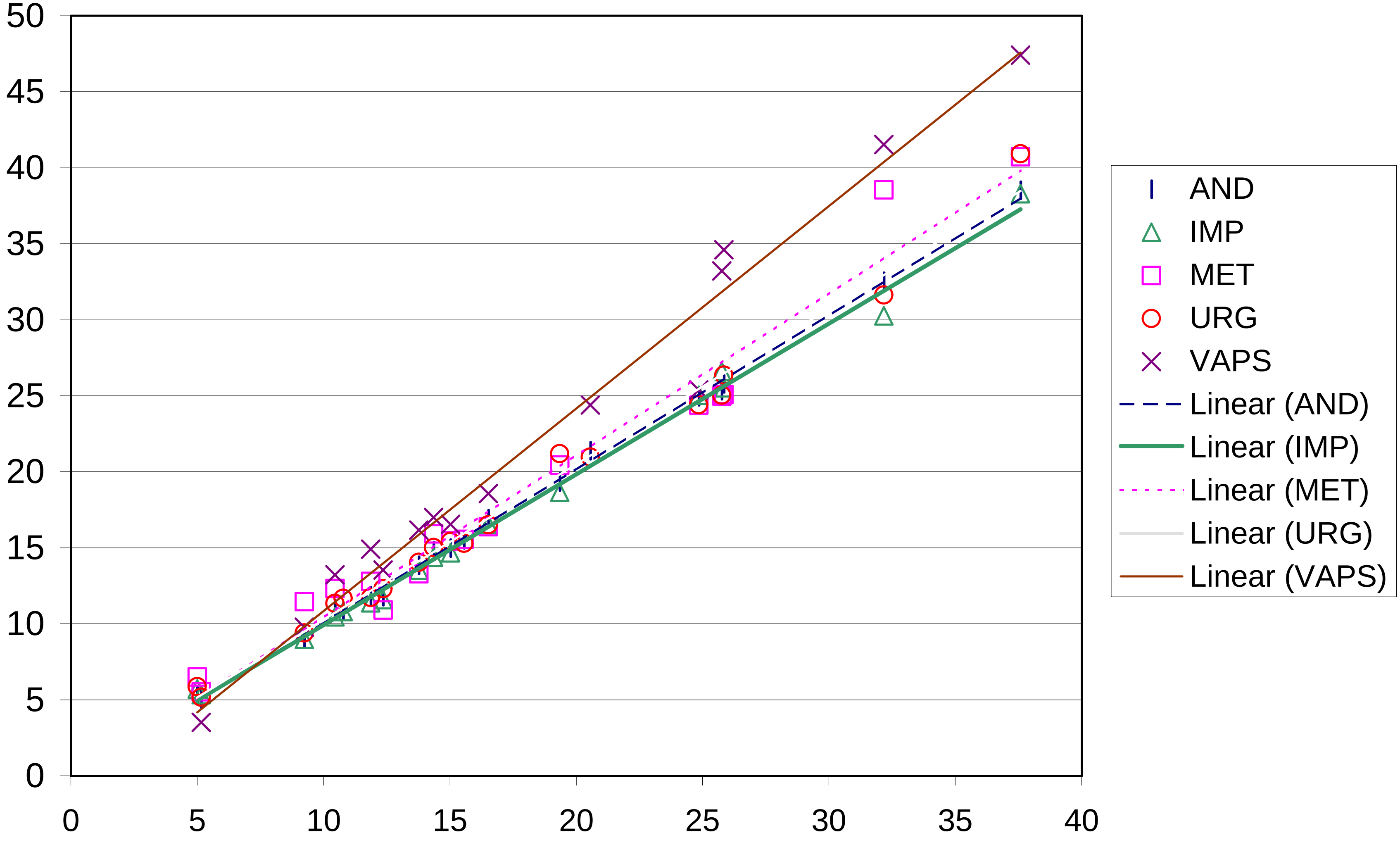
Appendix F

Regression Analysis Plots for All Species Measured in the 4-City Study

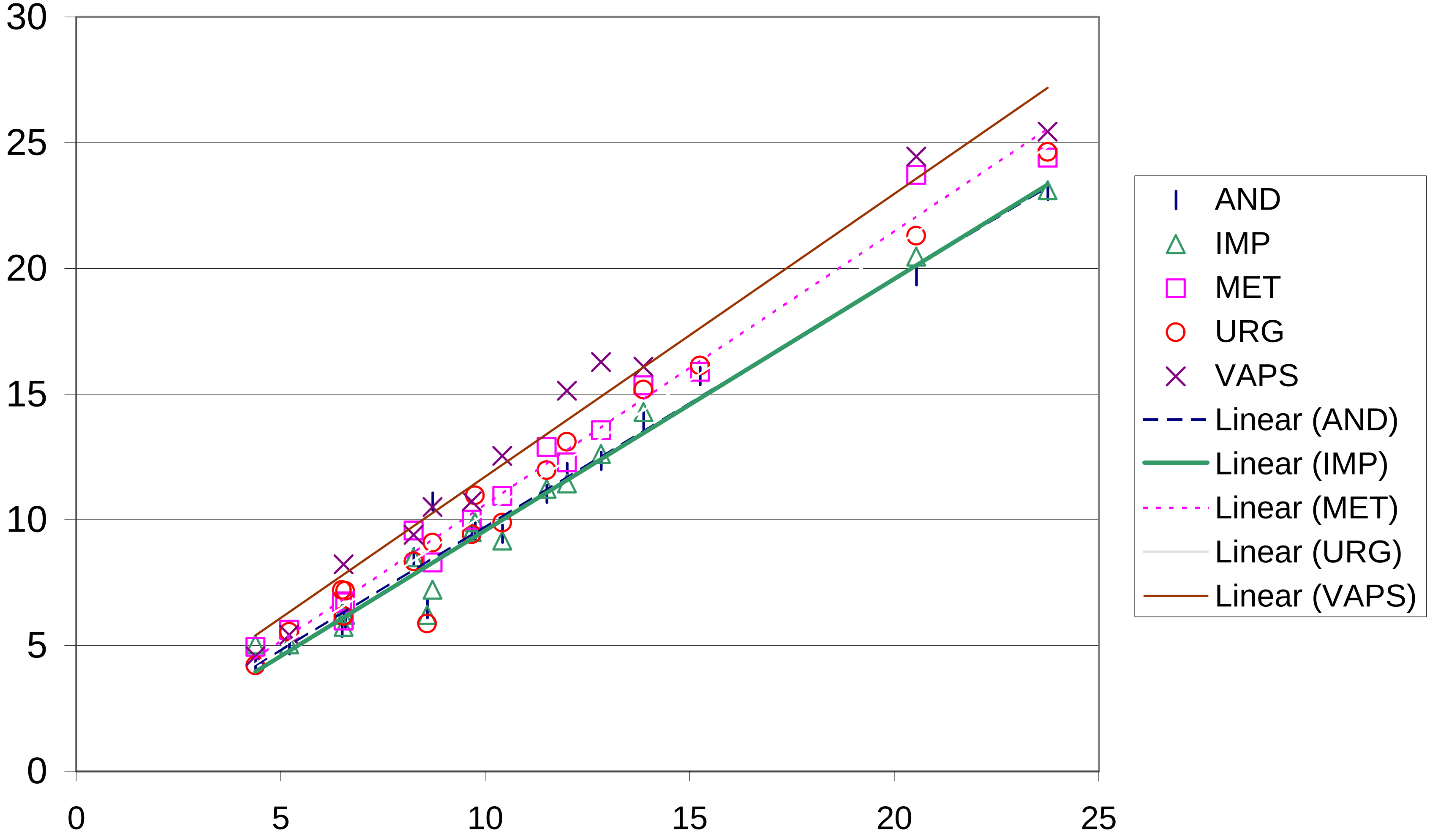

FRM vs Speciation Samplers for Mass at Rubidoux
Speciation Sampler (ug/m3)
FRM (ug/m3)
120
100
80
60
40
20
0
-20
0
10
20
30
40
50
60
70
80
AND
IMP
MET
URG
PTEMP
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (PTEMP)

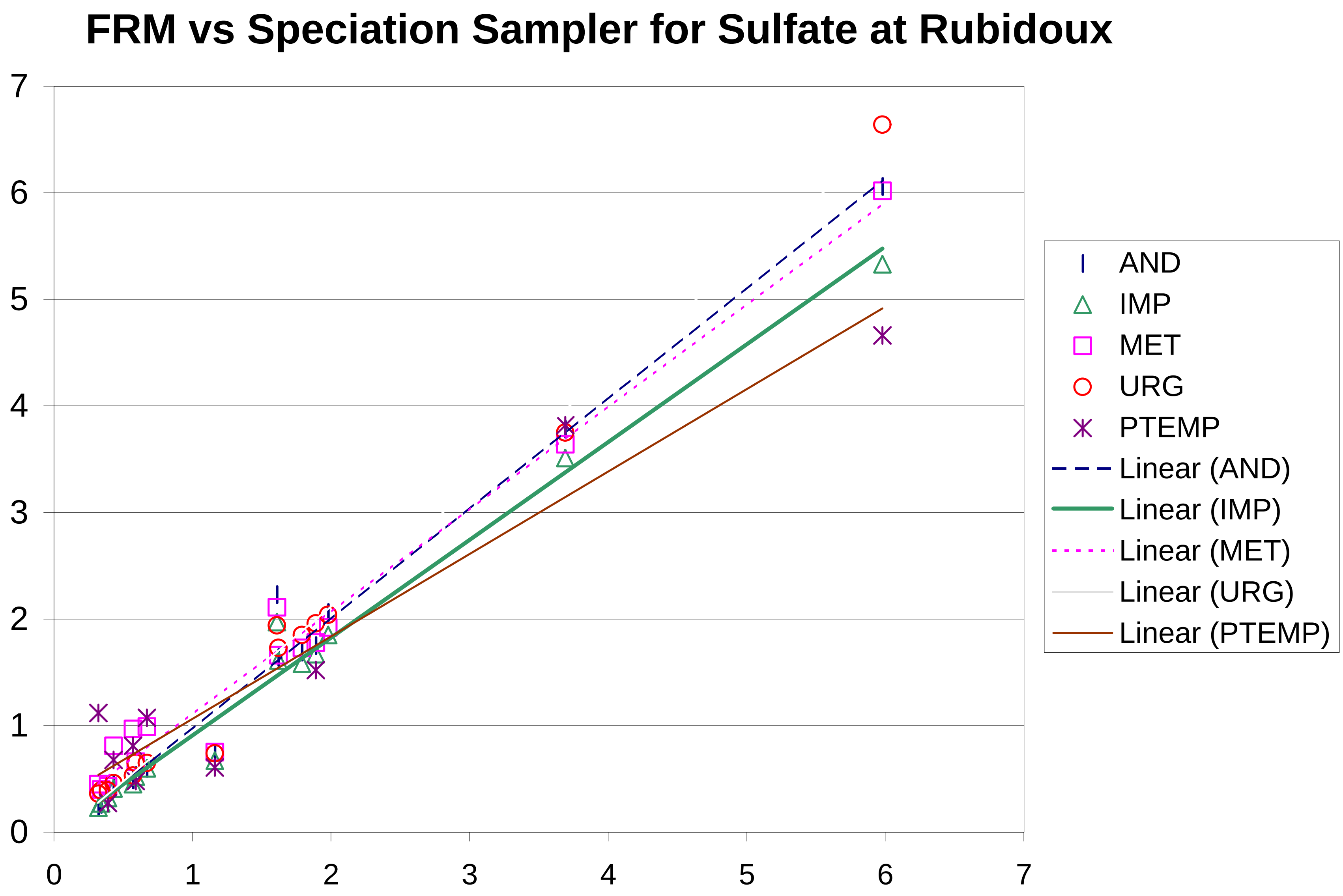

FRM vs Speciation Samplers for Mass at Phoenix
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

FRM vs Speciation Samplers for Mass at Philadelphia

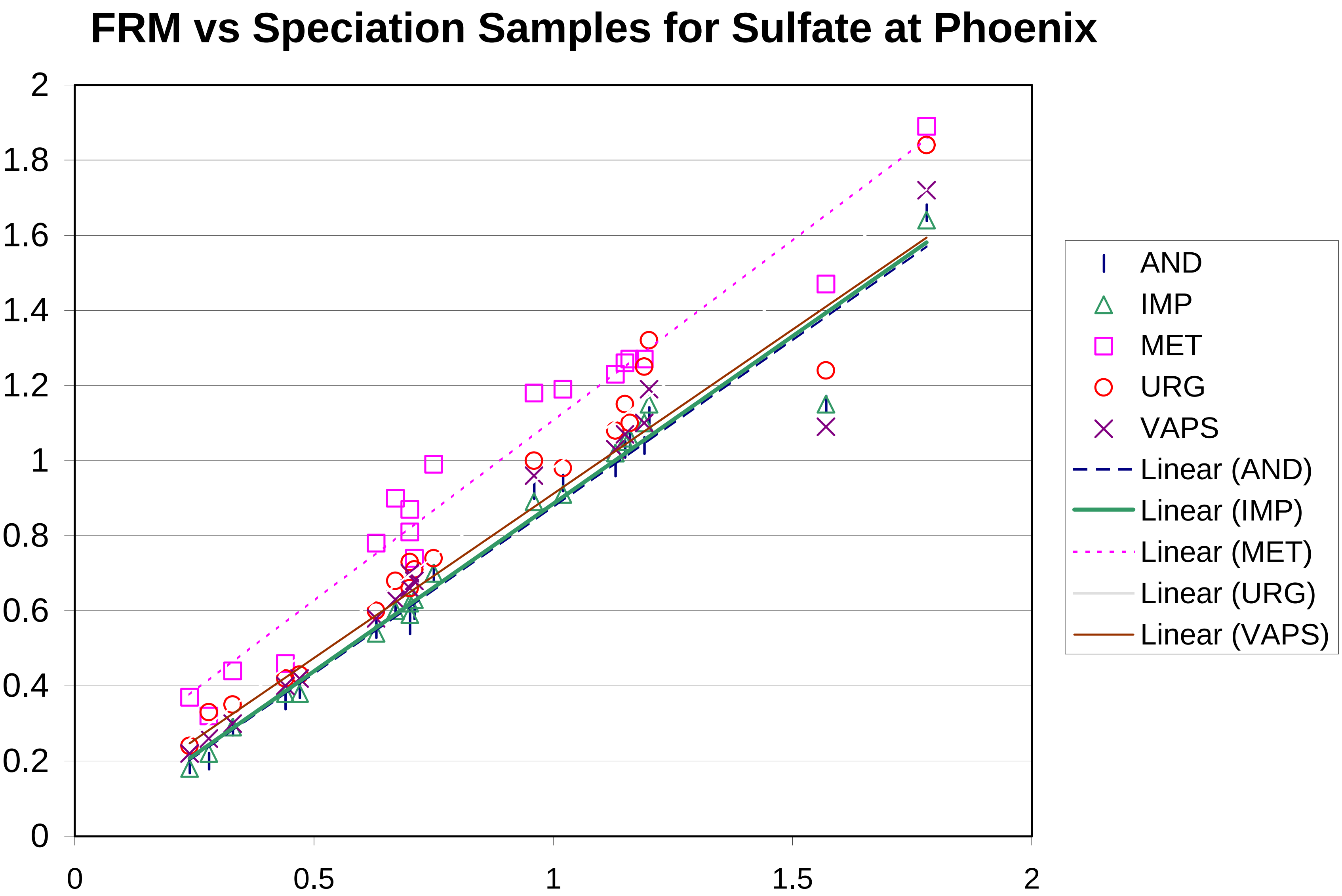


FRM vs Speciation Samplers for Mass at Research Triangle Park

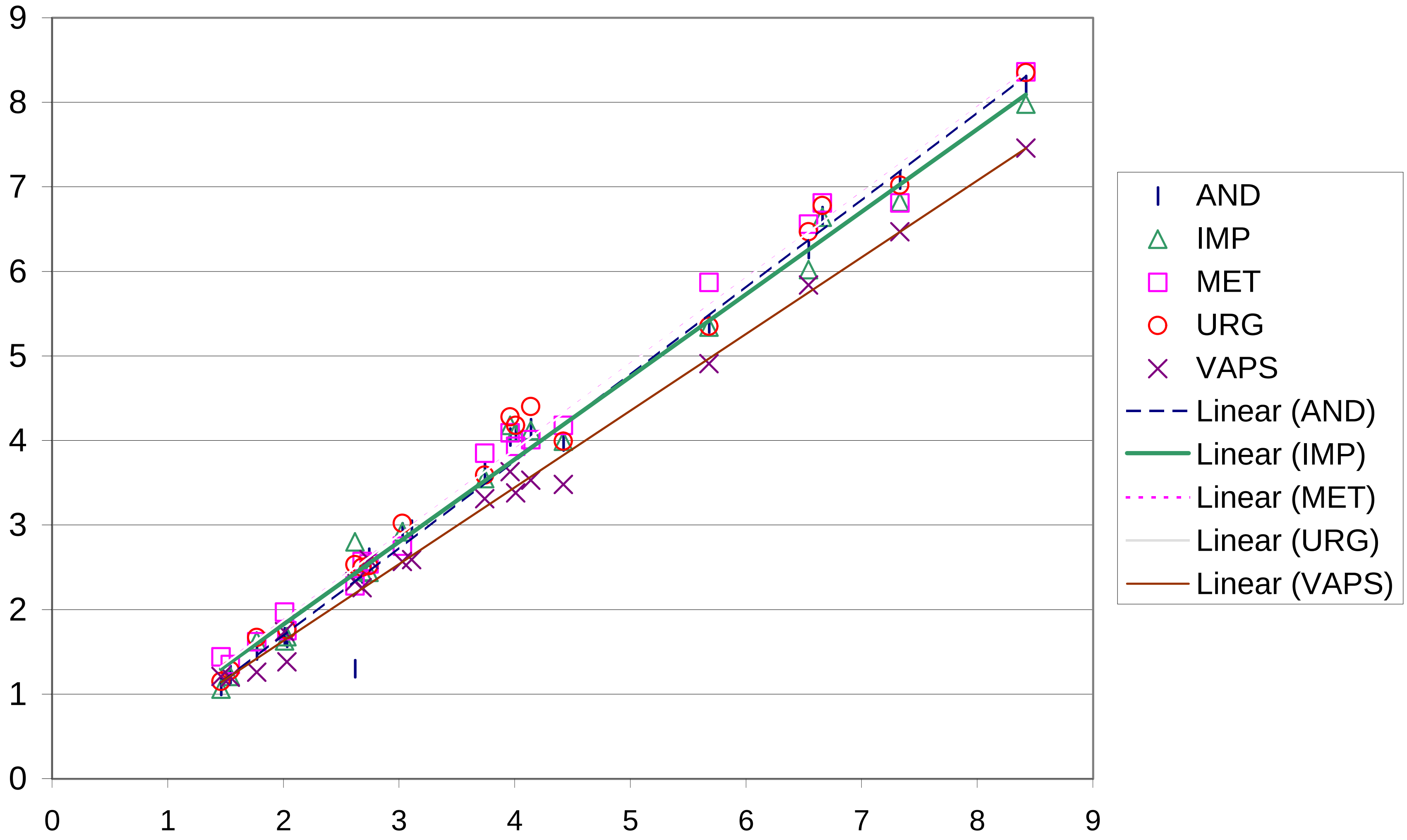




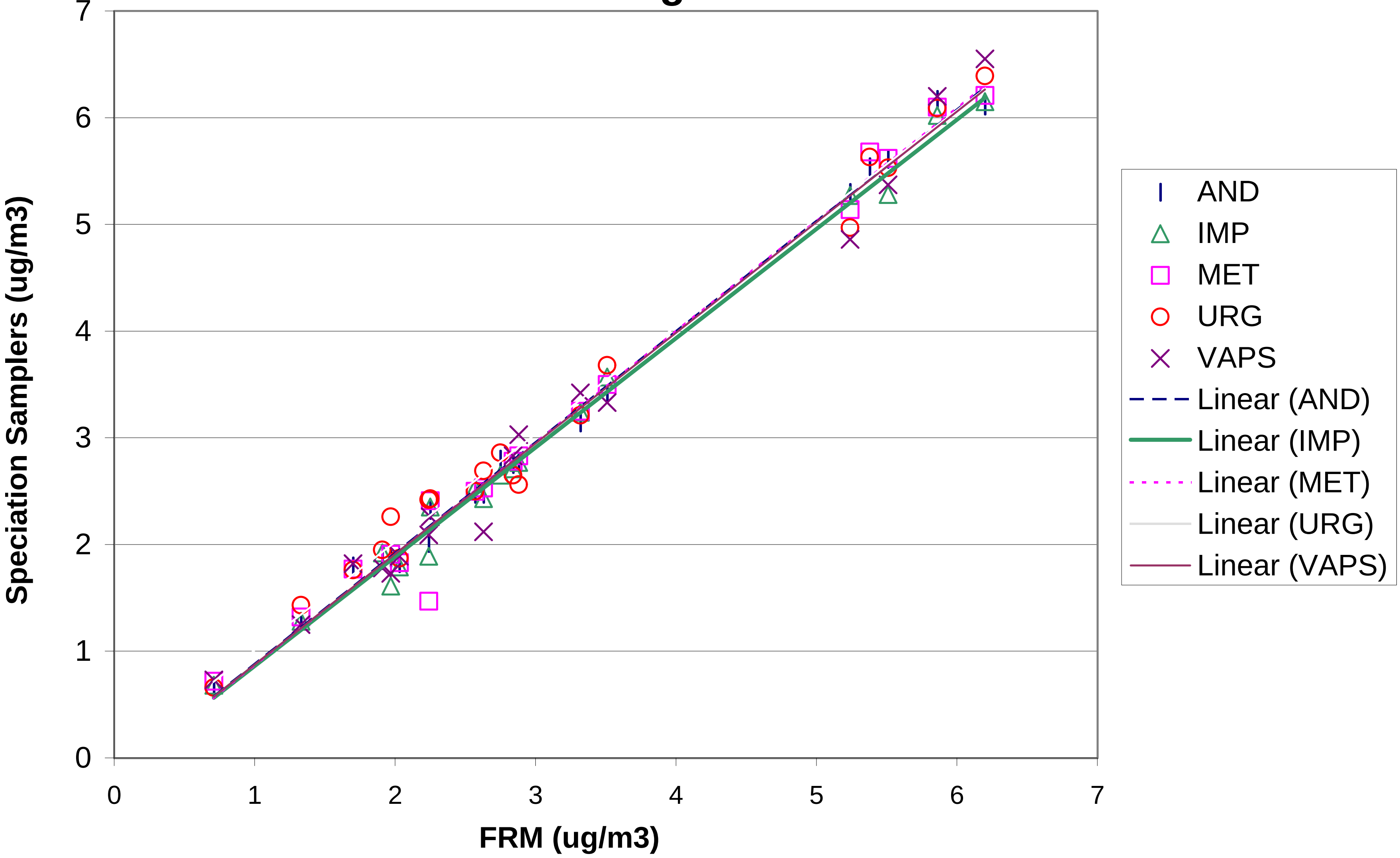
FRM vs Speciation Sampler for Sulfate at Rubidoux


FRM vs Speciation Samples for Sulfate at Phoenix
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

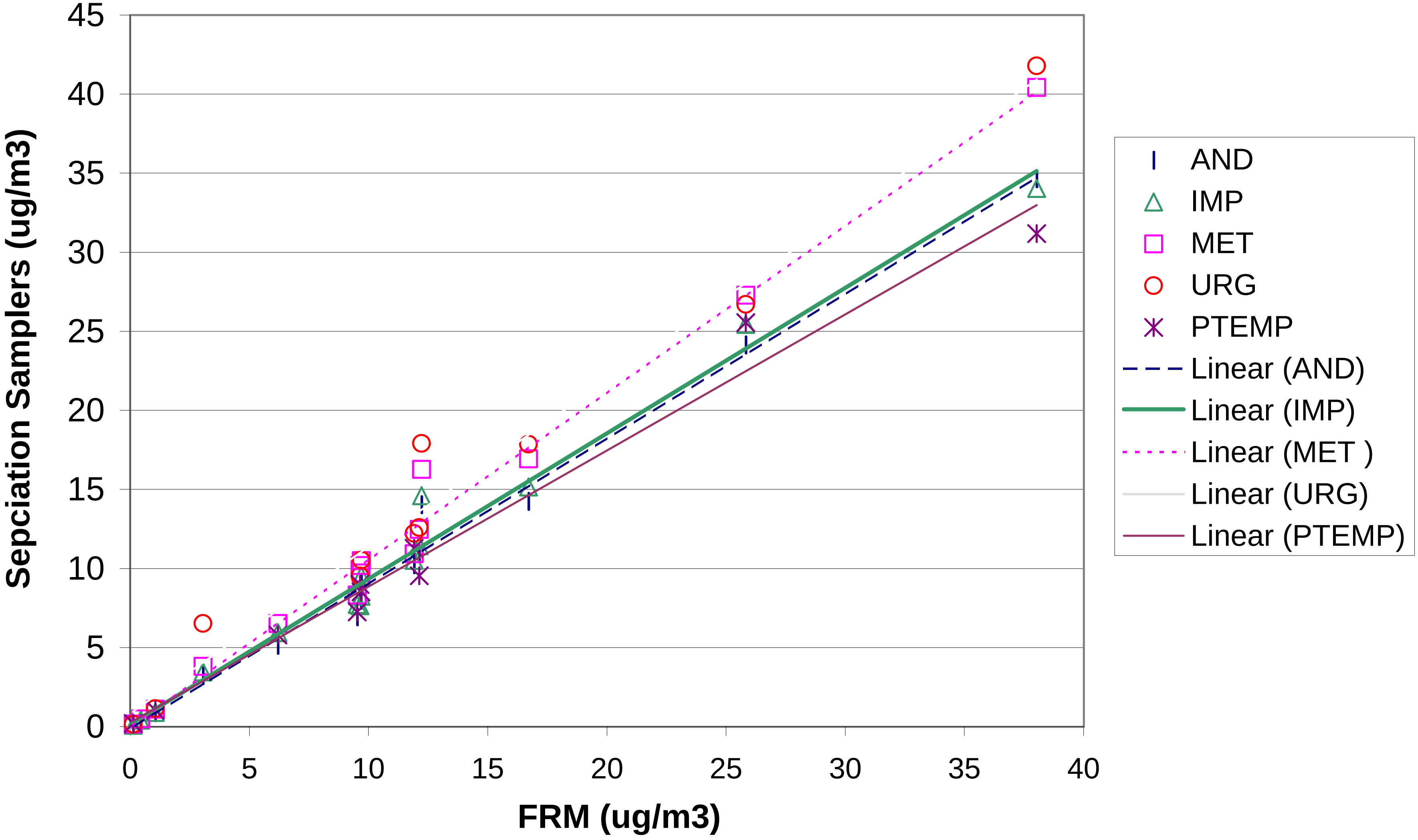
FRM vs Speciation Samplers for Sulfate in Philadelphia

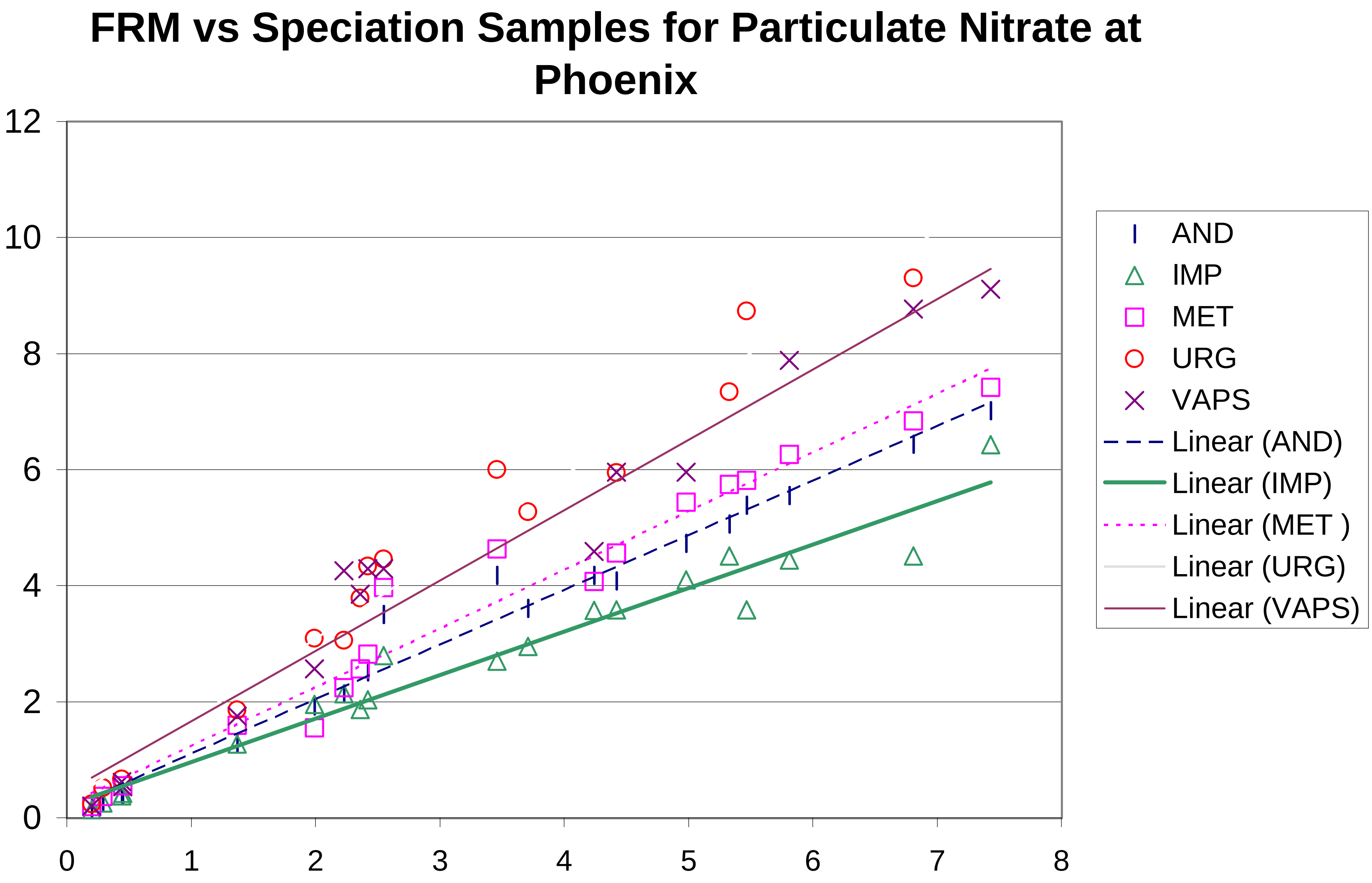


FRM vs Speciation Samplers for Sulfate at Research Triangle Park

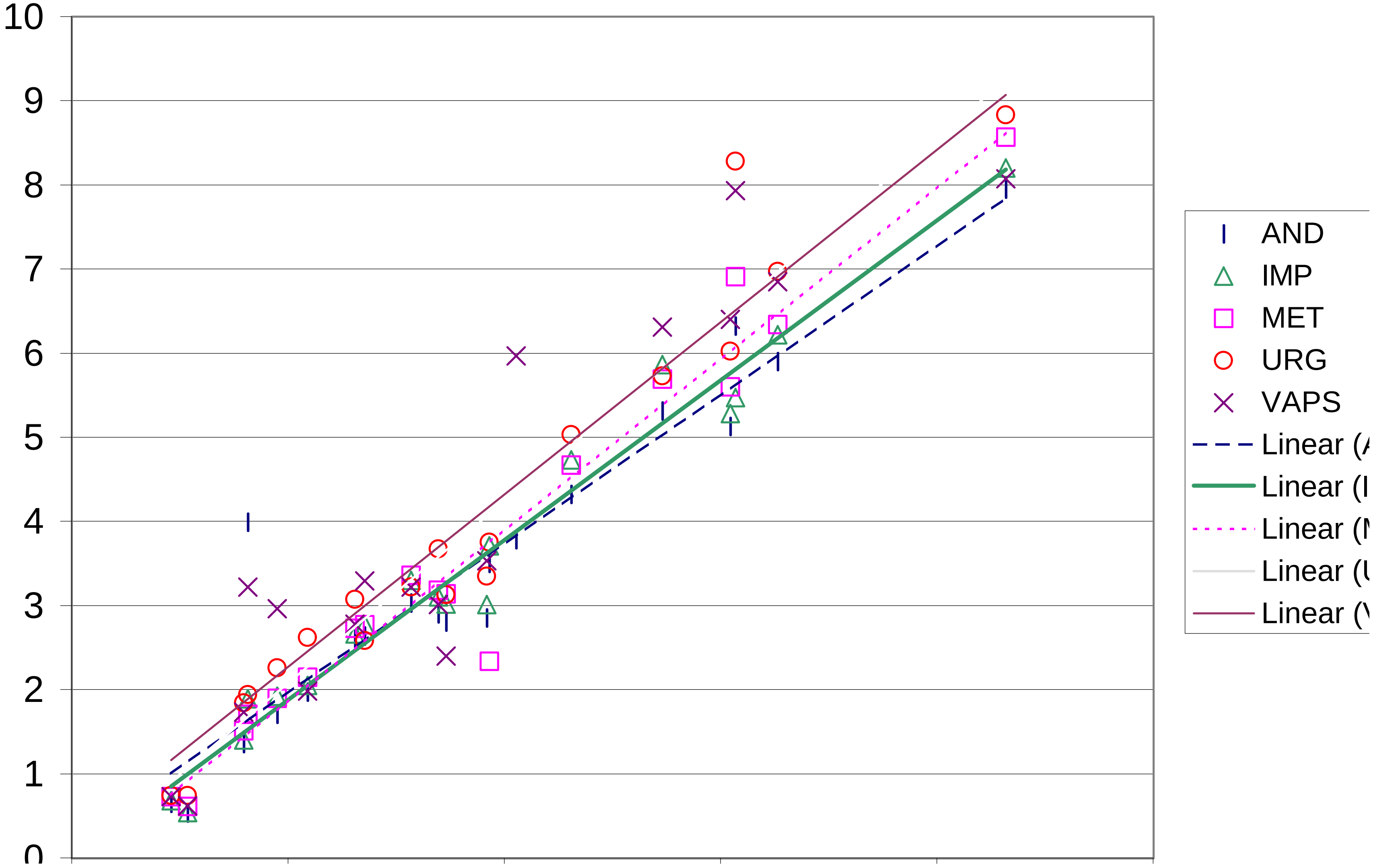


FRM vs Speciation Samplers for Particluate Nitrate at Rubidoux

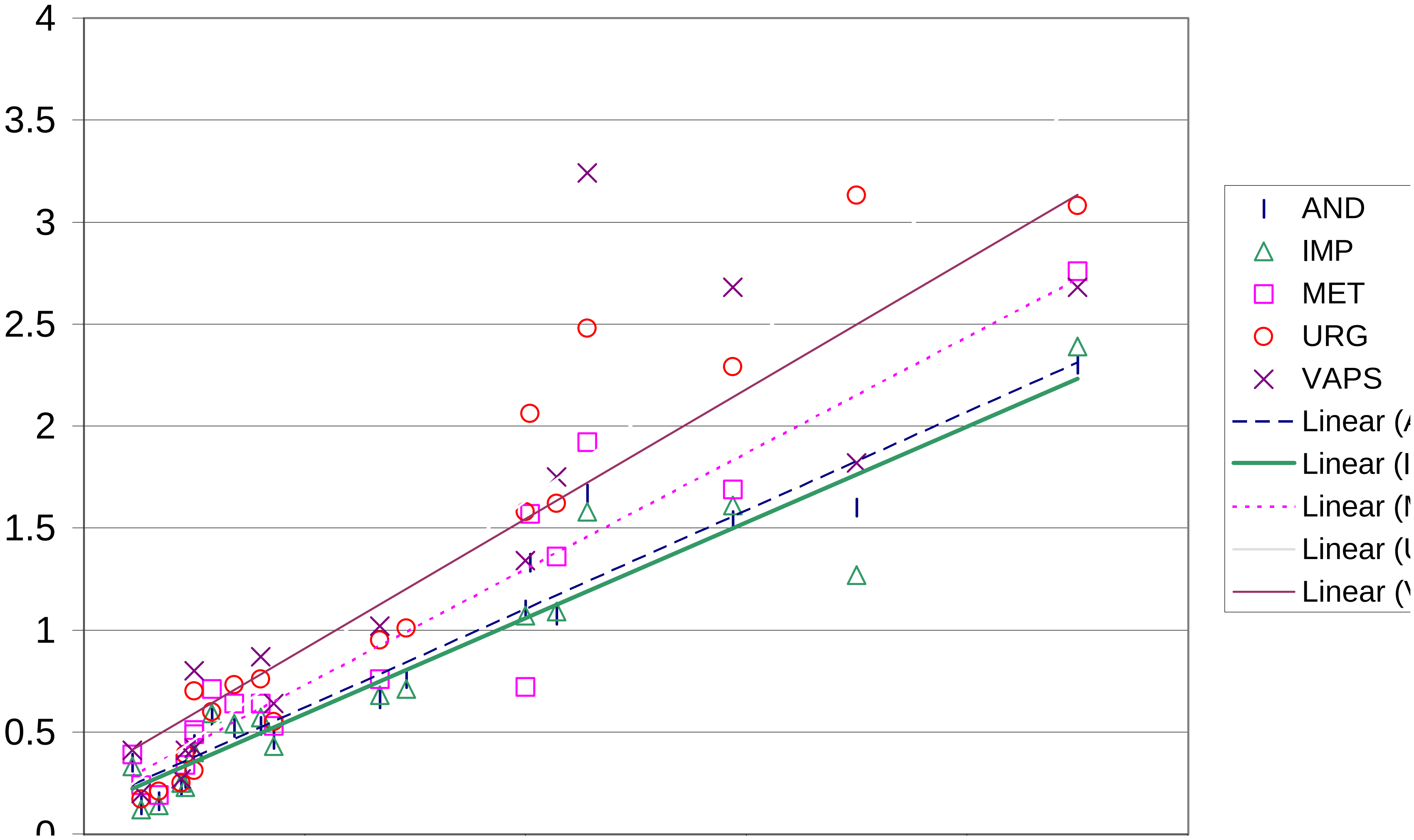



FRM vs Speciation Samples for Particulate Nitrate at Phoenix
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

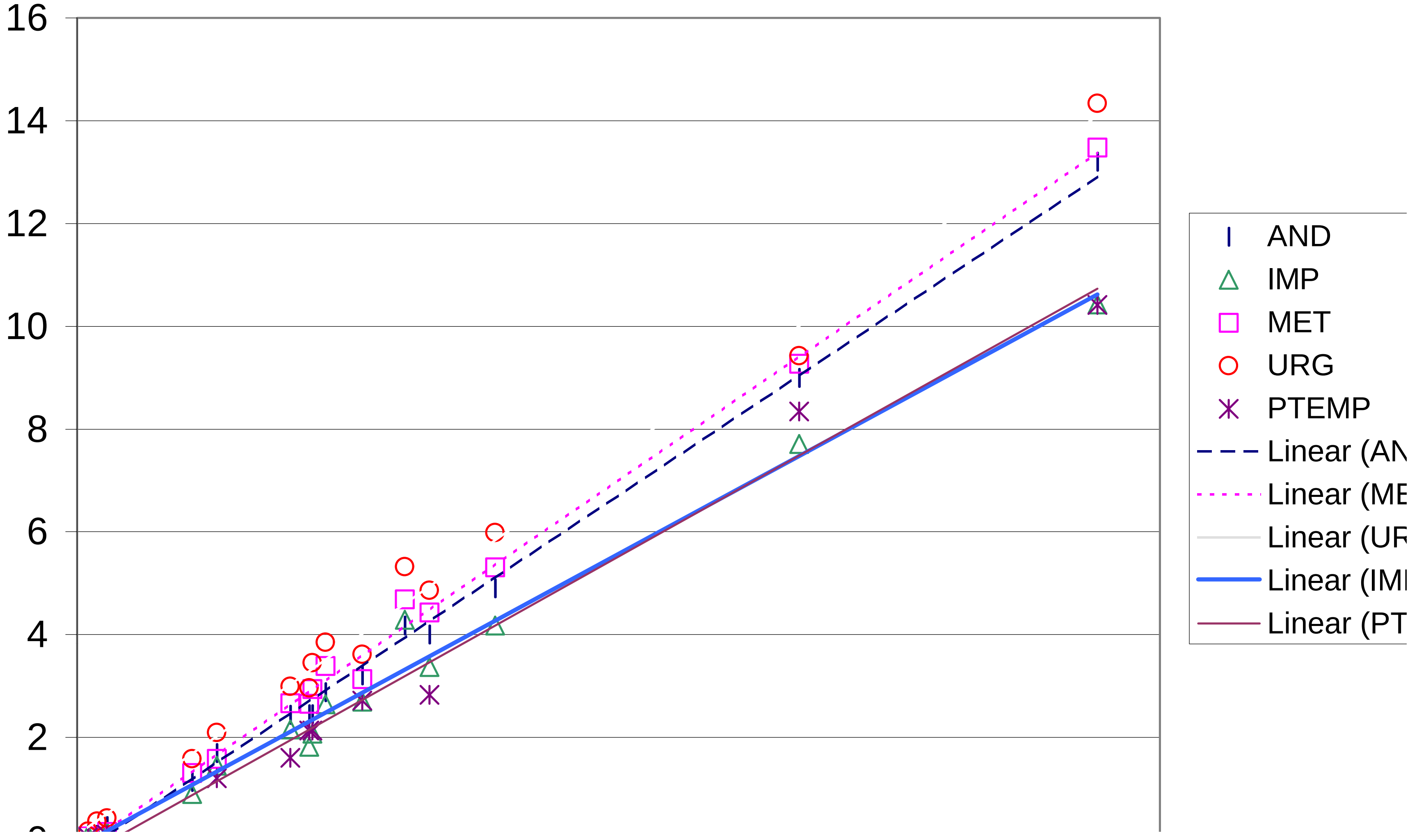
FRM vs Speciation Samplers for Particulate Nitrate at Philadelphia



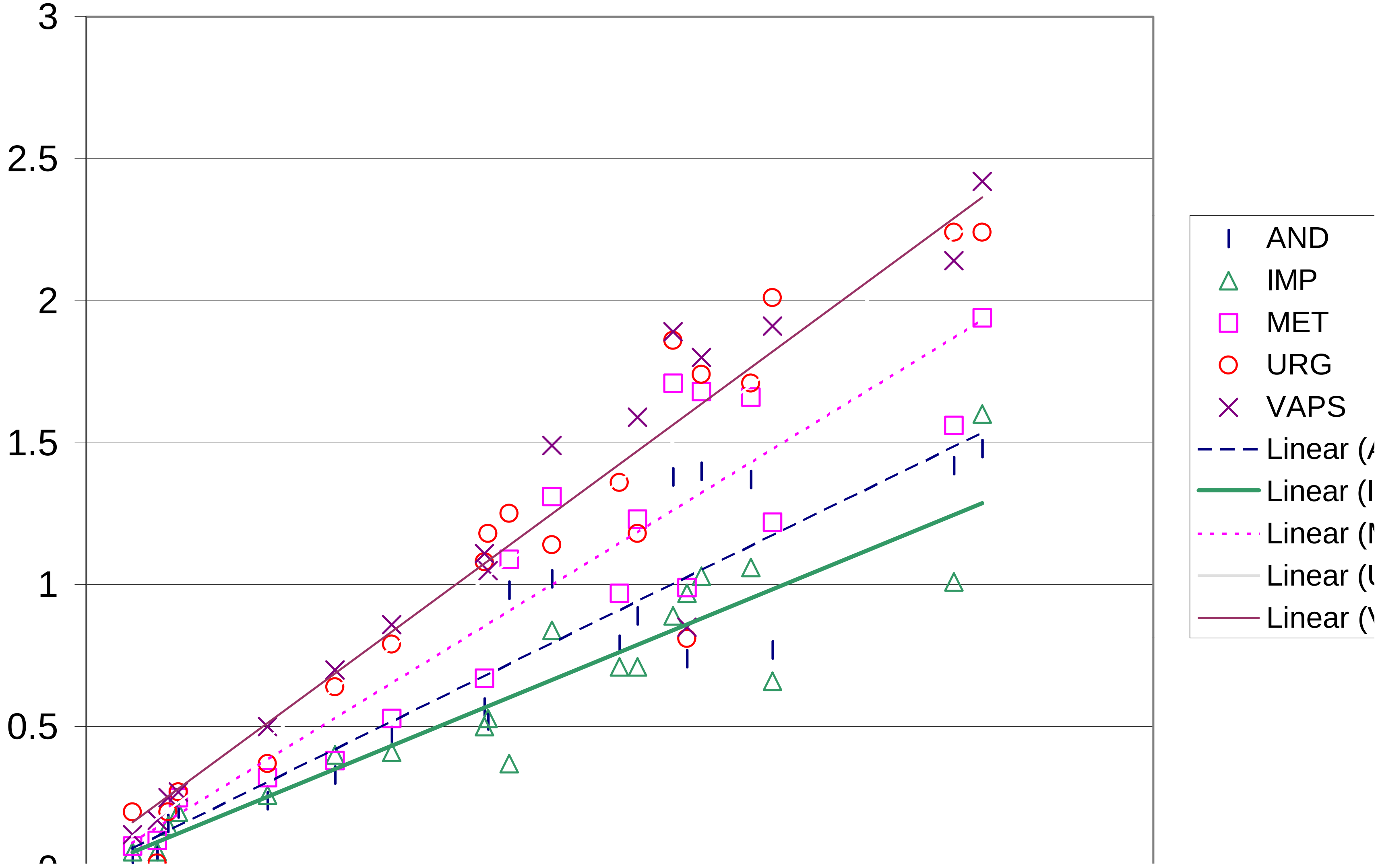
FRM vs Speciation Samplers for Particulate Nitrate at RTP



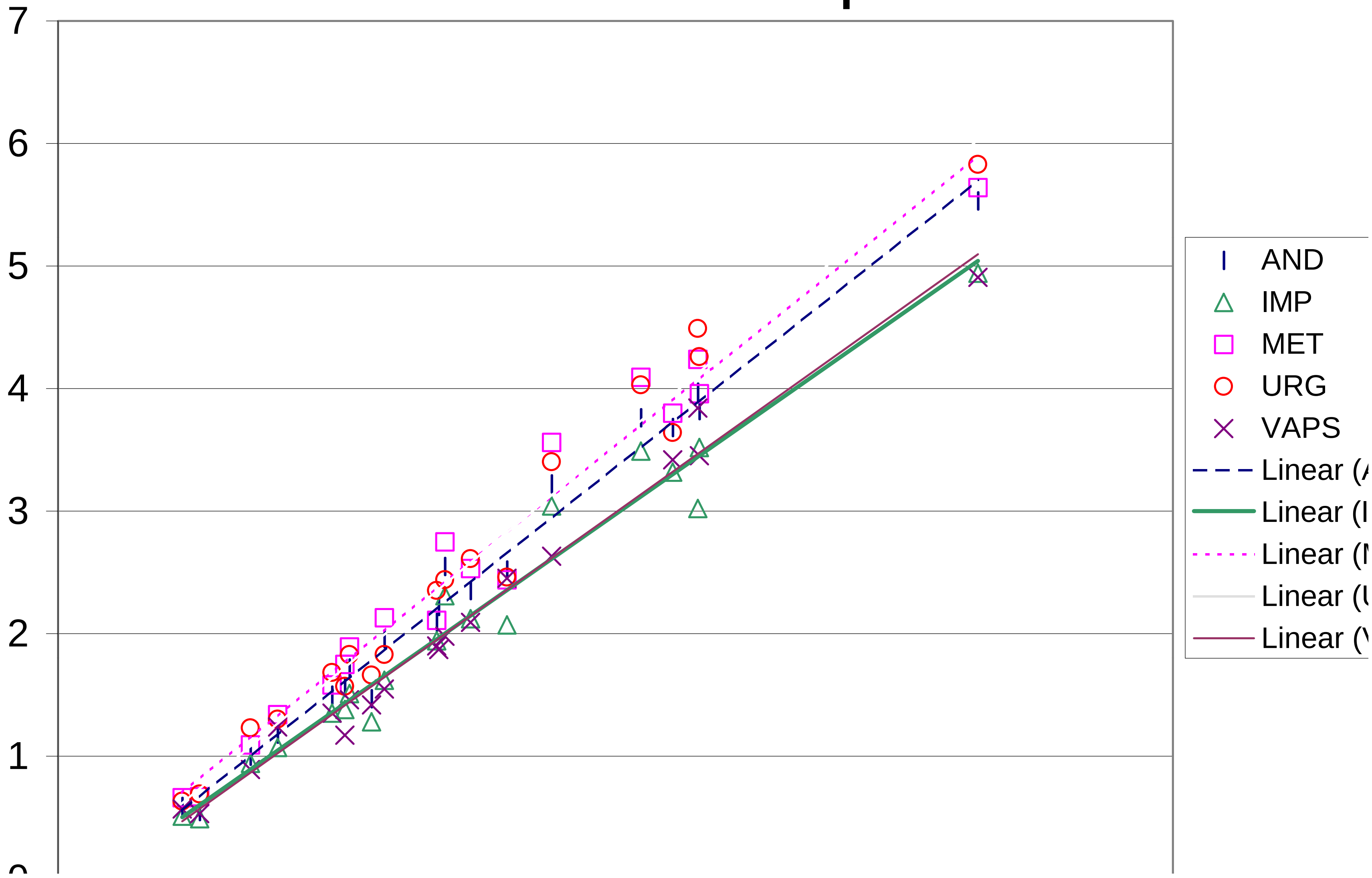
FRM vs Speciation Samplers for Ammonium at Rubidoux



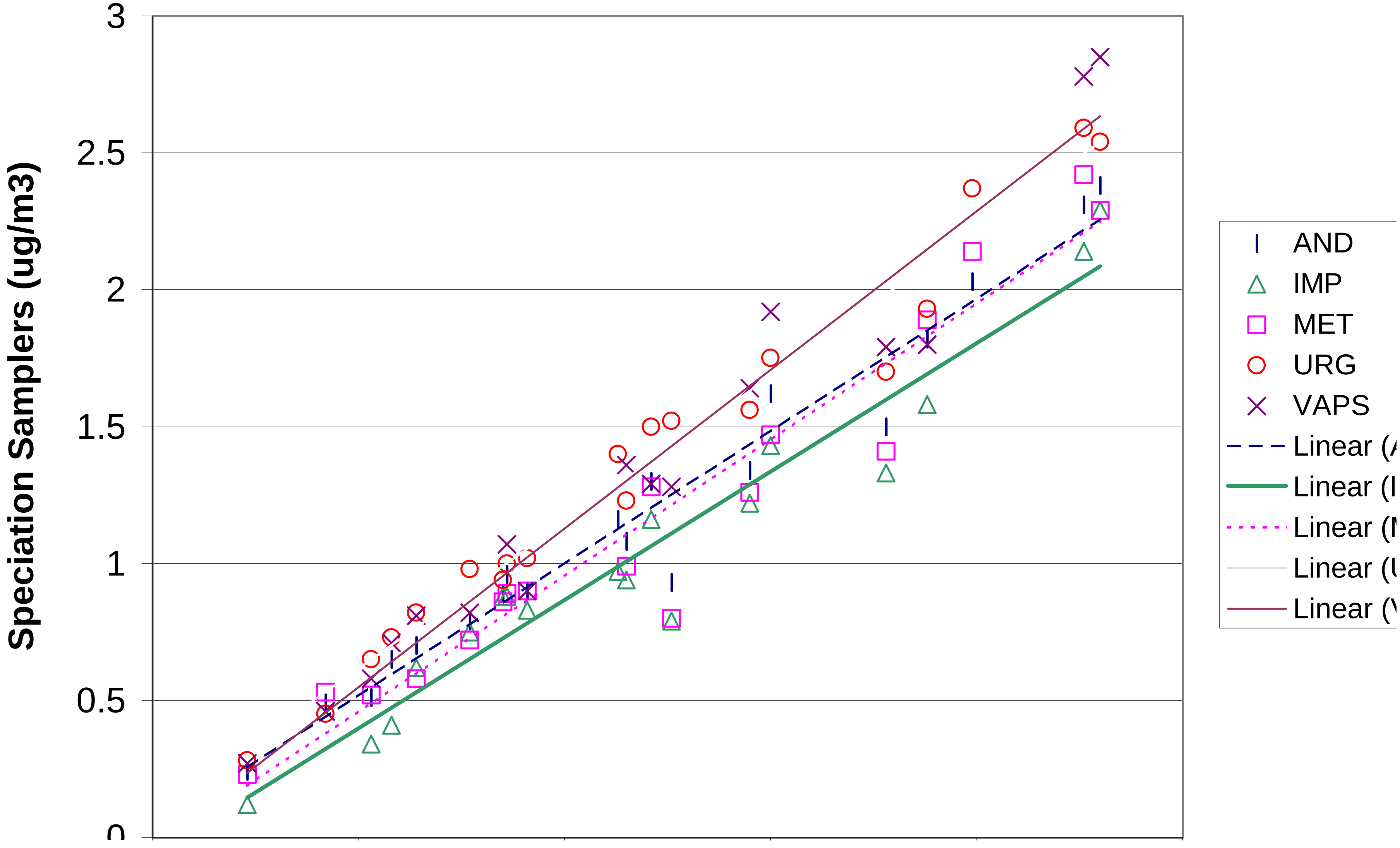
FRM vs Speciation Samplers for Particulate Ammonium at Phoenix

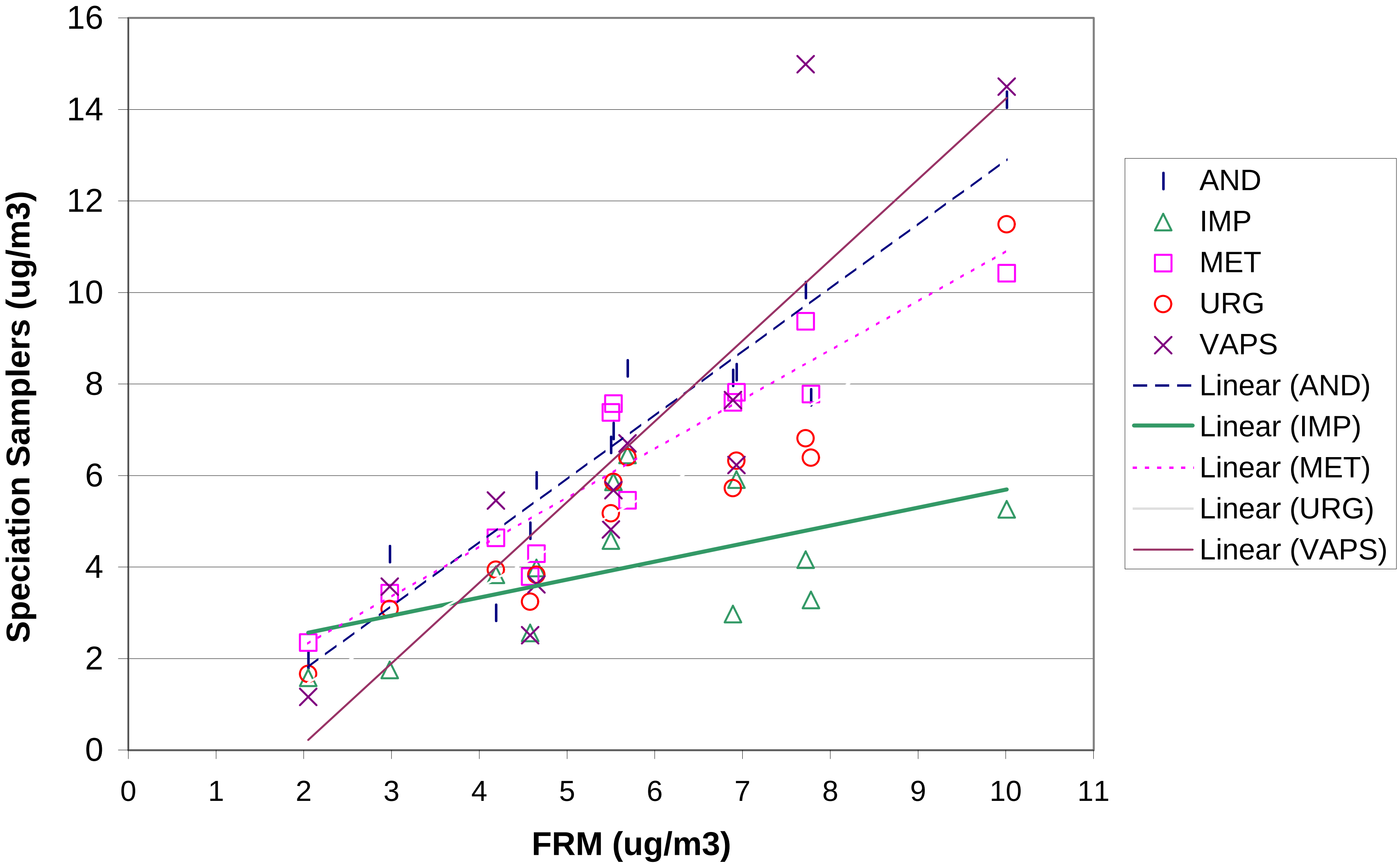


FRM vs Speciation Samplers for Particulate Ammonium at Philadelphia



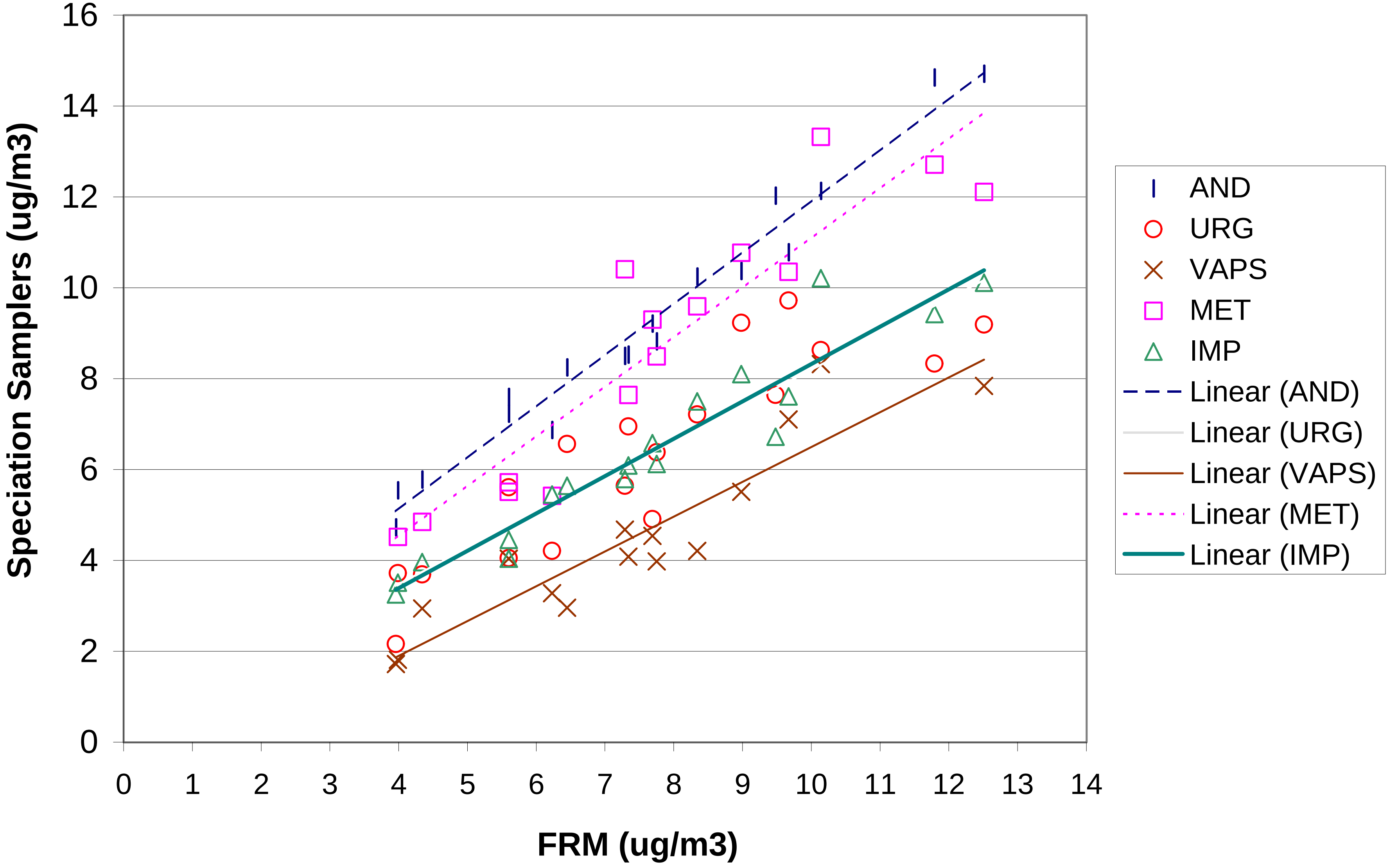
FRM vs Speciation Samplers for Particulate Ammonium at RTP



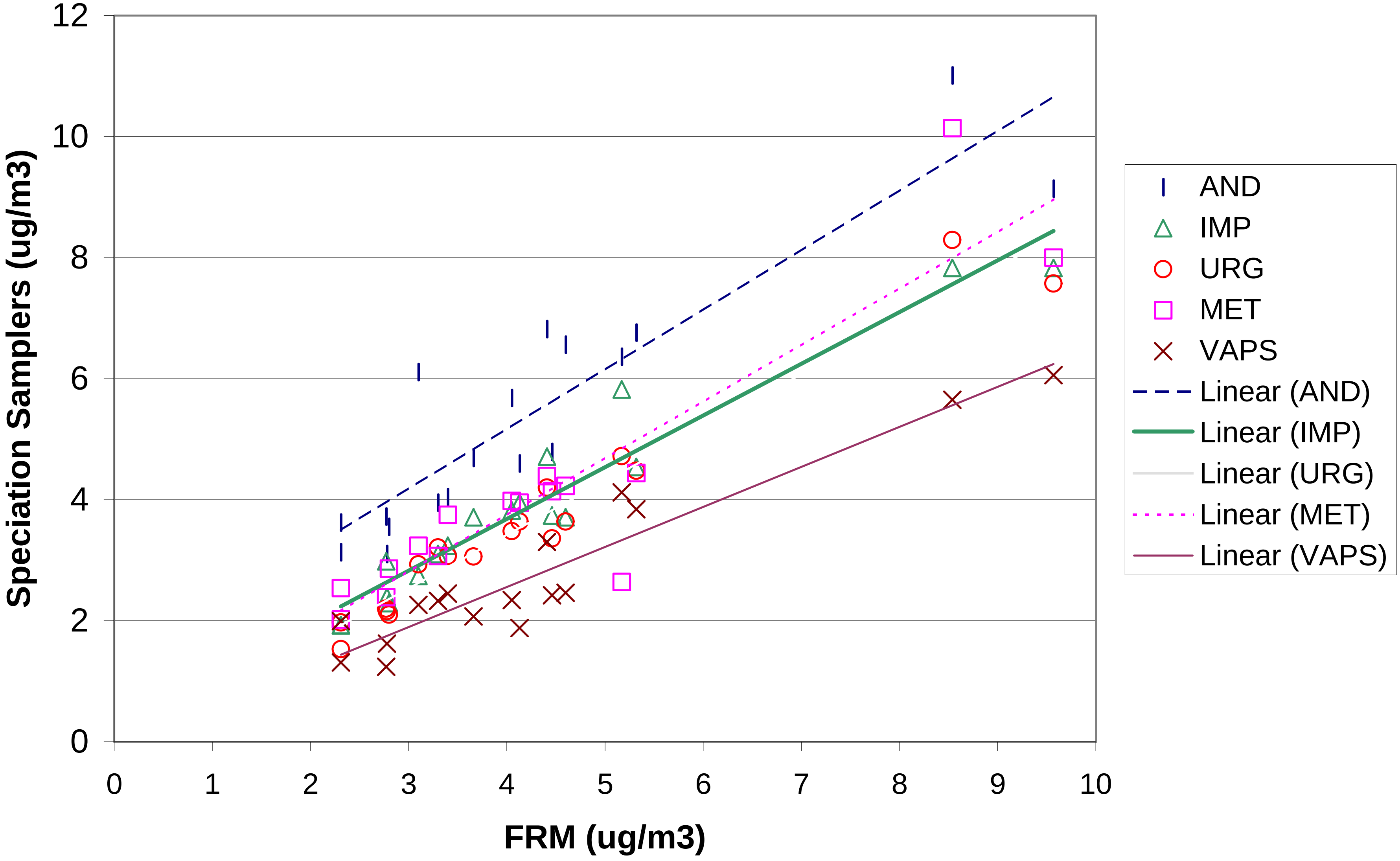


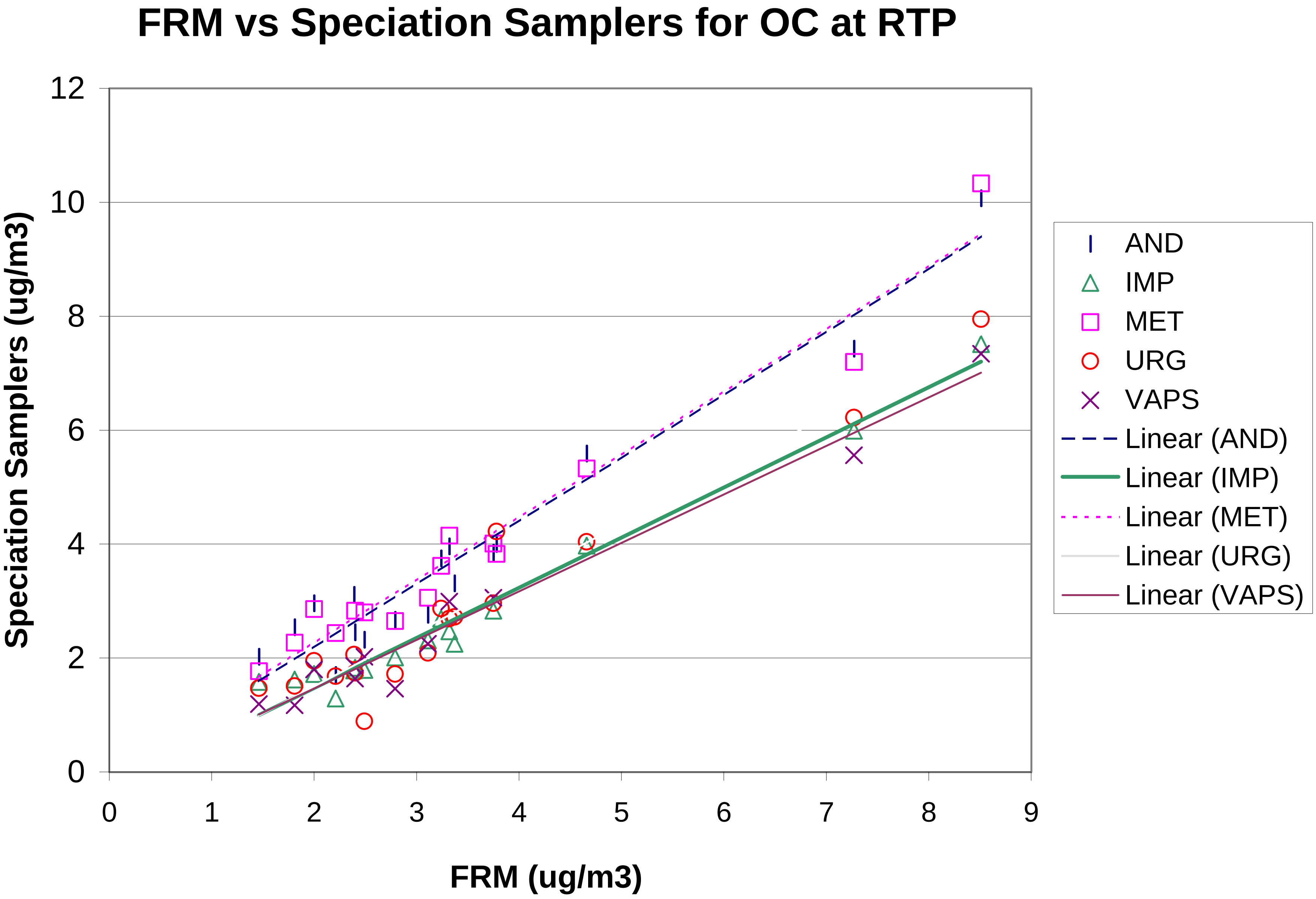
FRM vs Speciation Samplers for OC at Rubidoux

FRM vs Speciation Samplers for OC at Phoenix

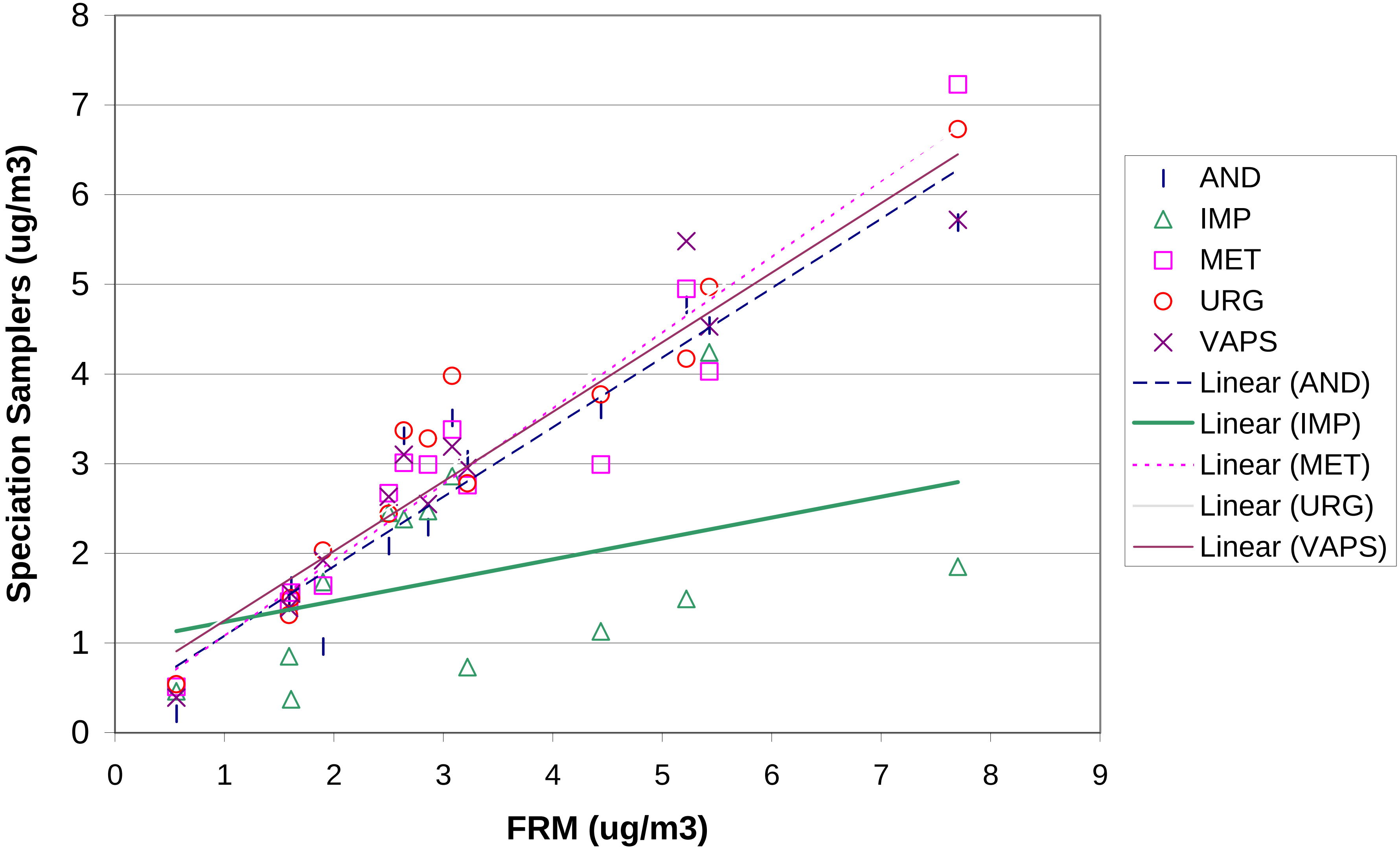


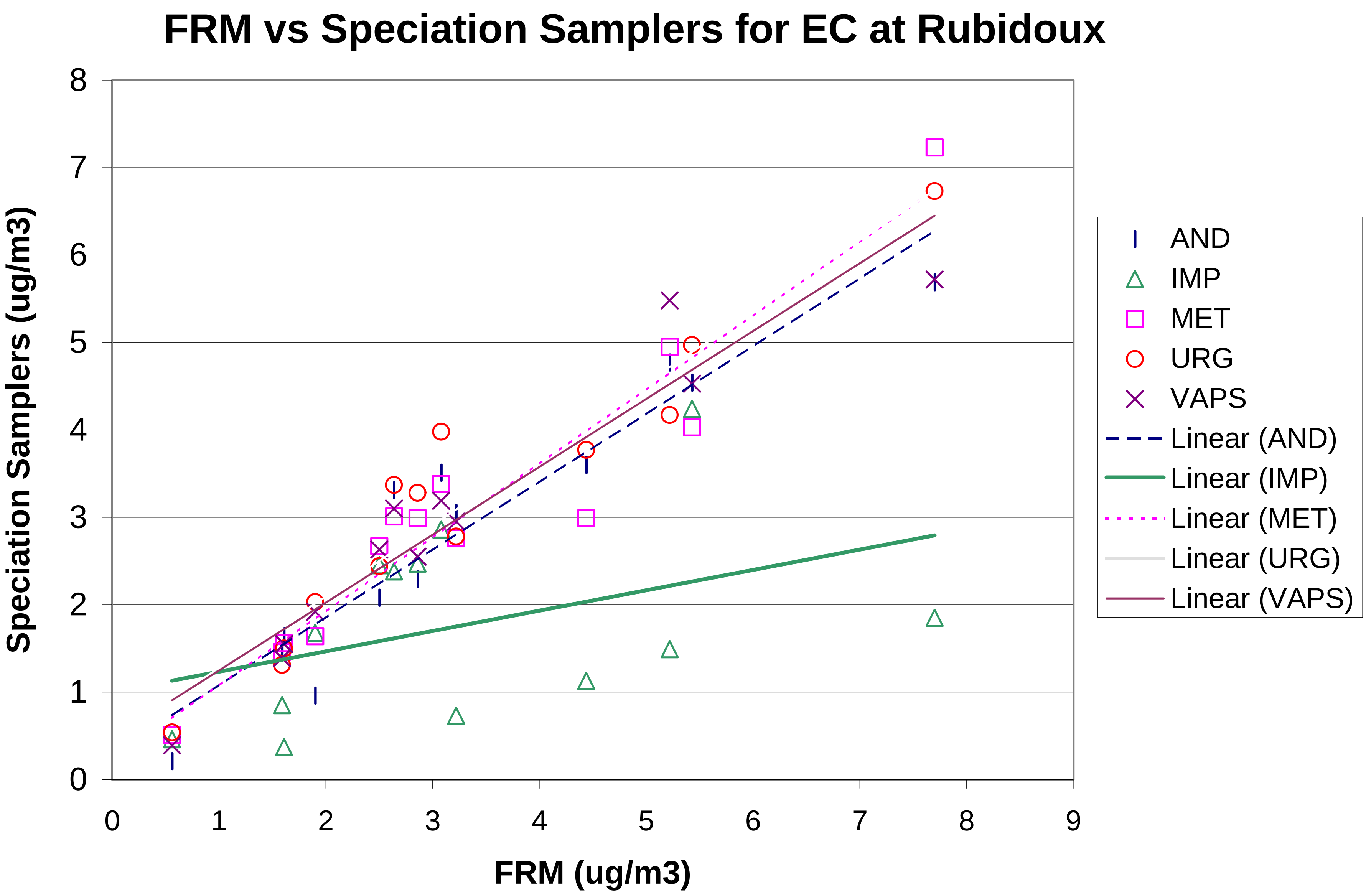
FRM vs Speciation Samplers for OC at Philadelphia



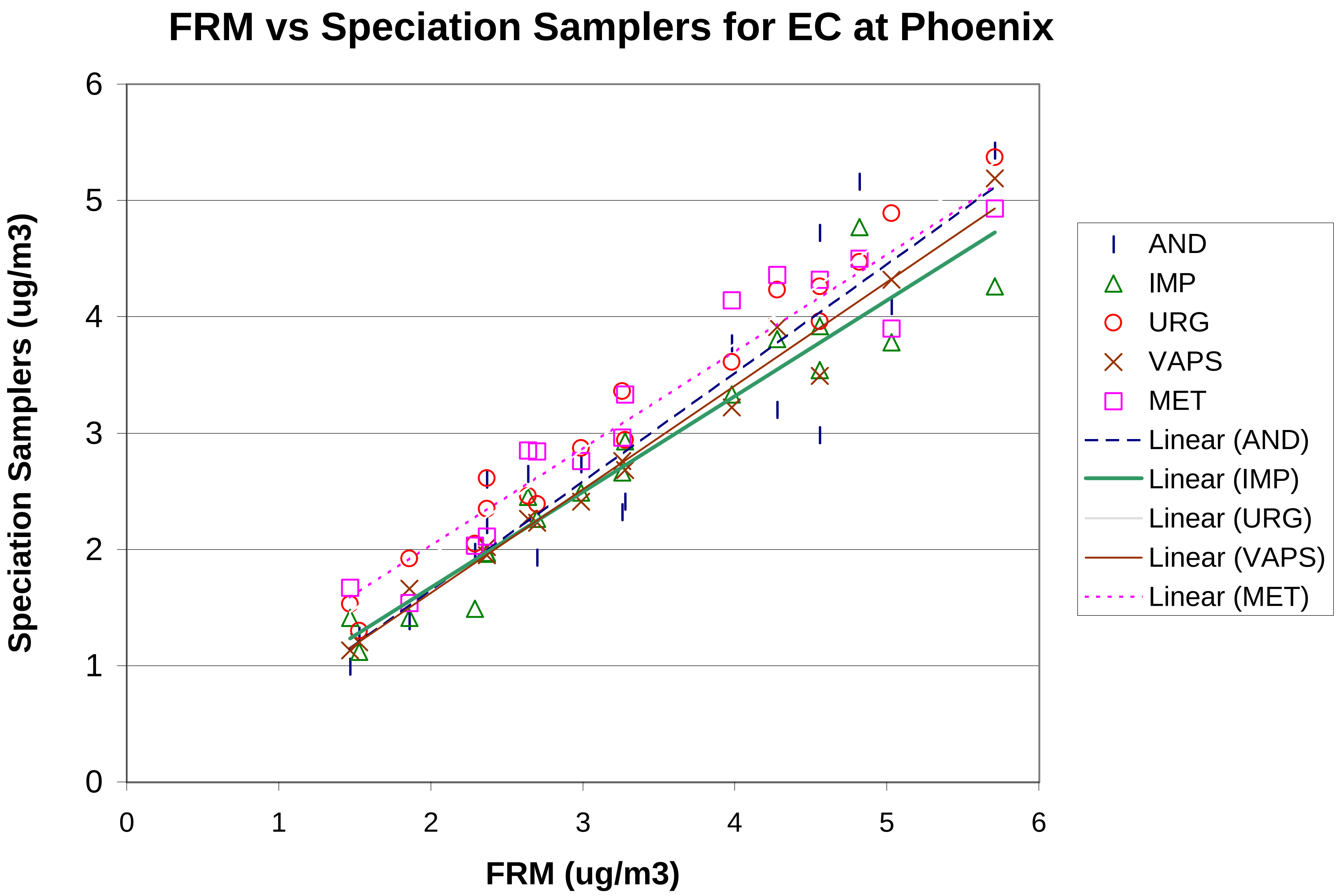

FRM vs Speciation Samplers for OC at RTP
Speciation Samplers (ug/m3)
FRM (ug/m3)
0
2
4
6
8
10
12
0
1
2
3
4
5
6
7
8
9
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

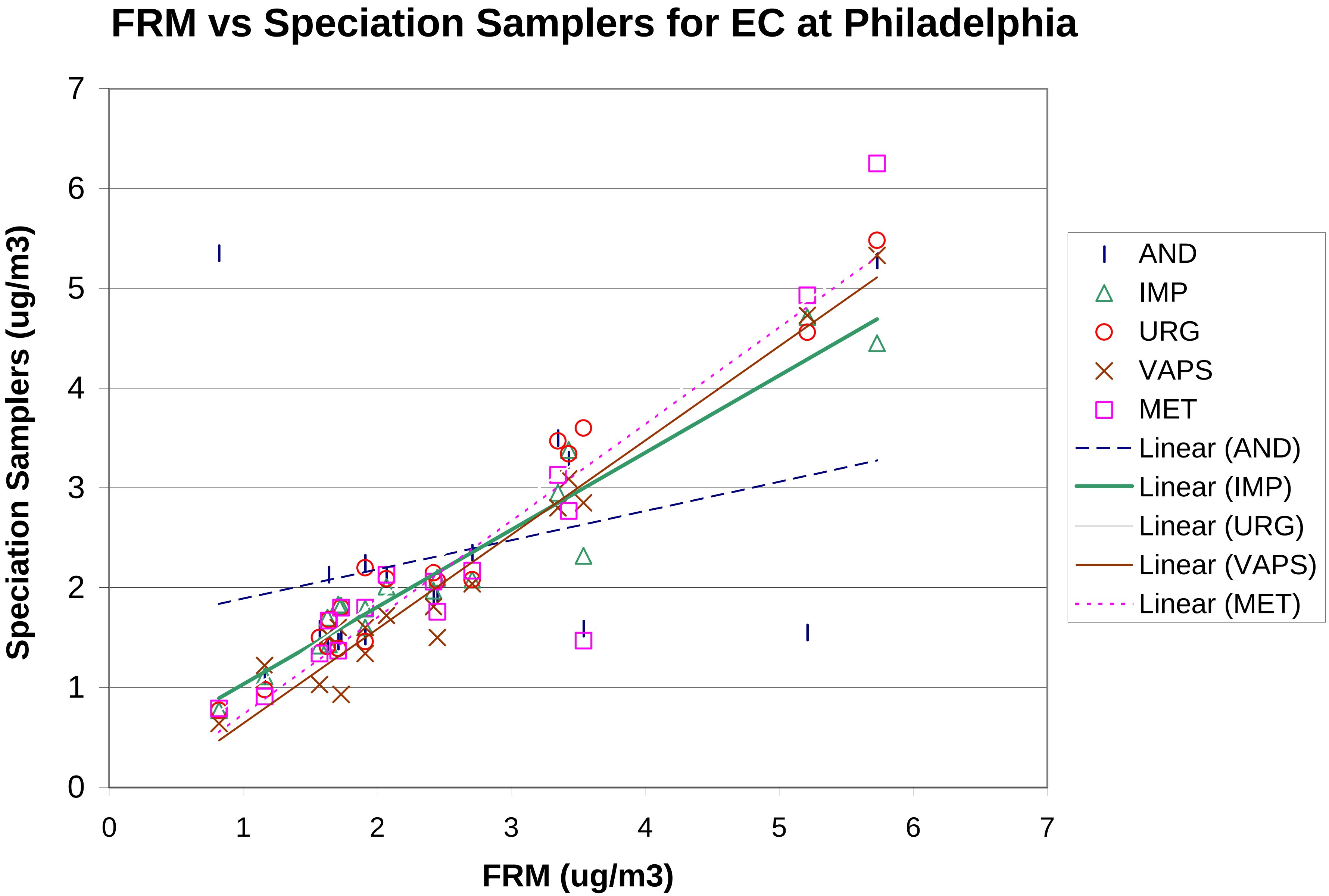
FRM vs Speciation Samplers for EC at Rubidoux

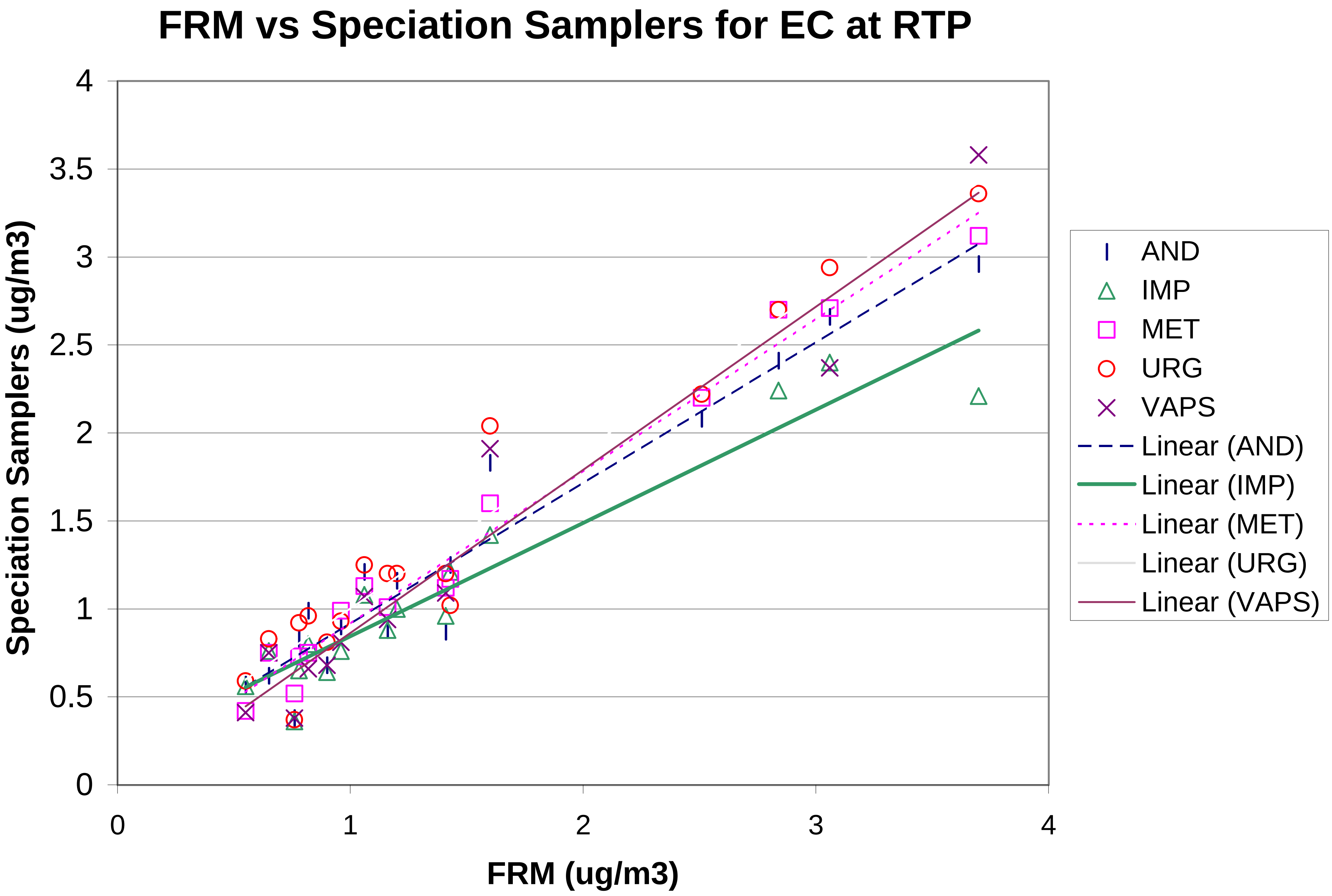


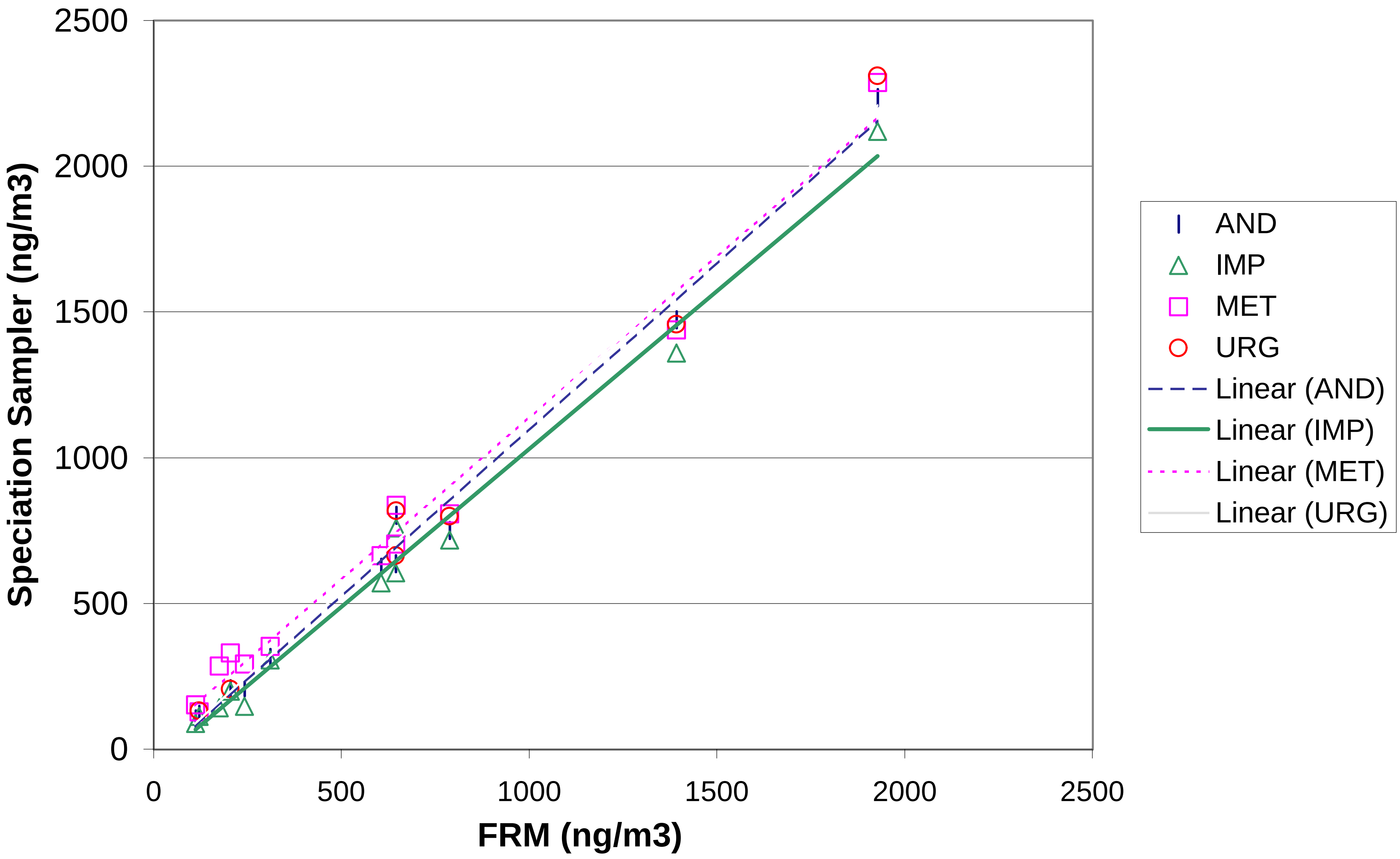


FRM vs Speciation Samplers for EC at Rubidoux


FRM vs Speciation Samplers for EC at Phoenix
Speciation Samplers (ug/m3)
FRM (ug/m3)
0
1
2
3
4
5
6
AND
IMP
URG
VAPS
MET
Linear (AND)
Linear (IMP)
Linear (URG)
Linear (VAPS)
Linear (MET)

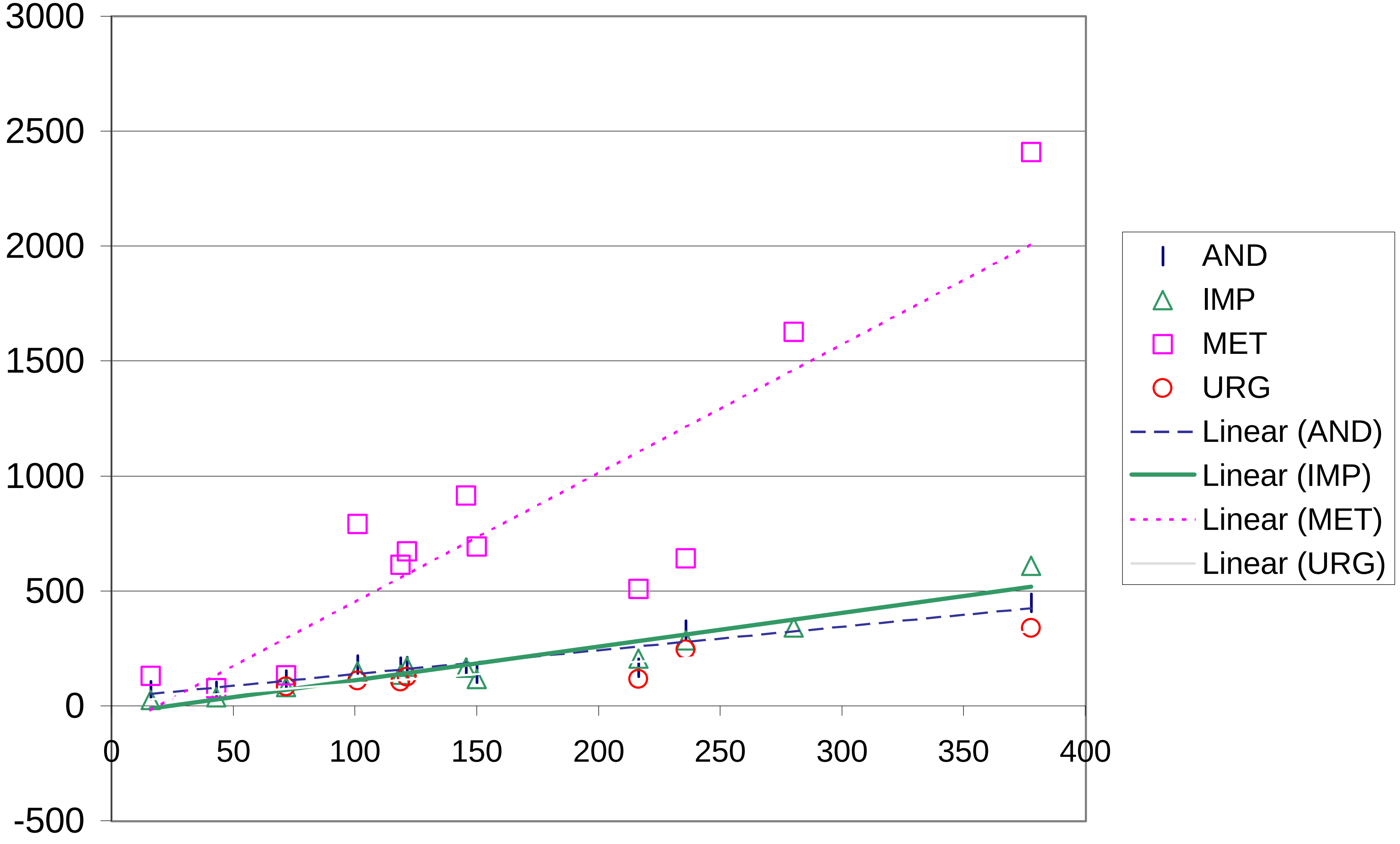

FRM vs Speciation Samplers for EC at Philadelphia
Speciation Samplers (ug/m3)
FRM (ug/m3)
0
1
2
3
4
5
6
7
AND
IMP
URG
VAPS
MET
Linear (AND)
Linear (IMP)
Linear (URG)
Linear (VAPS)
Linear (MET)

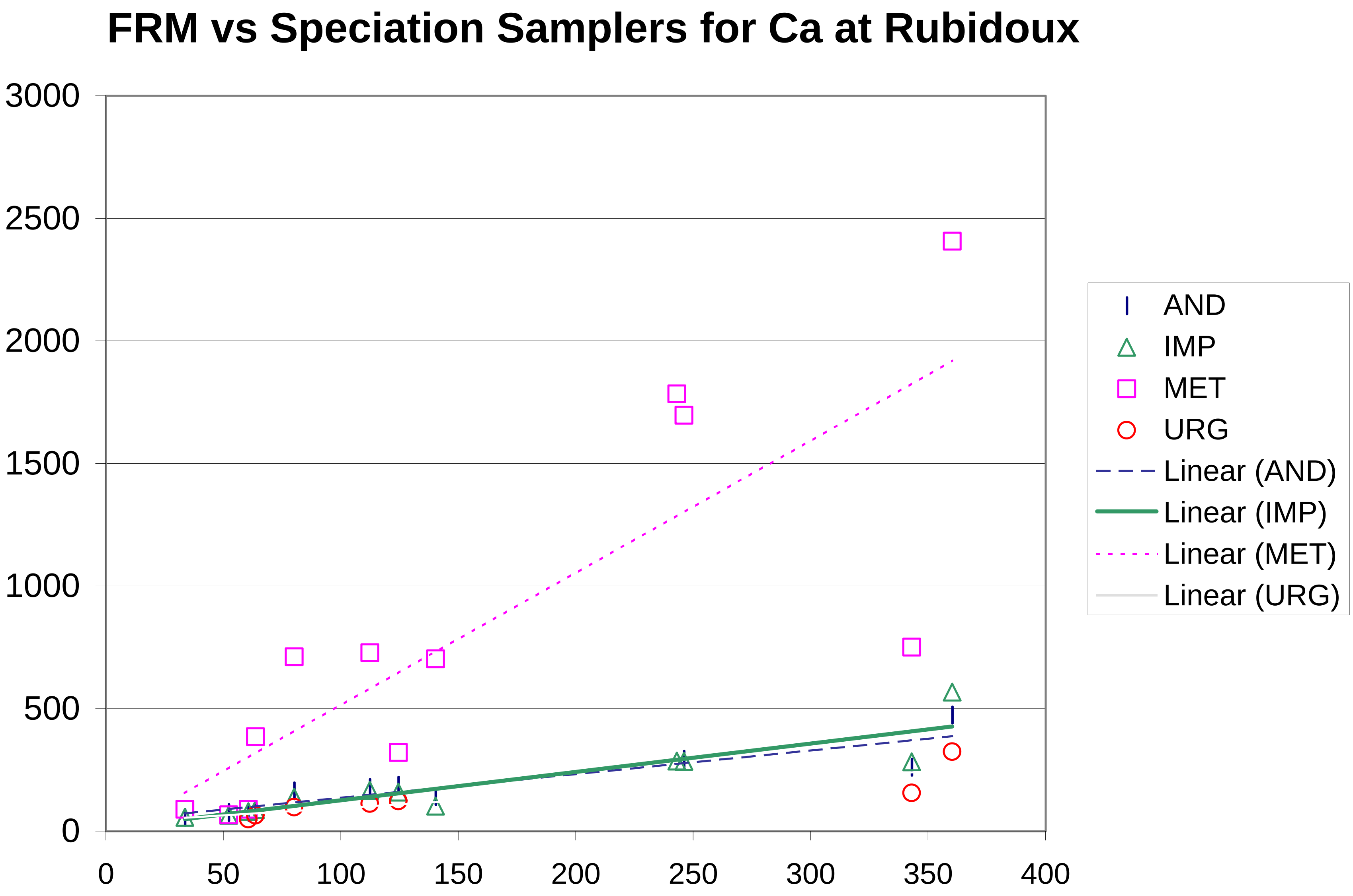

FRM vs Speciation Samplers for EC at RTP
Speciation Samplers (ug/m3)
0
0.5
1
1.5
2
2.5
3
3.5
4
FRM (ug/m3)
0
1
2
3
4
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

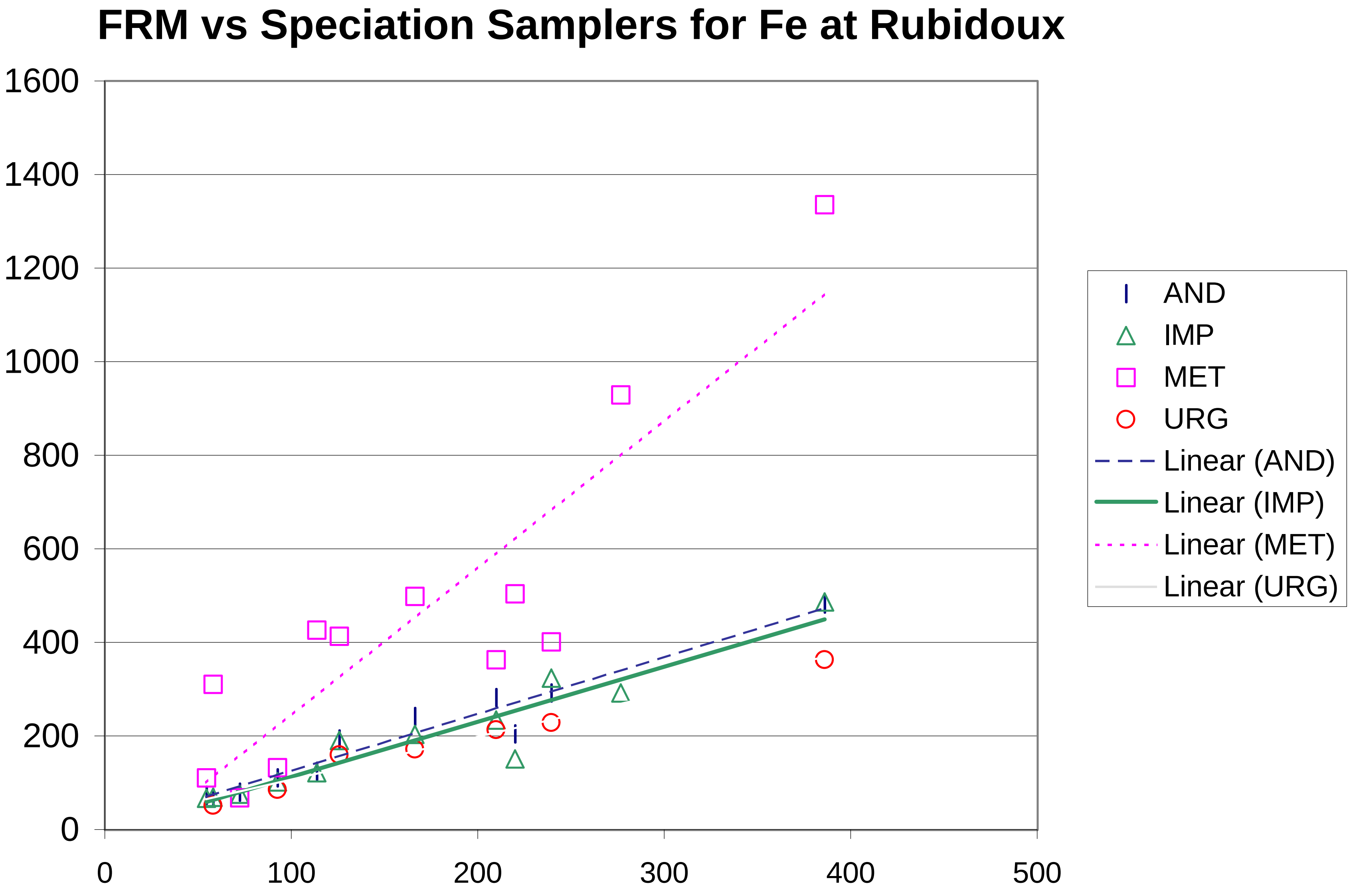


FRM vs Speciation Samplers for Sulfur at Rubidoux

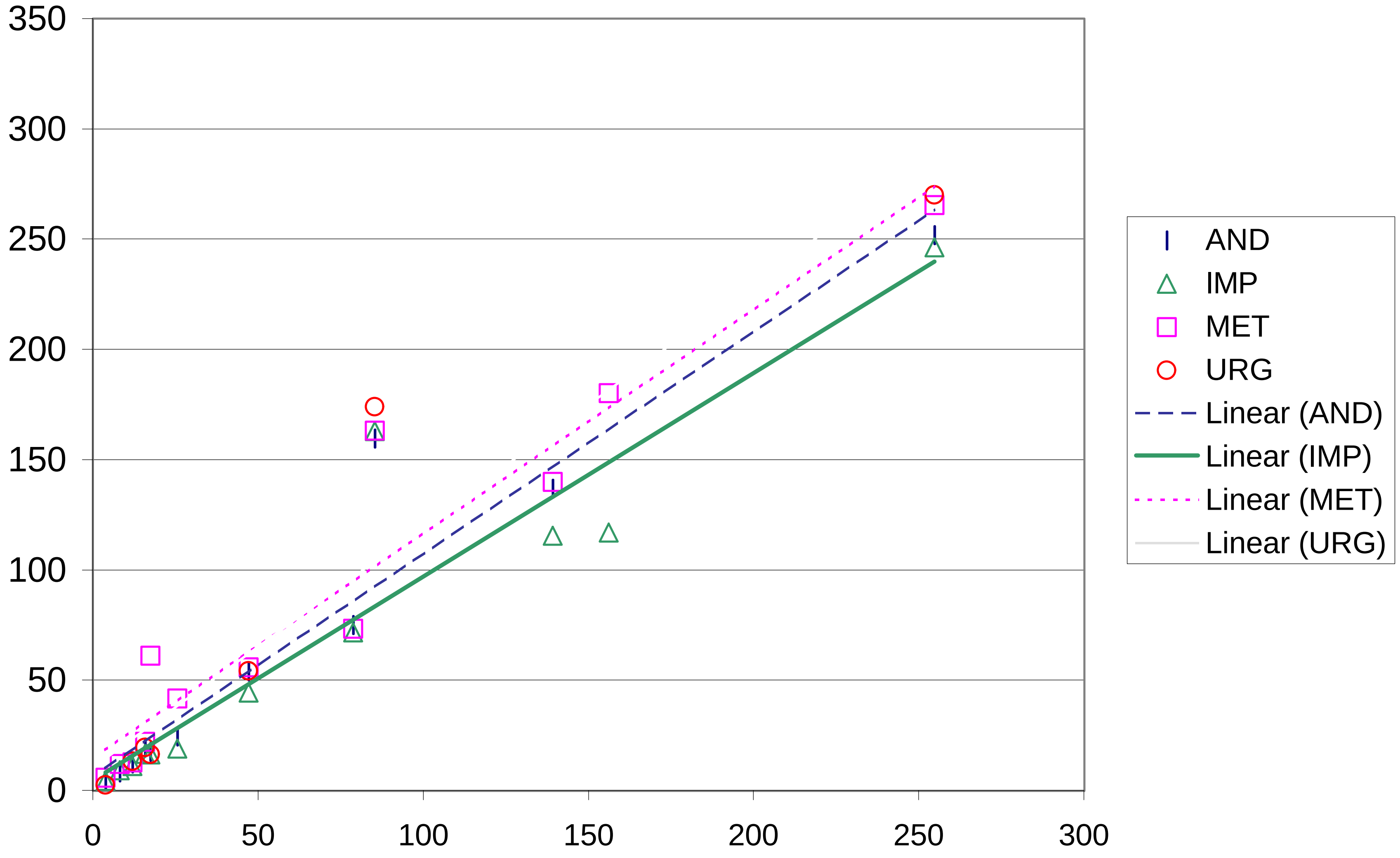
FRM vs Speciation Samplers for Si at Rubidoux

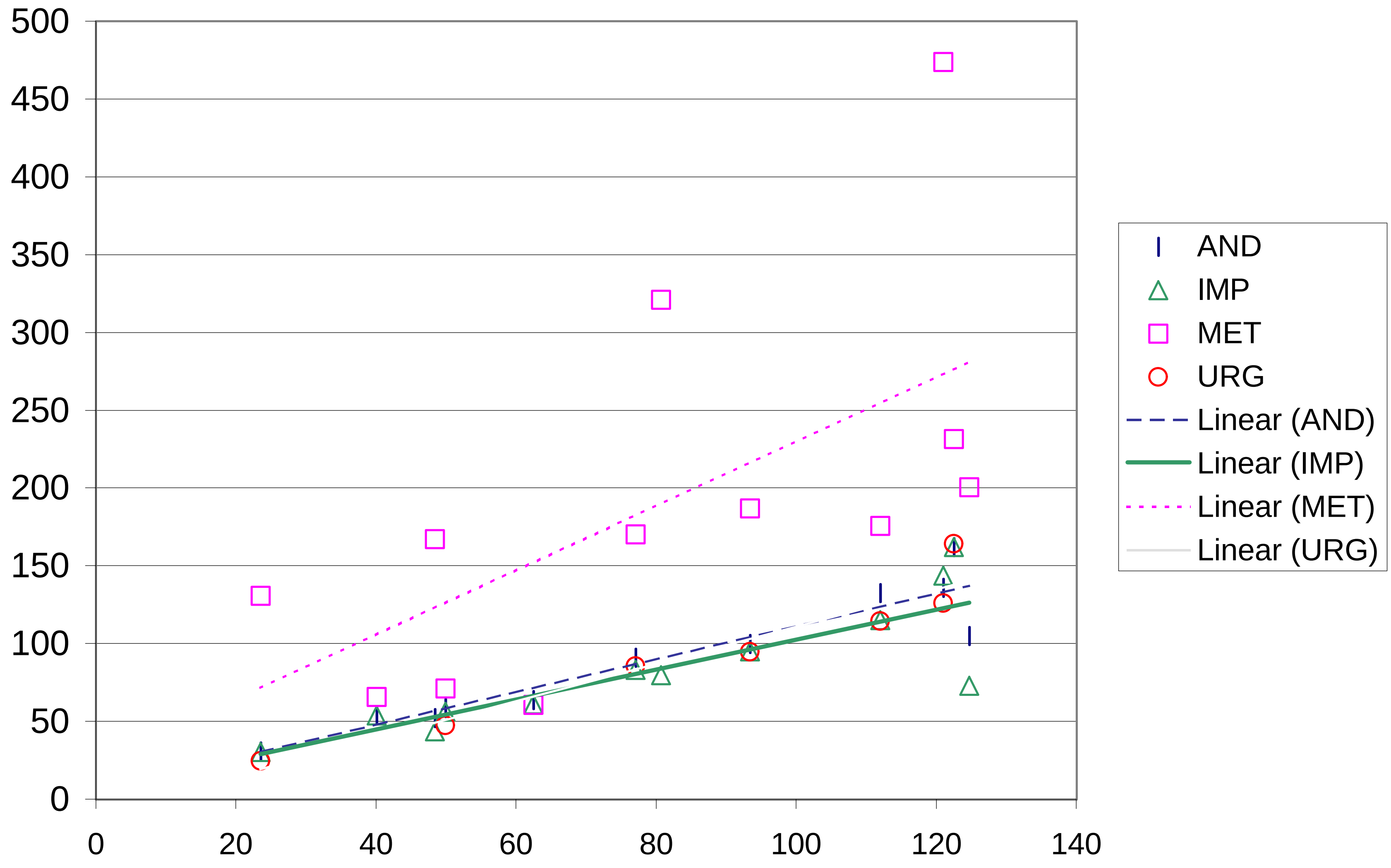



FRM vs Speciation Samplers for Ca at Rubidoux

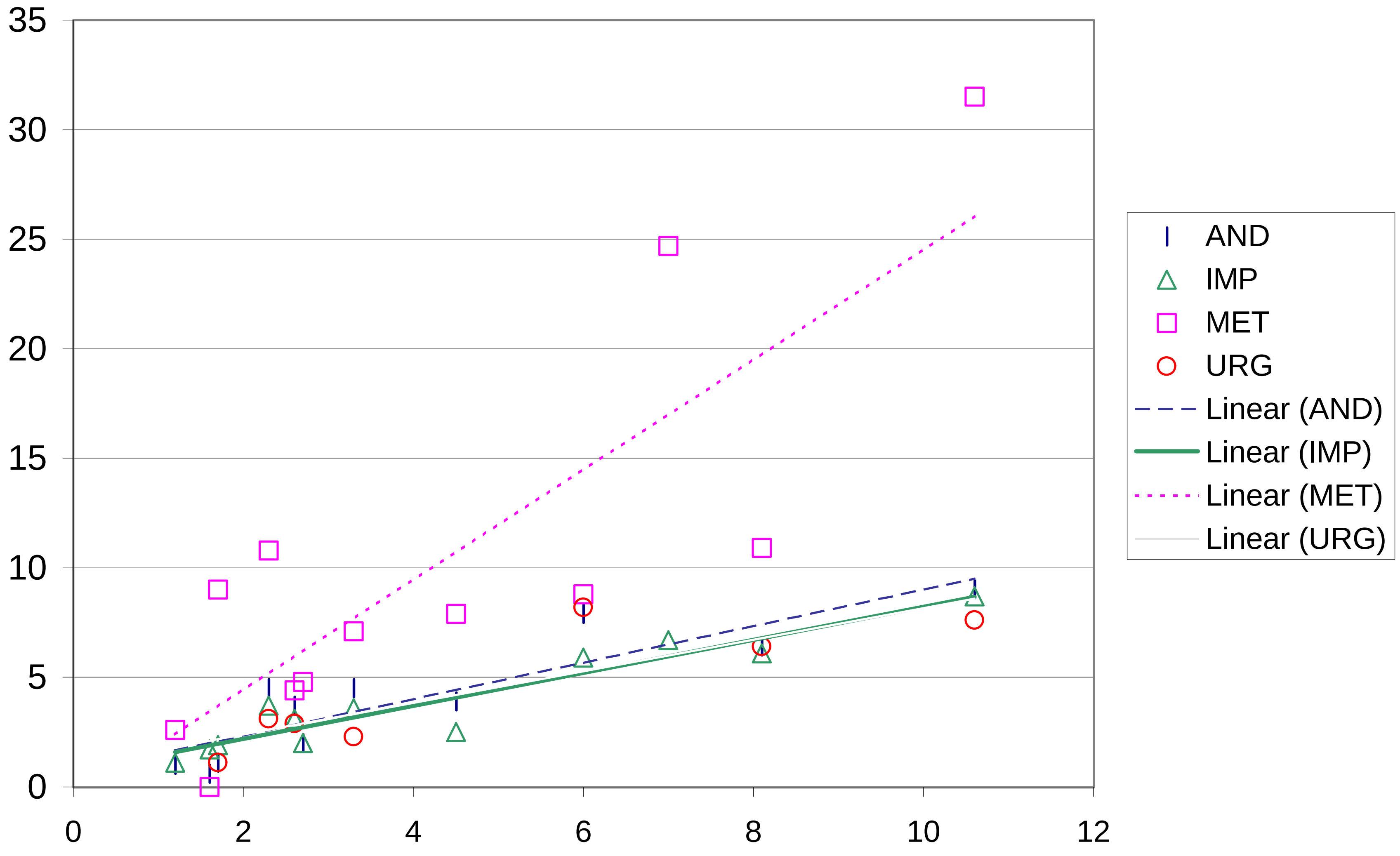

FRM vs Speciation Samplers for Fe at Rubidoux
1600
1400
1200
1000
800
600
400
200
0
0
100
200
300
400
500
AND
IMP
MET
URG
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)

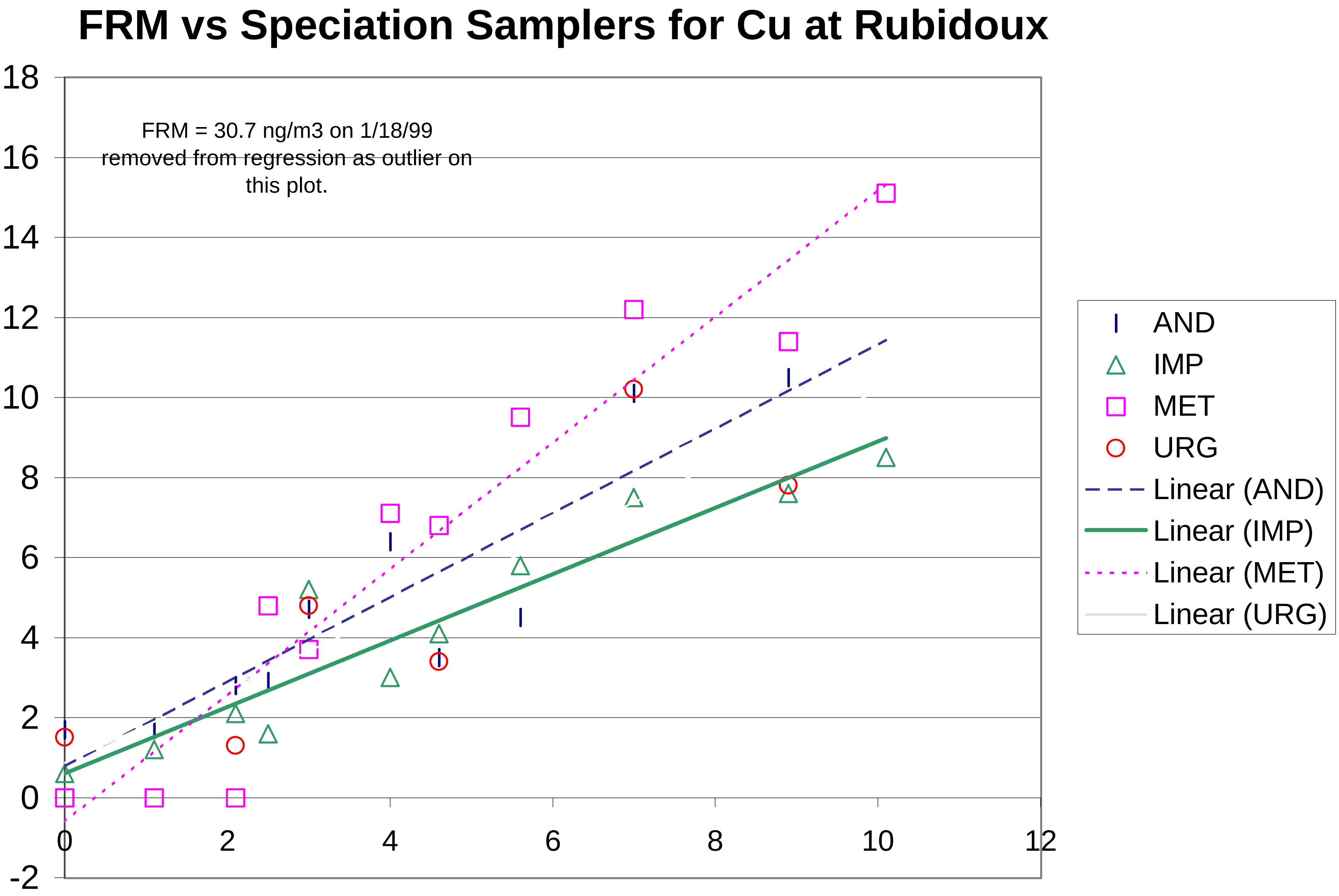
FRM vs Speciation Samplers for Zn at Rubidoux




FRM vs Speciation Samplers for K at Rubidoux

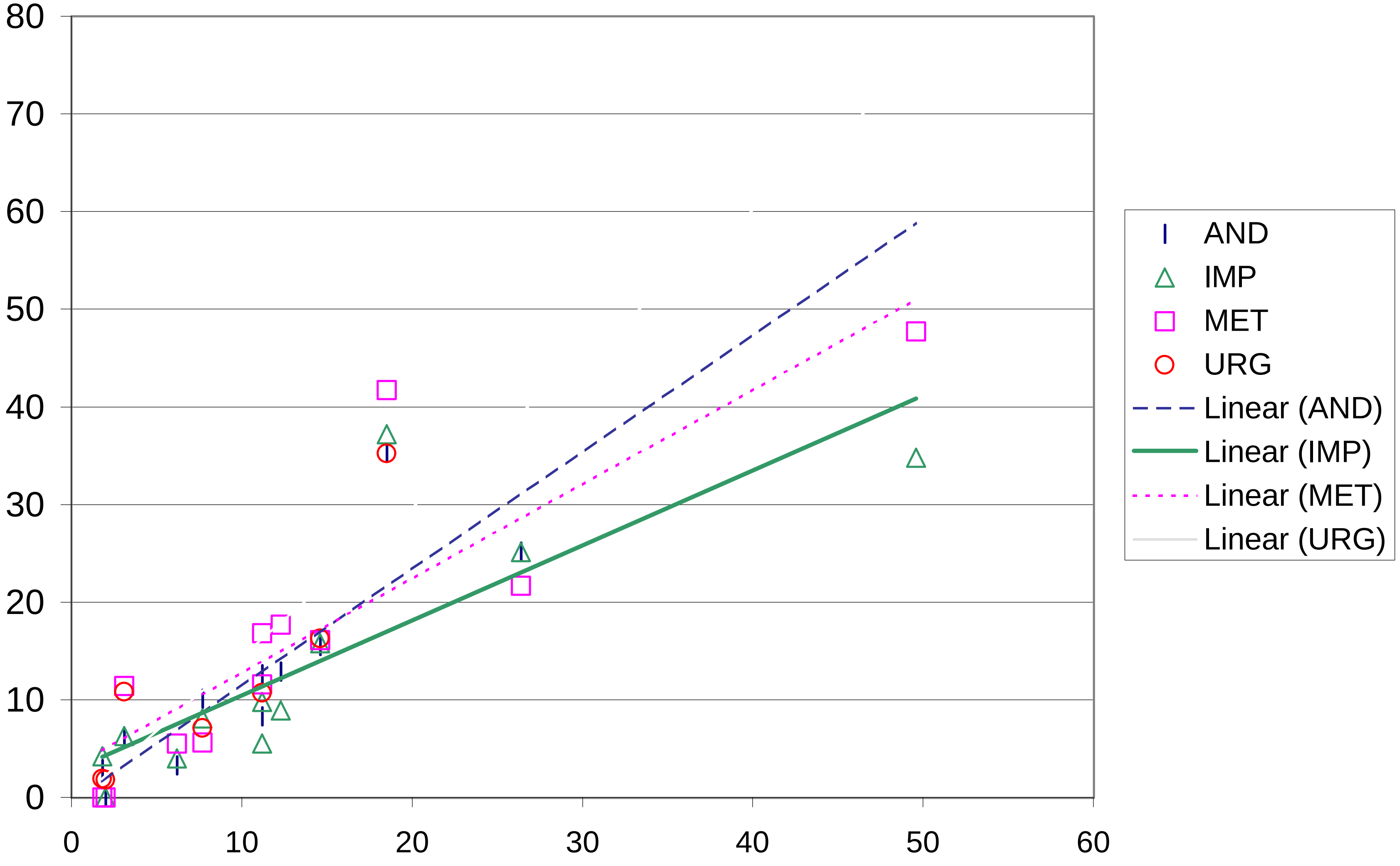
FRM vs Speciation Samplers for Mn at Rubidoux

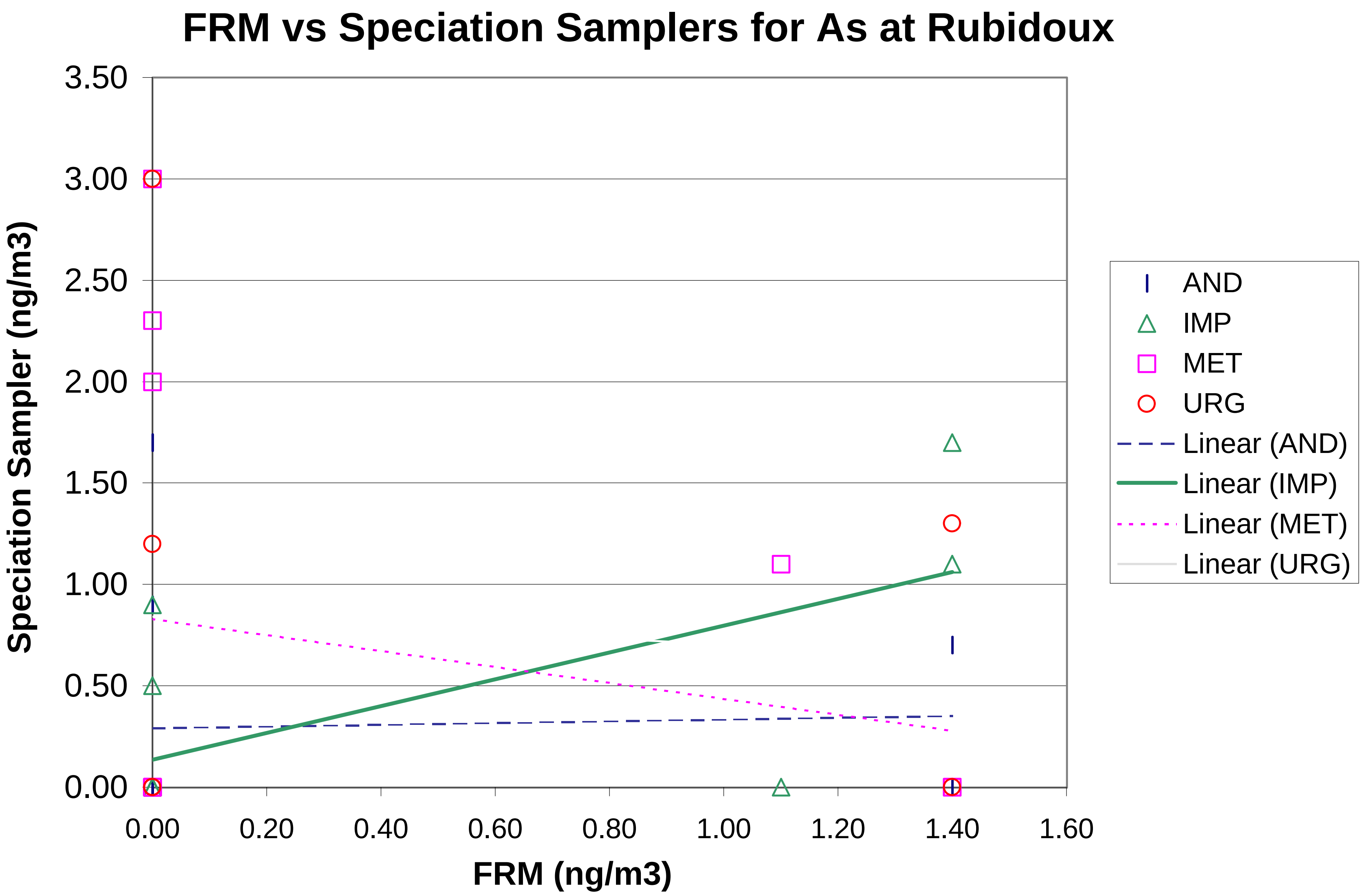




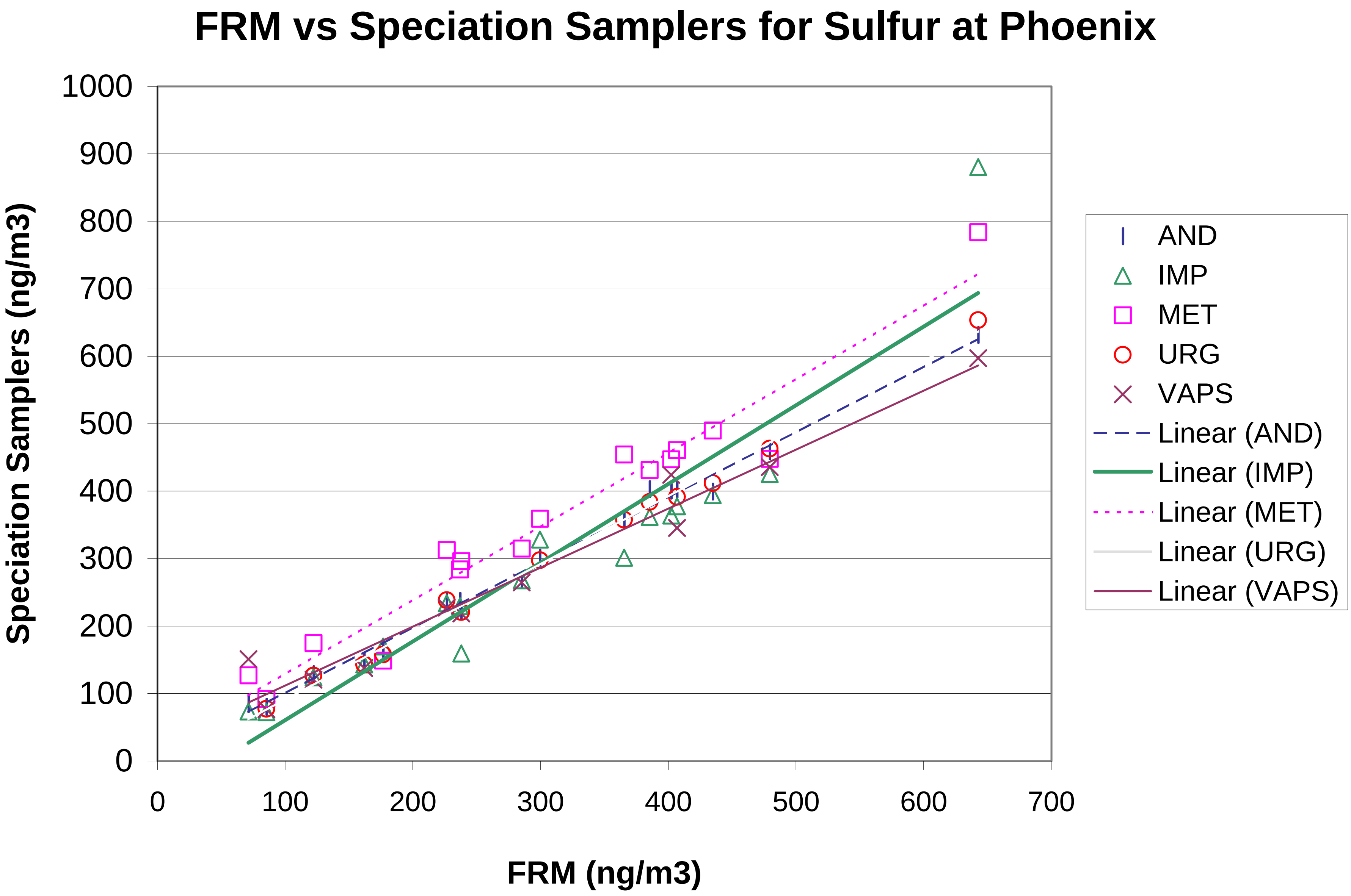
FRM vs Speciation Samplers for Cu at Rubidoux
FRM = 30.7 ng/m3 on 1/18/99 removed from regression as outlier on this plot.
18
16
14
12
10
8
6
4
2
0
-2
0
2
4
6
8
10
12
AND
IMP
MET
URG
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)

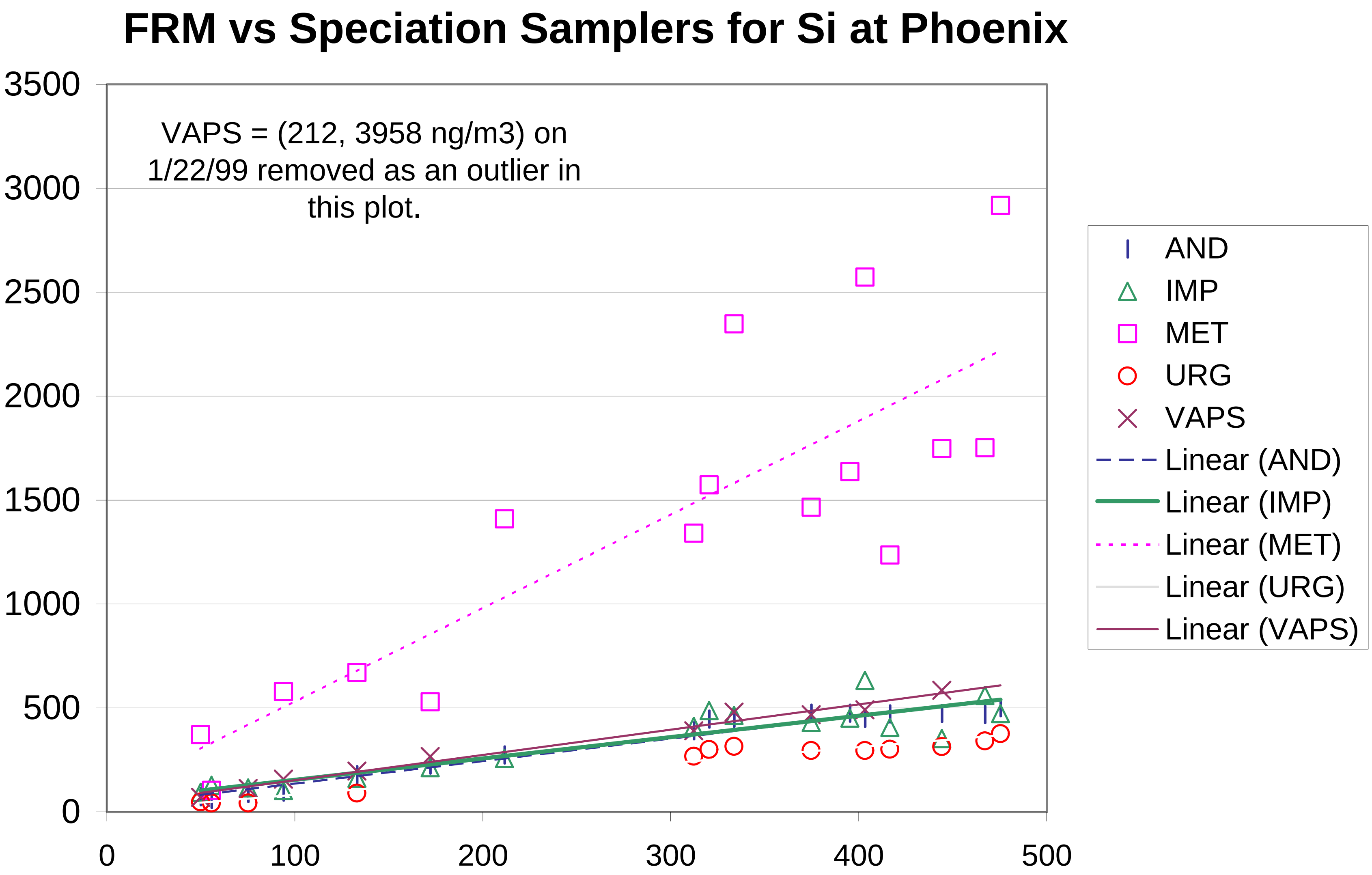
FRM vs Speciation Samplers for Pb at Rubidoux



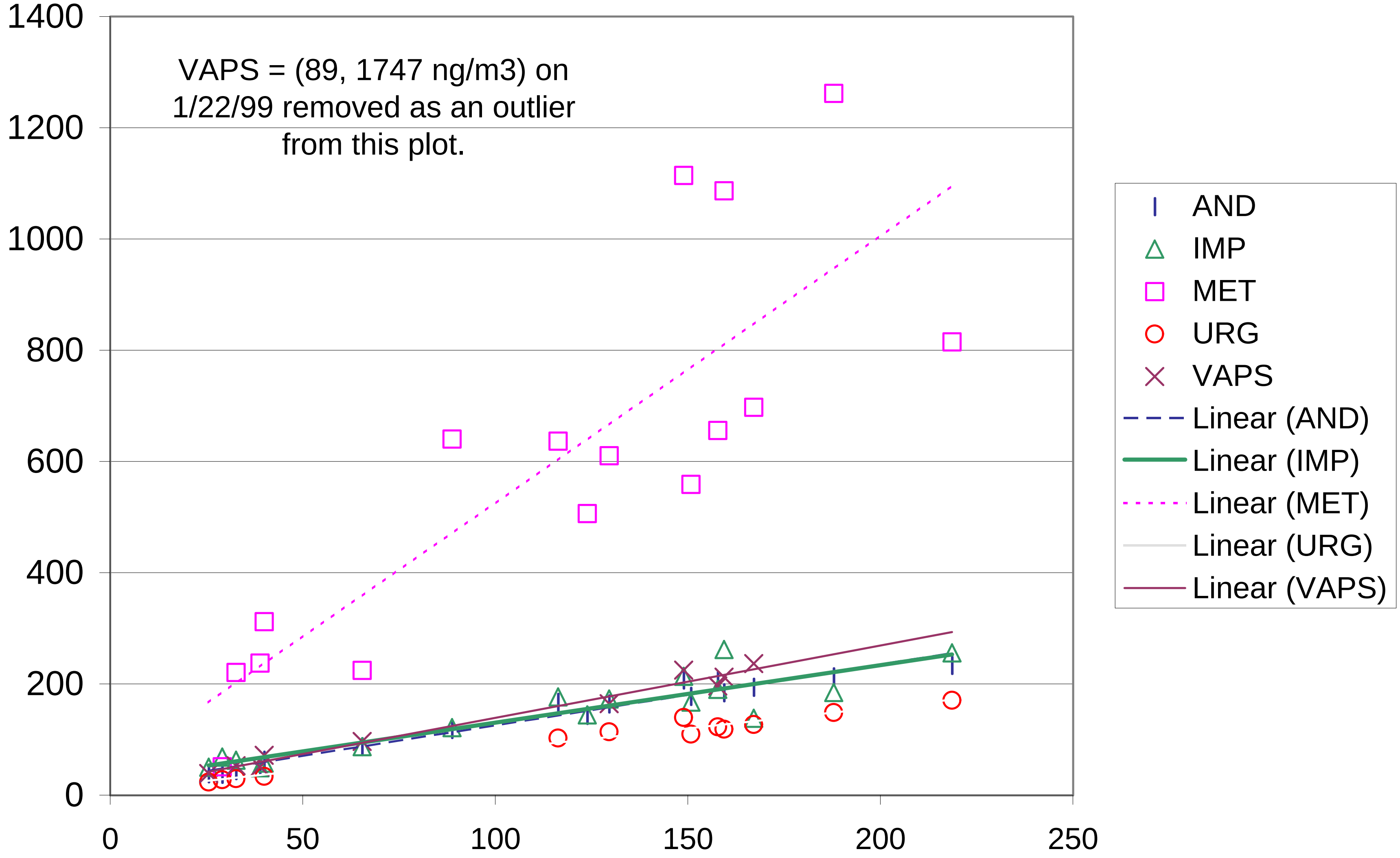


FRM vs Speciation Samplers for As at Rubidoux
Speciation Sampler (ng/m3)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
FRM (ng/m3)
AND
IMP
MET
URG
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)


FRM vs Speciation Samplers for Sulfur at Phoenix
Speciation Samplers (ng/m3)
1000
900
800
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
700
FRM (ng/m3)
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

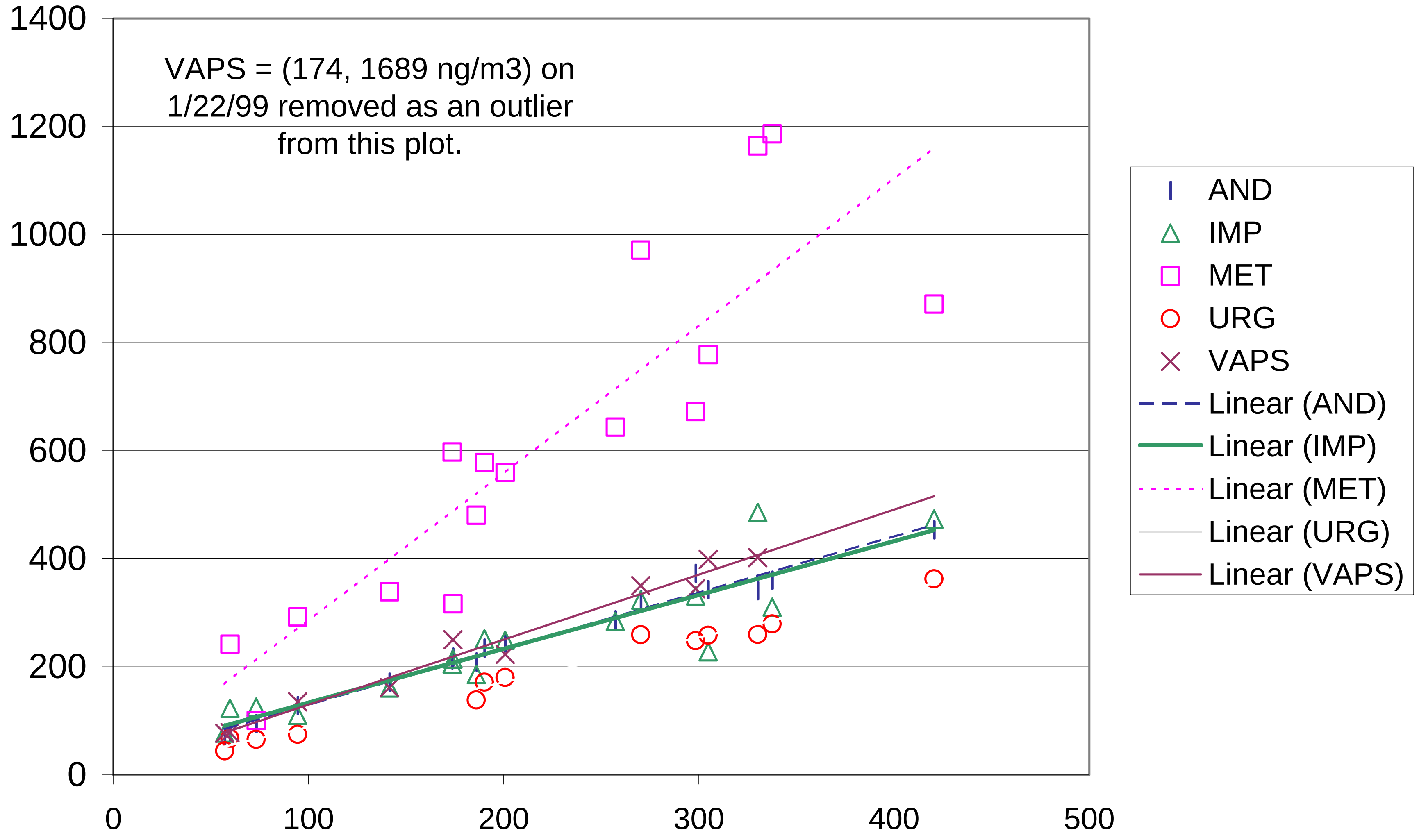

FRM vs Speciation Samplers for Si at Phoenix
VAPS = (212, 3958 ng/m3) on 1/22/99 removed as an outlier in this plot.
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

FRM vs Speciation Samplers for Ca at Phoenix

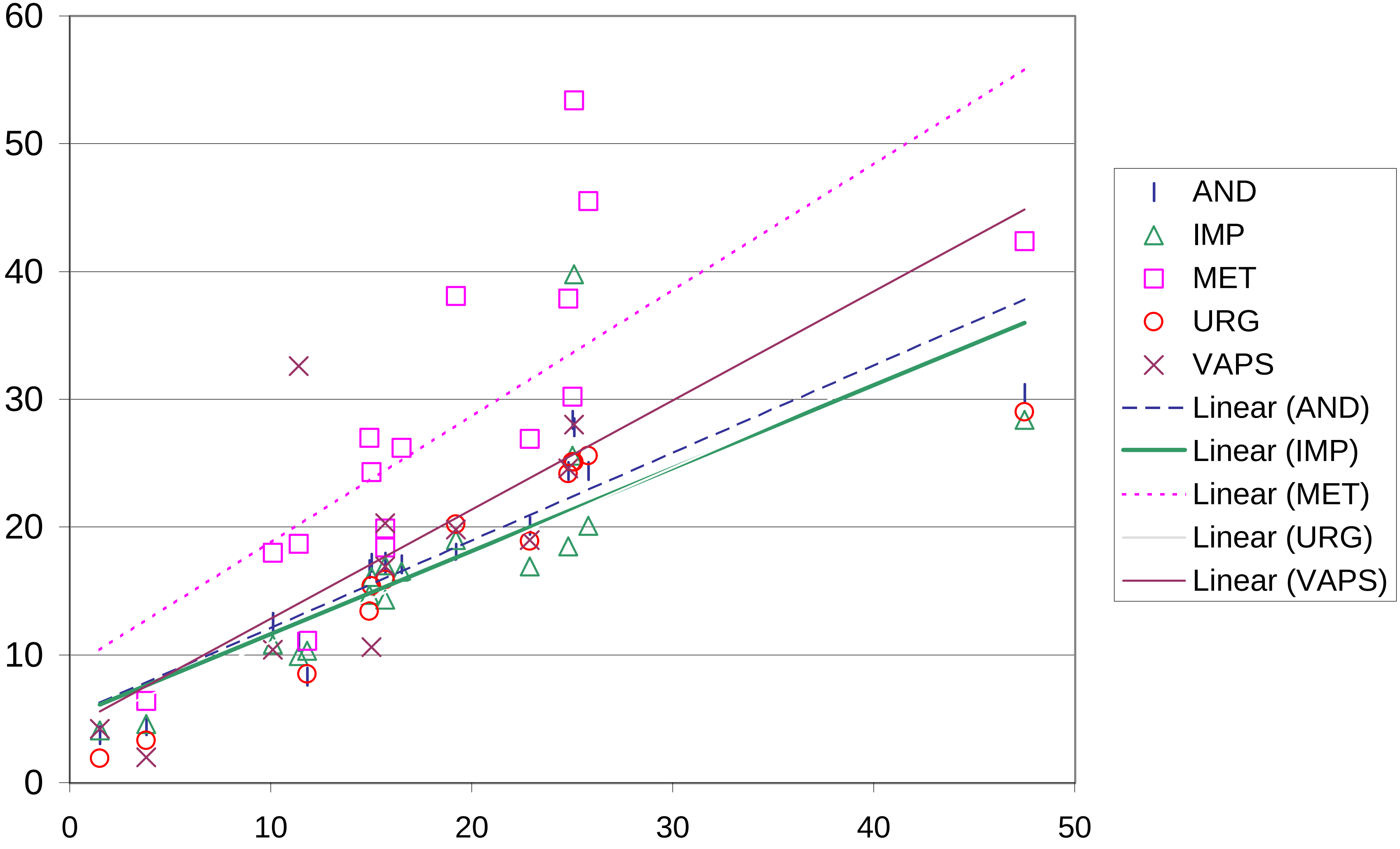


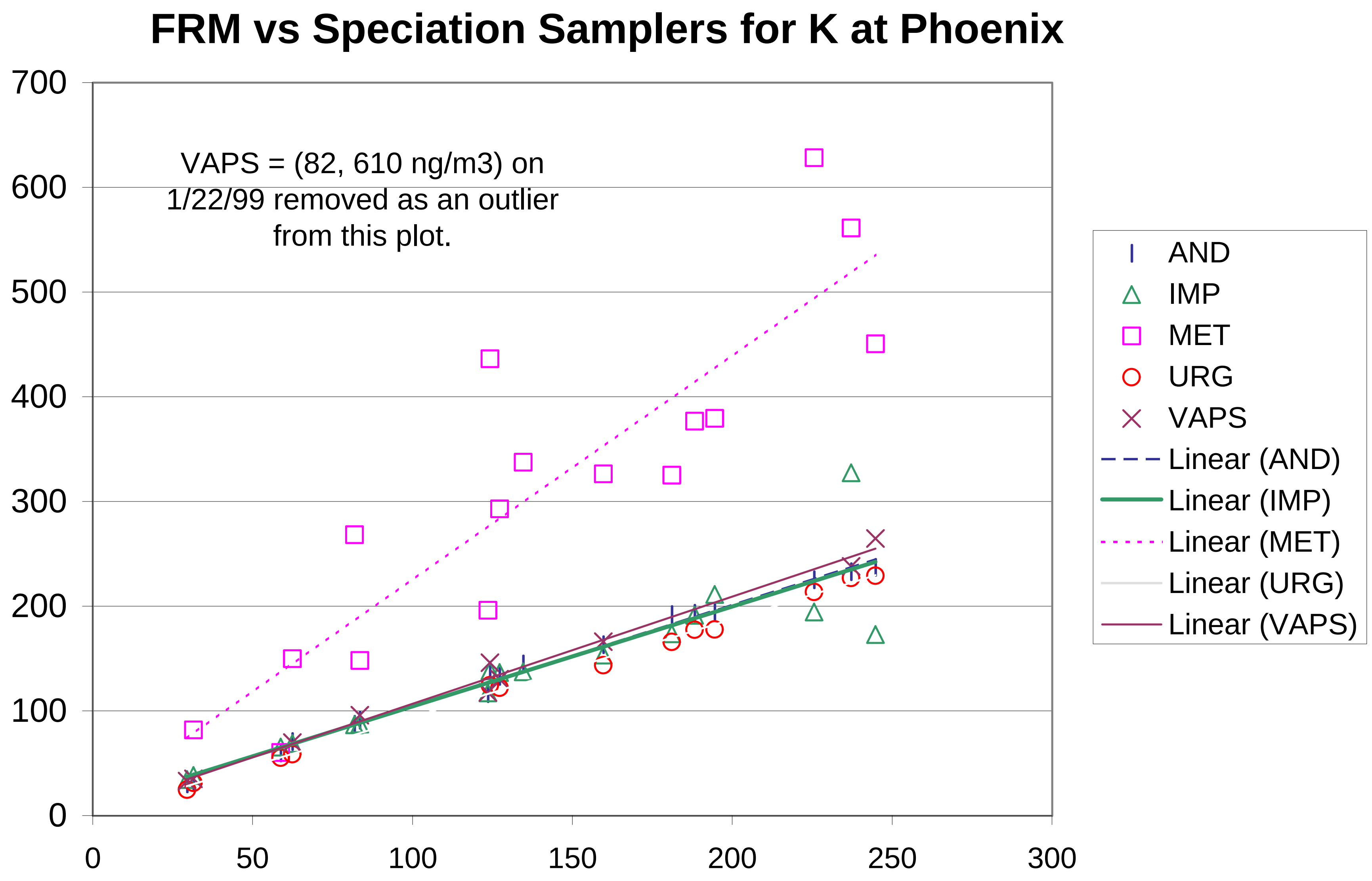
VAPS = (89, 1747 ng/m3) on 1/22/99 removed as an outlier from this plot.

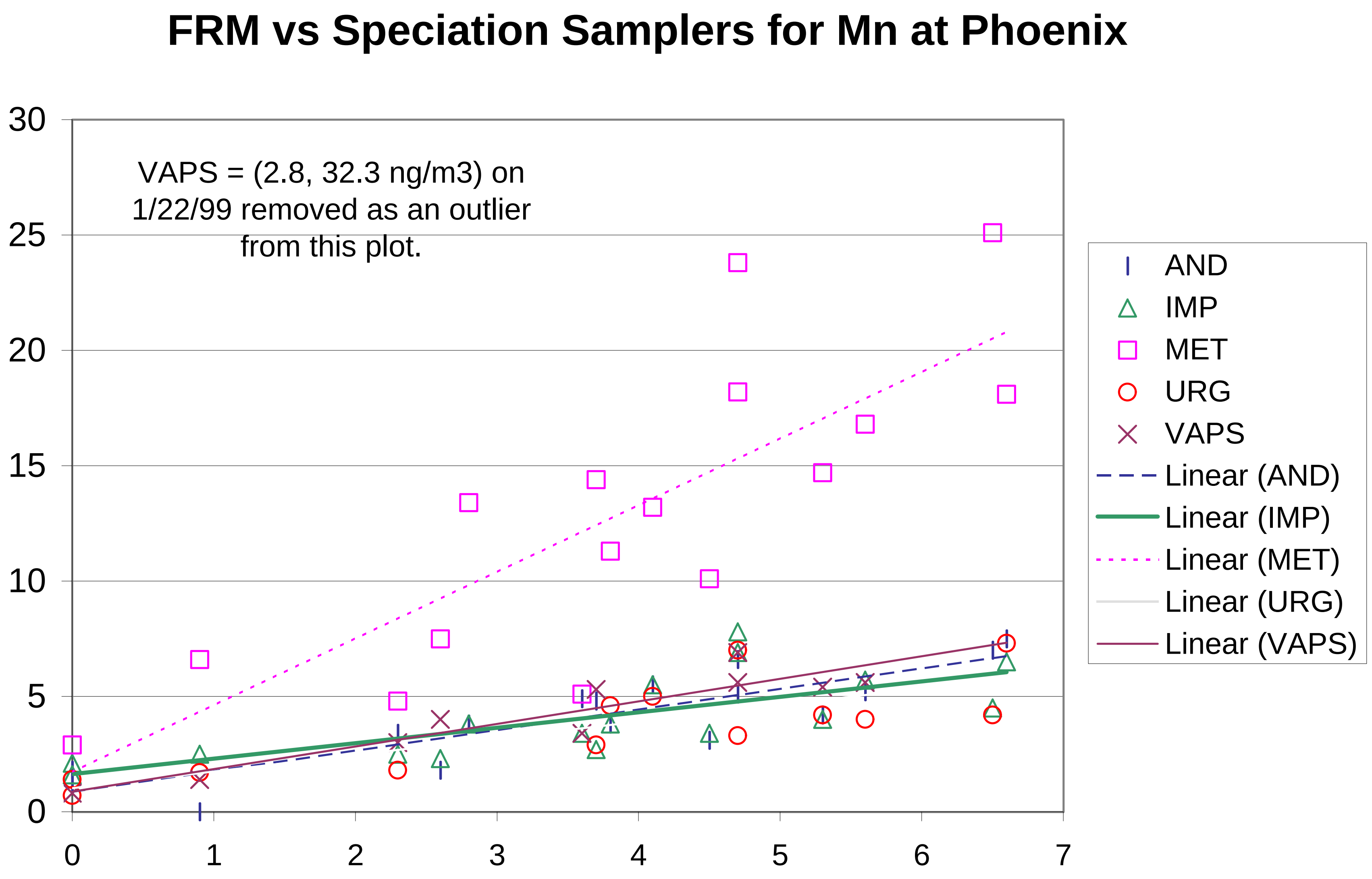
FRM vs Speciation Samplers for Fe at Phoenix



FRM vs Speciation Samplers for Zn at Phoenix



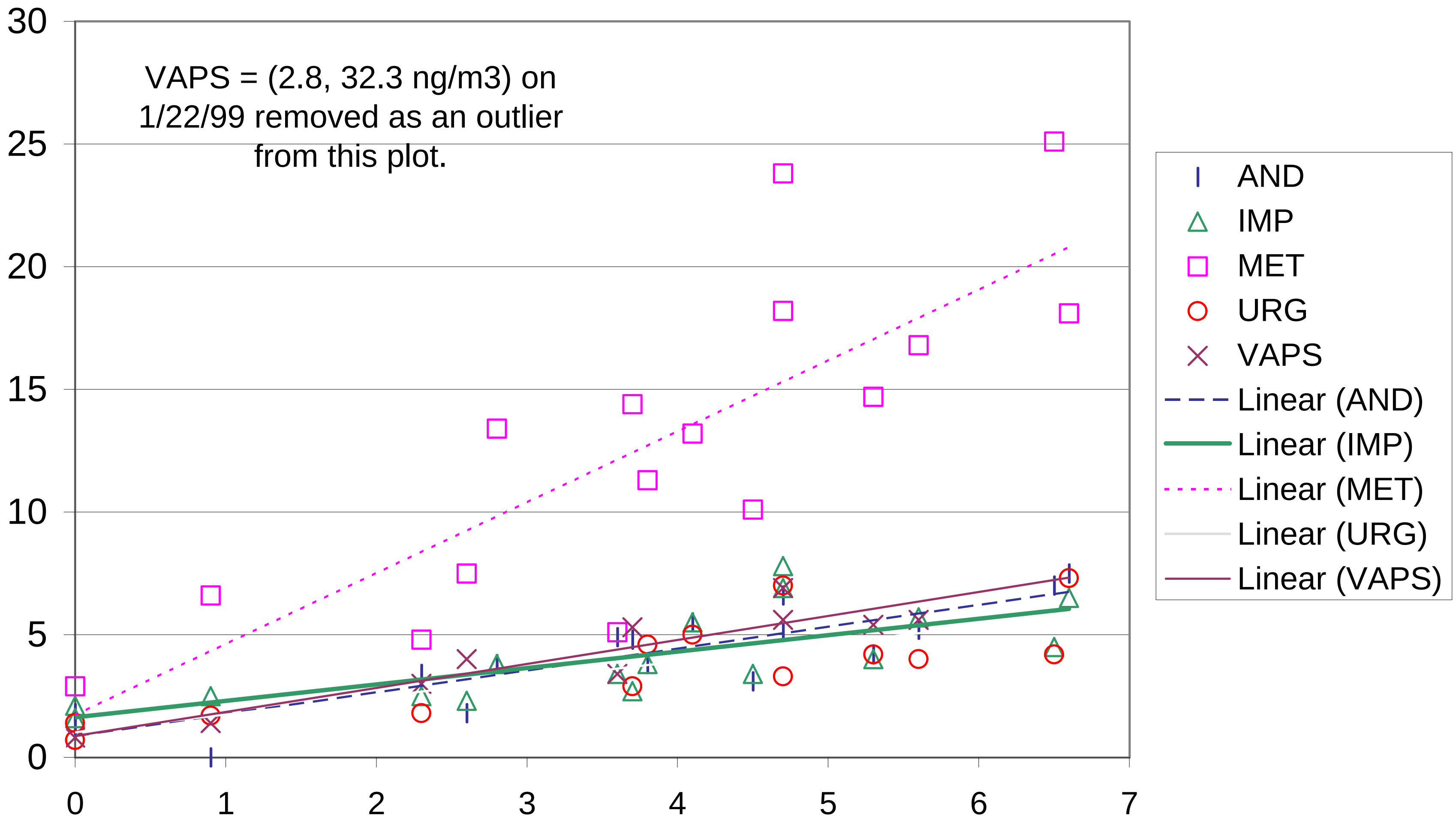

FRM vs Speciation Samplers for K at Phoenix
VAPS = (82, 610 ng/m3) on 1/22/99 removed as an outlier from this plot.
0
100
200
300
400
500
600
700
0
50
100
150
200
250
300
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

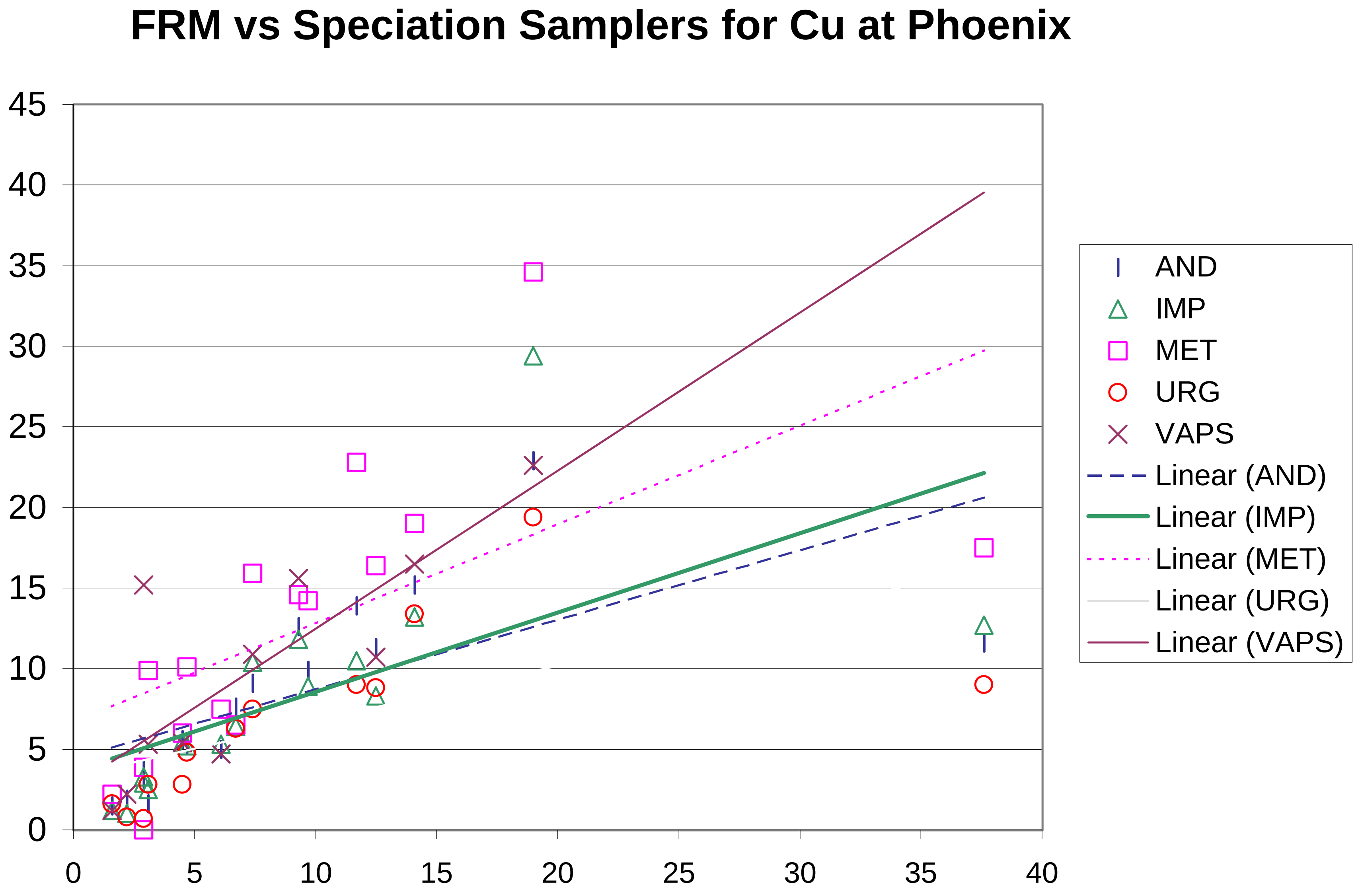


FRM vs Speciation Samplers for Mn at Phoenix

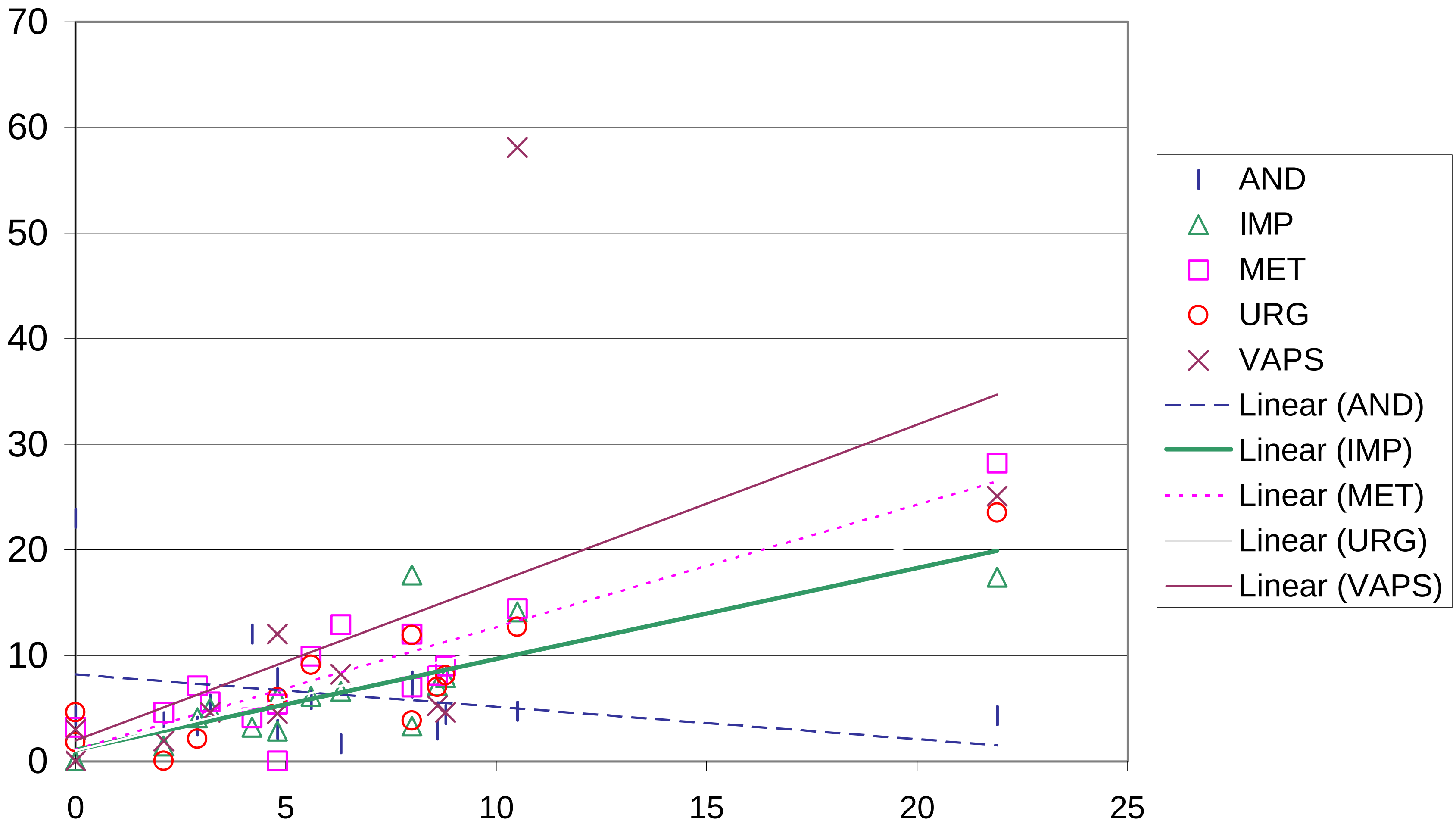
VAPS = (2.8, 32.3 ng/m3) on 1/22/99 removed as an outlier from this plot.

FRM vs Speciation Samplers for Mn at Phoenix

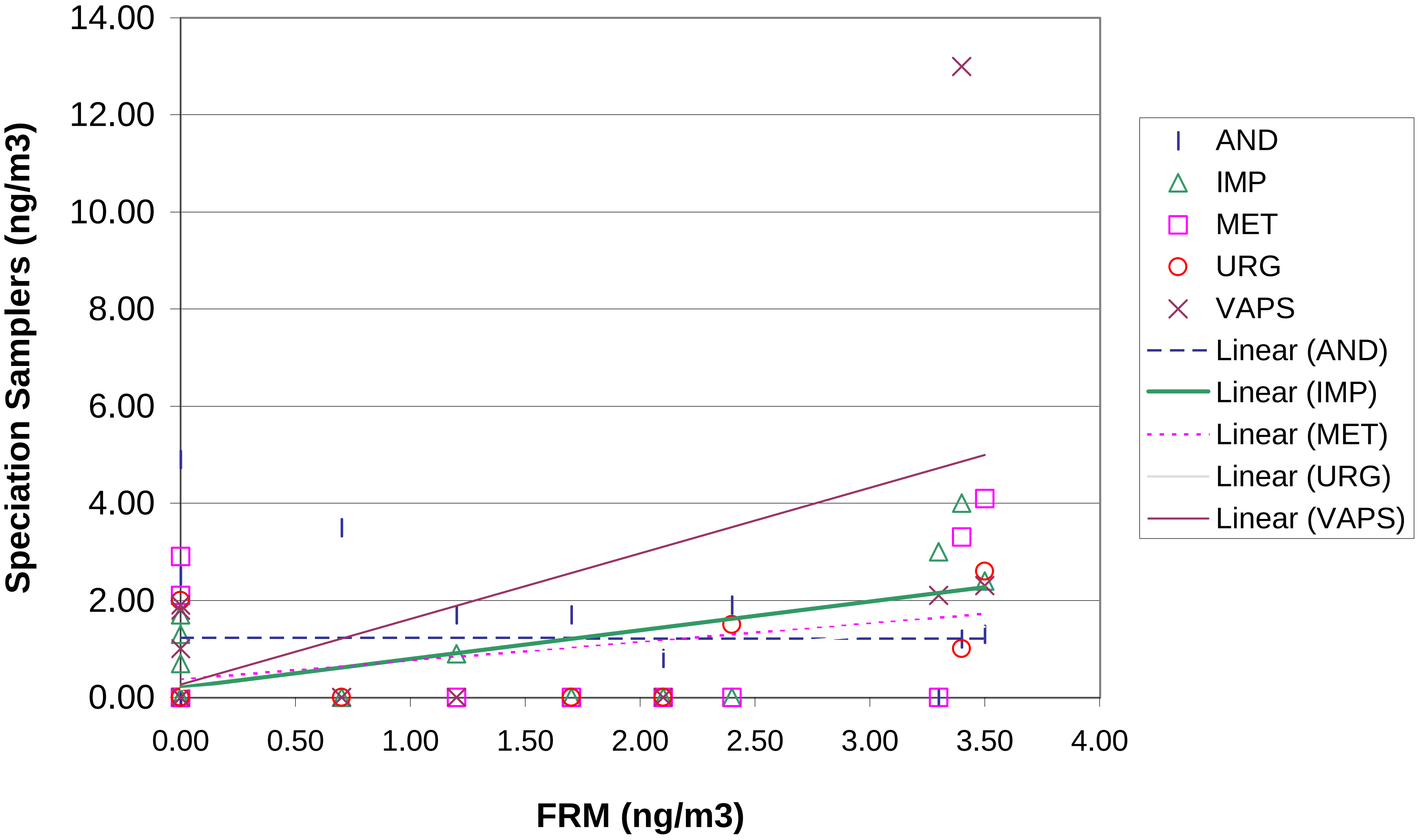

VAPS = (2.8, 32.3 ng/m3) on 1/22/99 removed as an outlier from this plot.


FRM vs Speciation Samplers for Cu at Phoenix
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
40
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

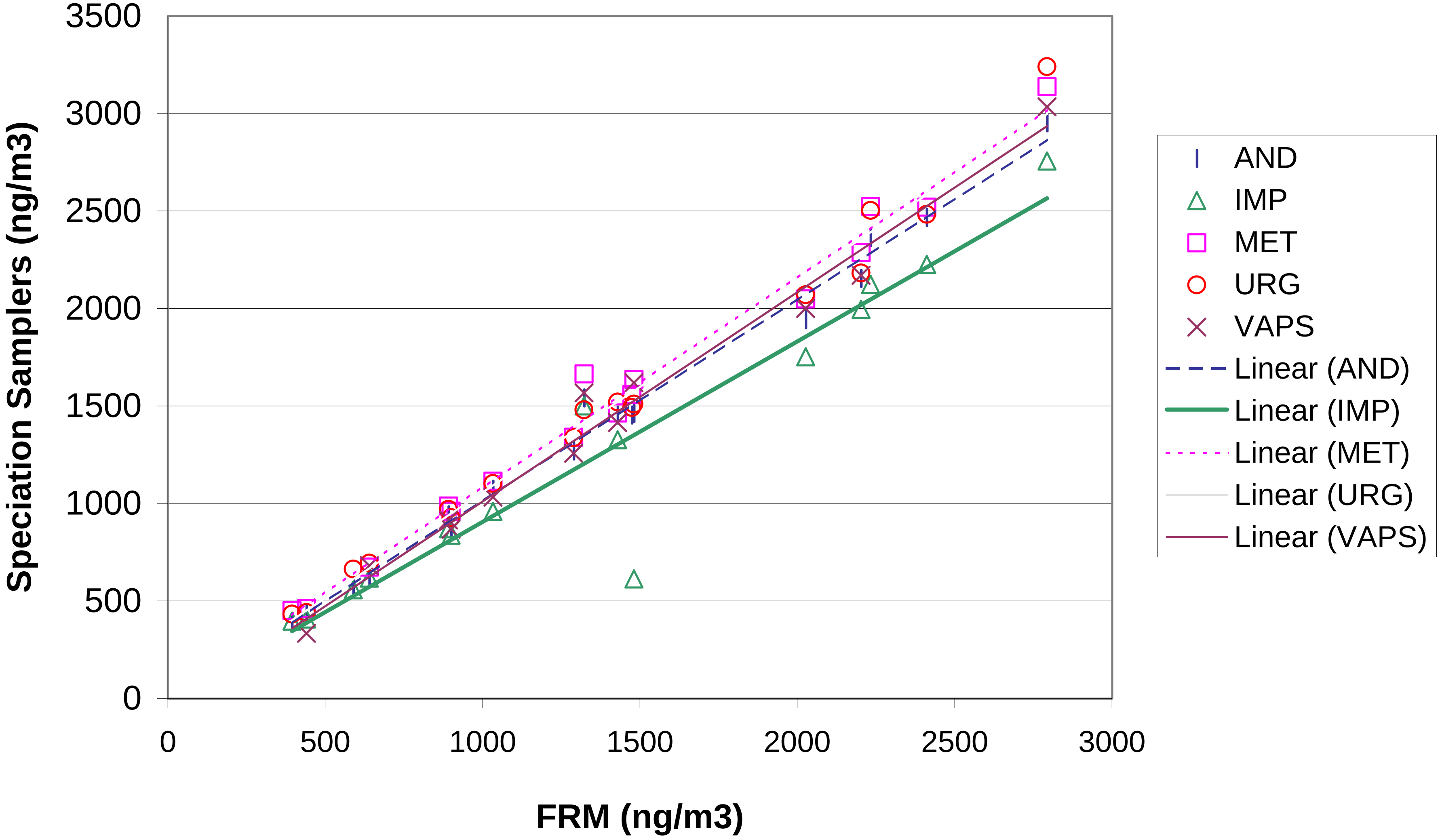
FRM vs Speciation Samplers for Pb at Phoenix

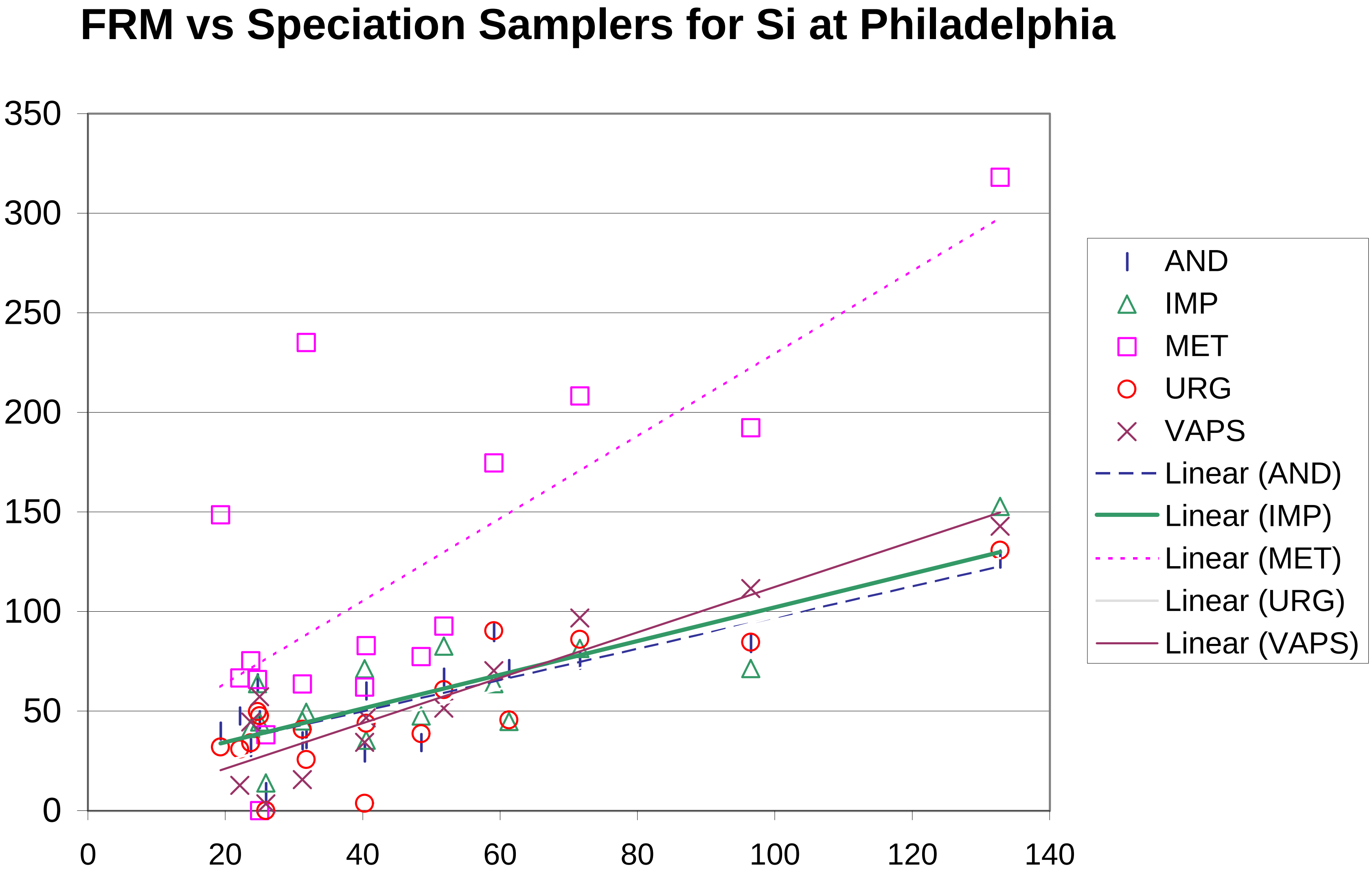


FRM vs Speciation Samplers for As at Phoenix

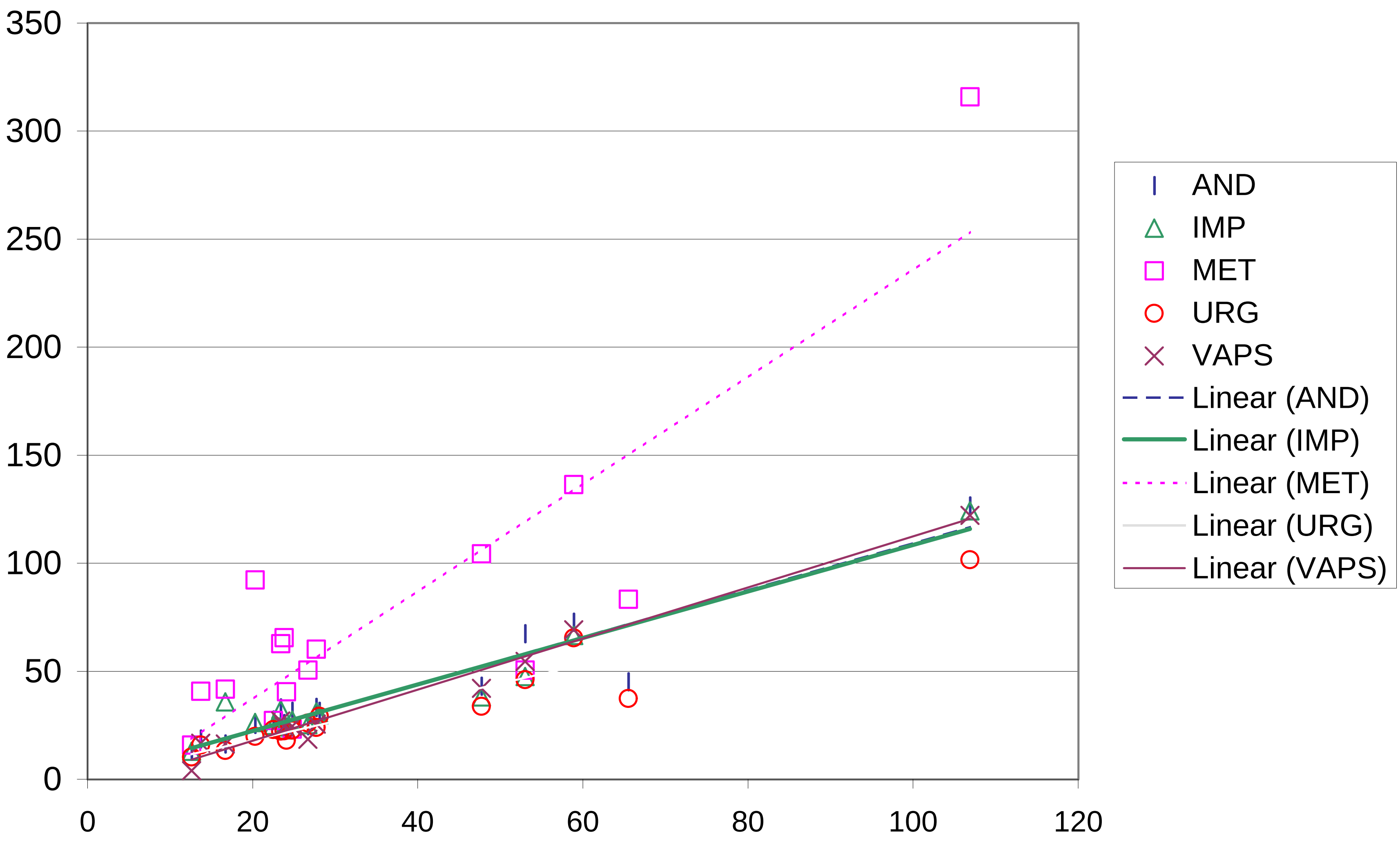


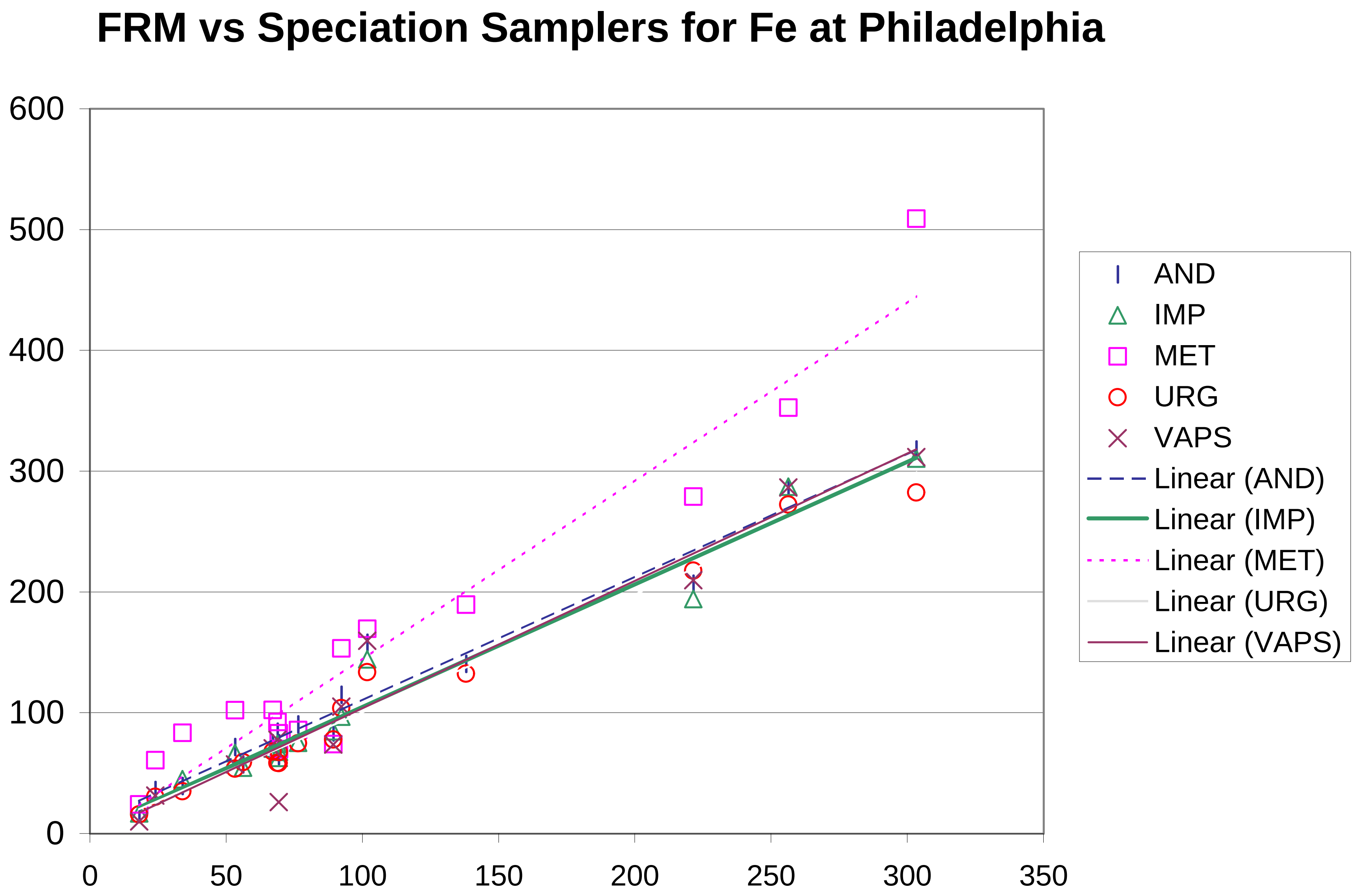
FRM vs Speciation Samplers for Sulfur at Philadelphia




FRM vs Speciation Samplers for Si at Philadelphia
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
140
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

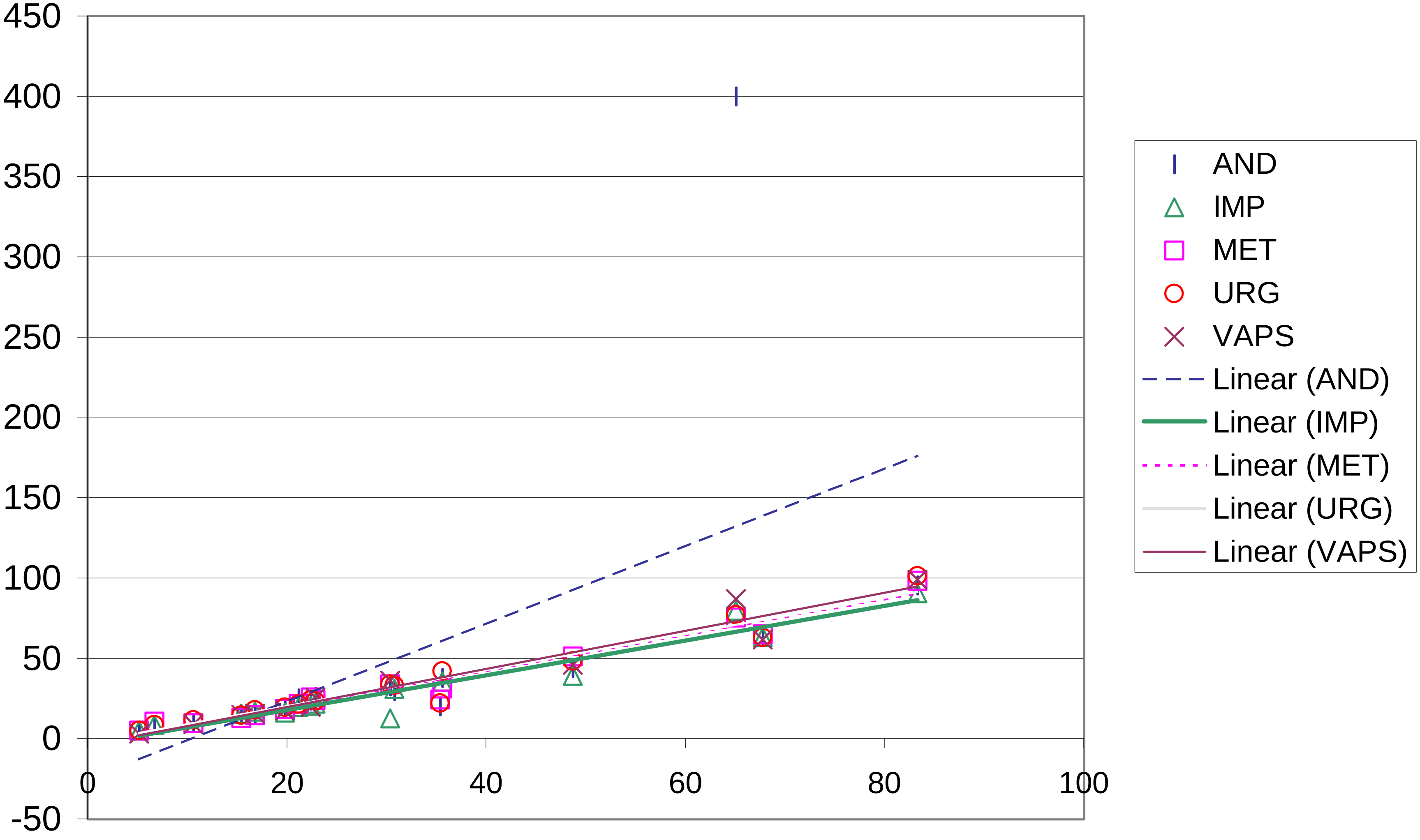
FRM vs Speciation Samplers for Ca at Philadelphia



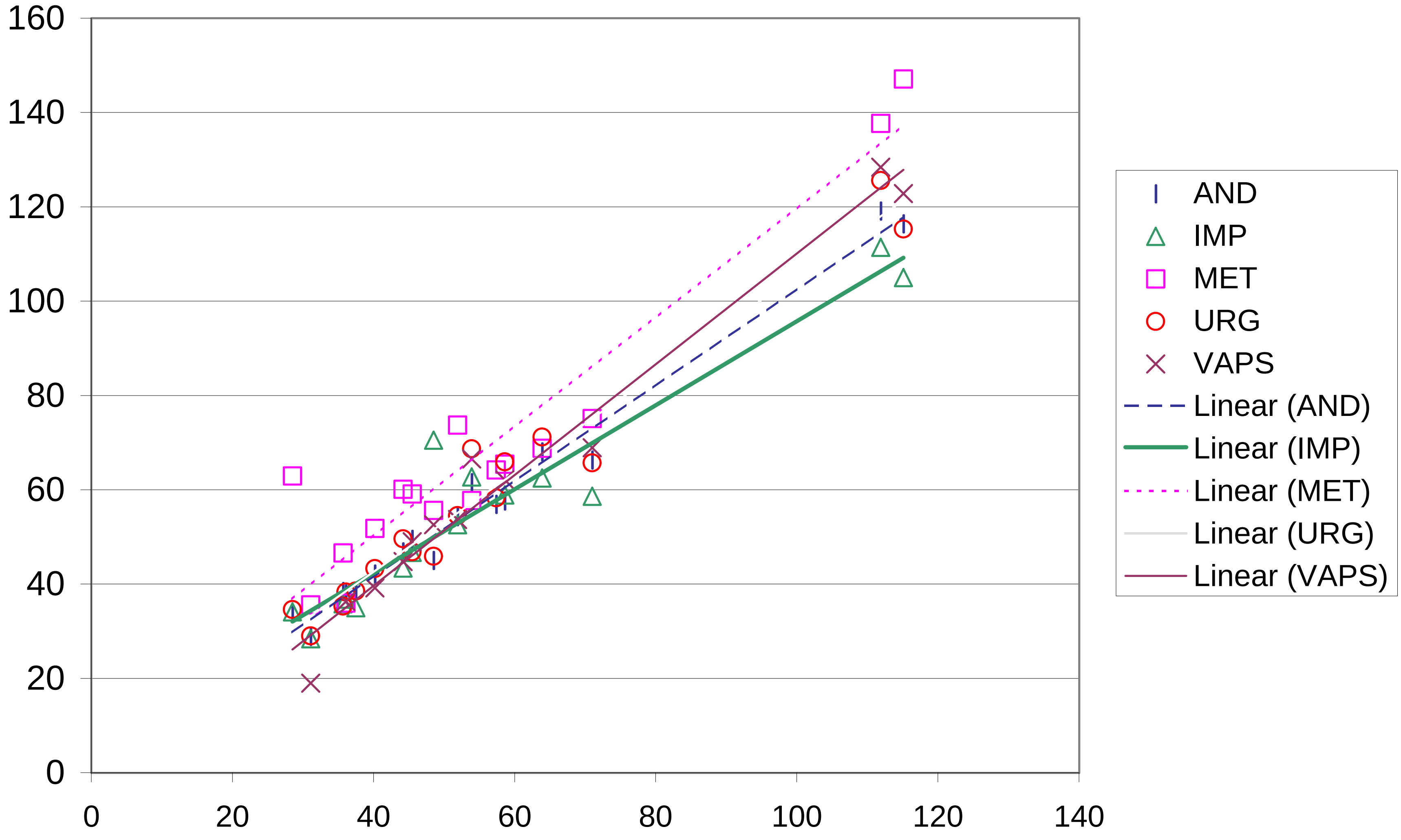


FRM vs Speciation Samplers for Fe at Philadelphia
0
100
200
300
400
500
600
0
50
100
150
200
250
300
350
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

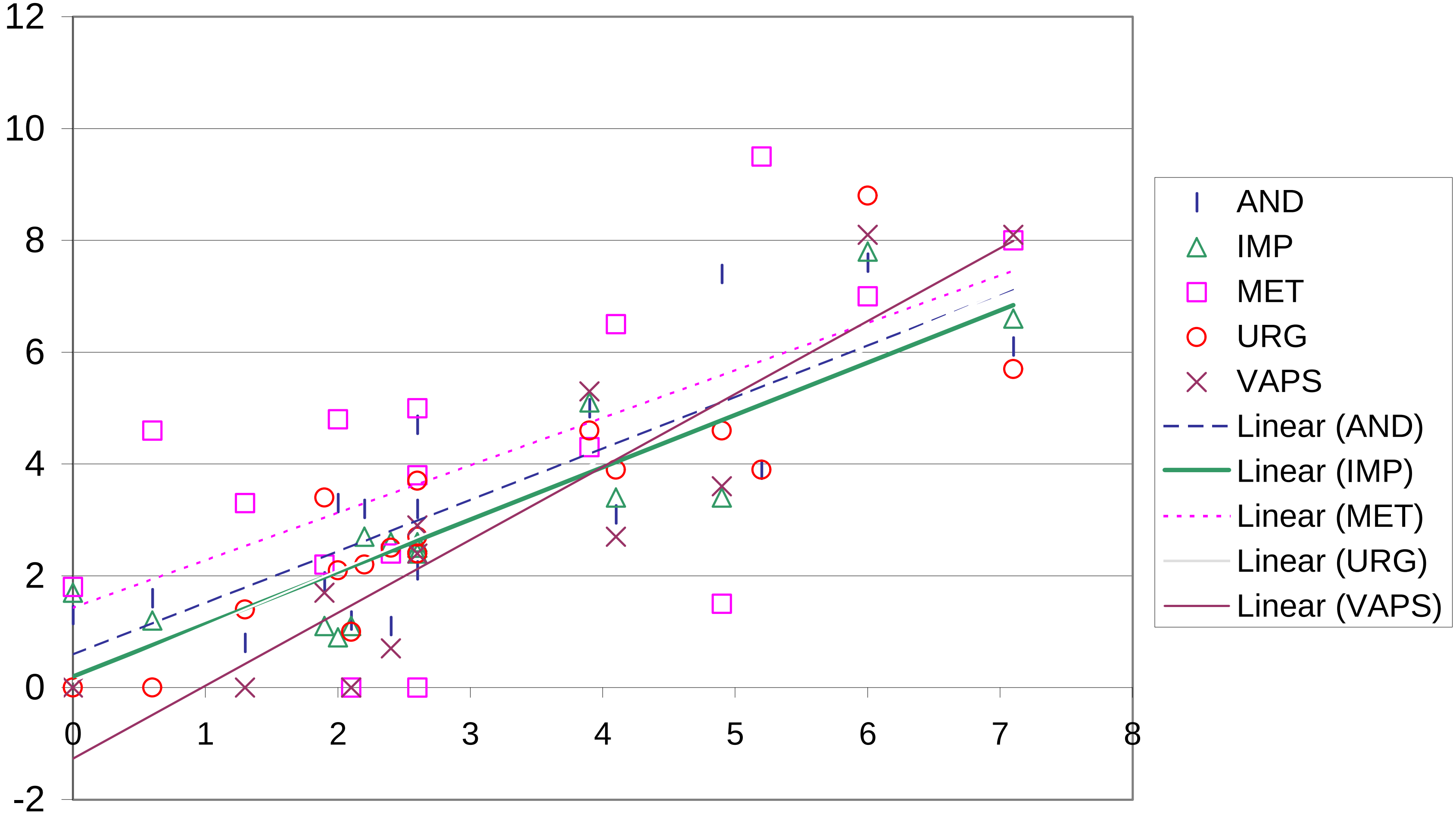
FRM vs Speciation Samplers for Zn at Philadelphia



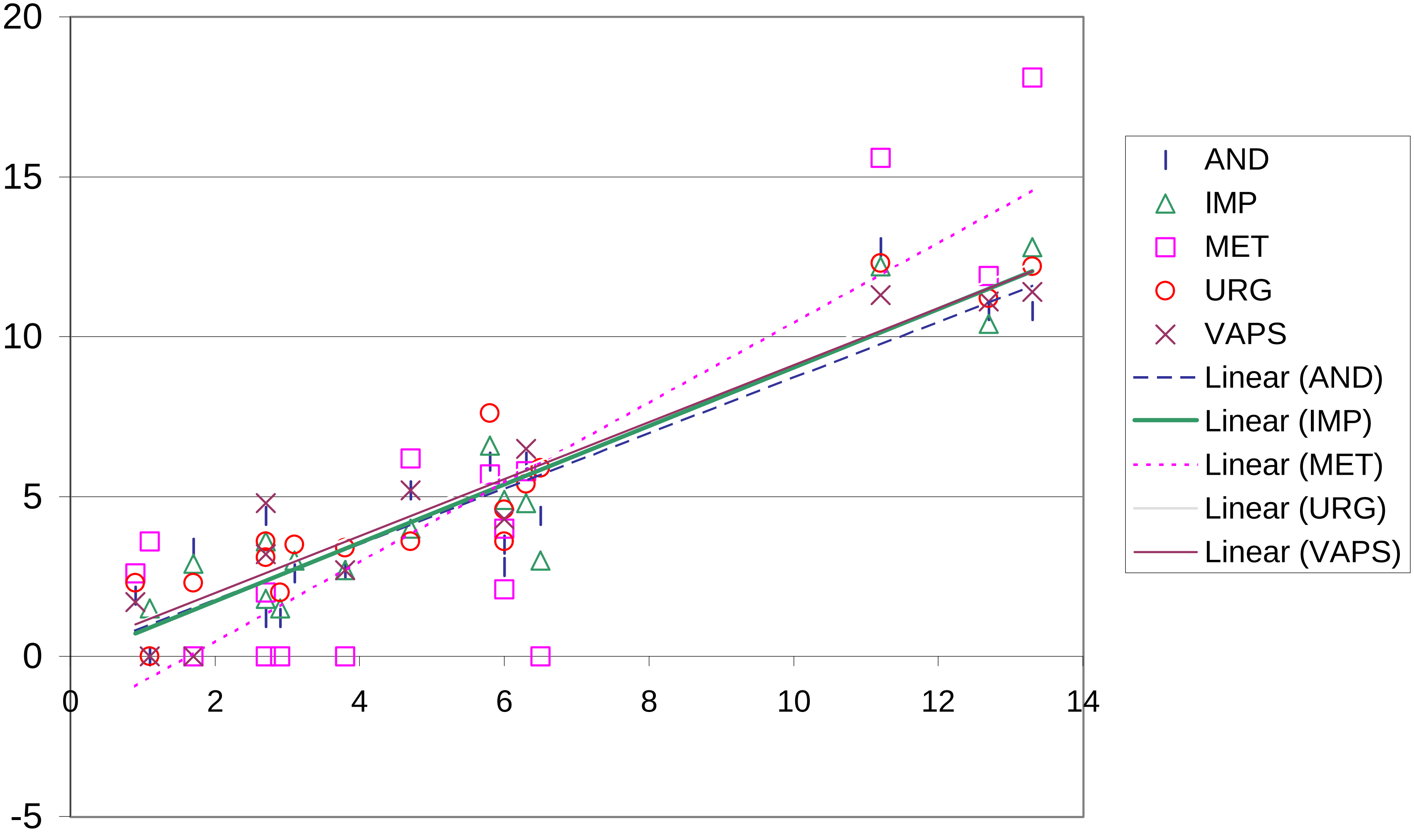
FRM vs Speciation Samplers for K at Philadelphia



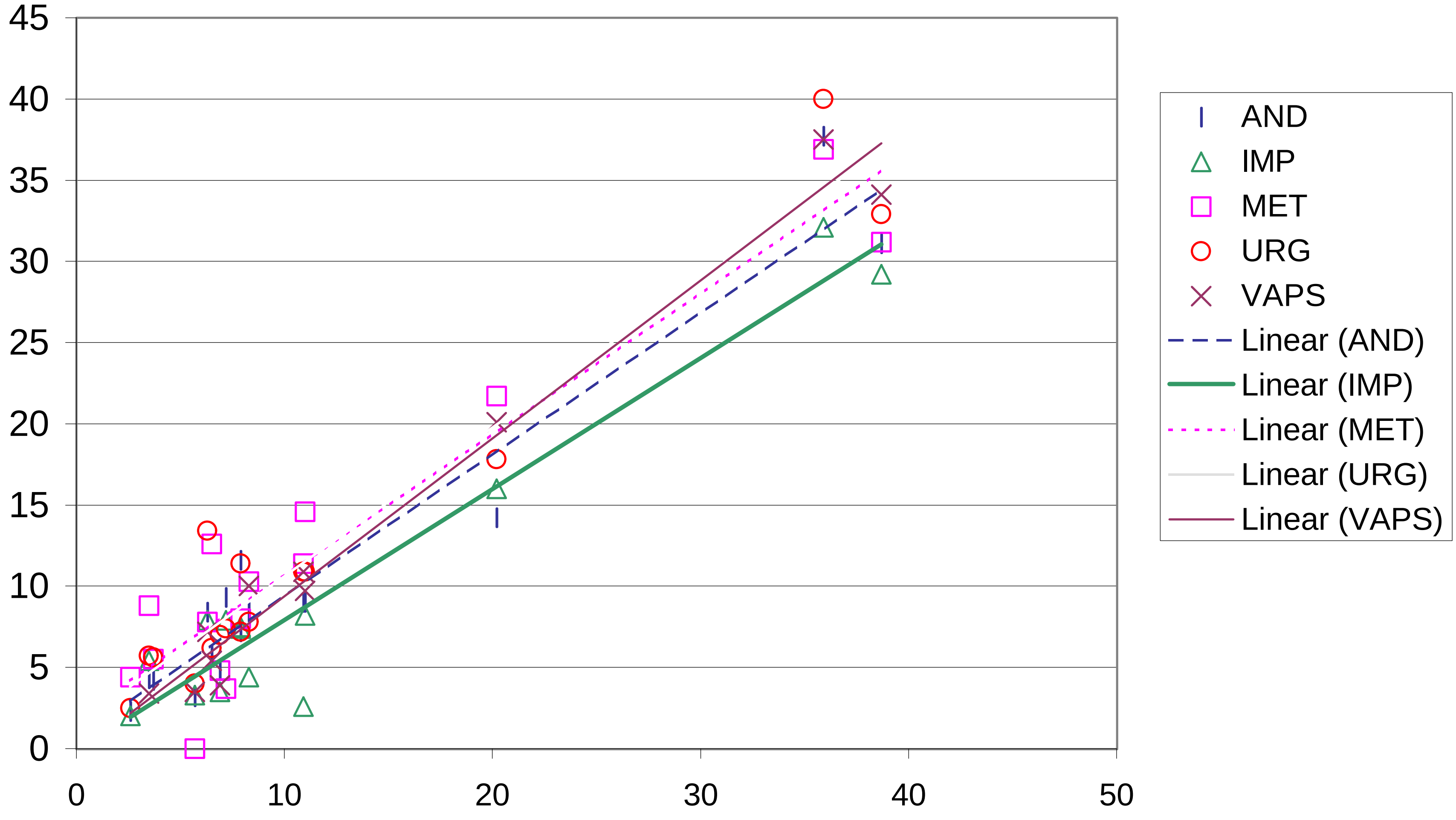
FRM vs Speciation Samplers for Mn at Philadelphia



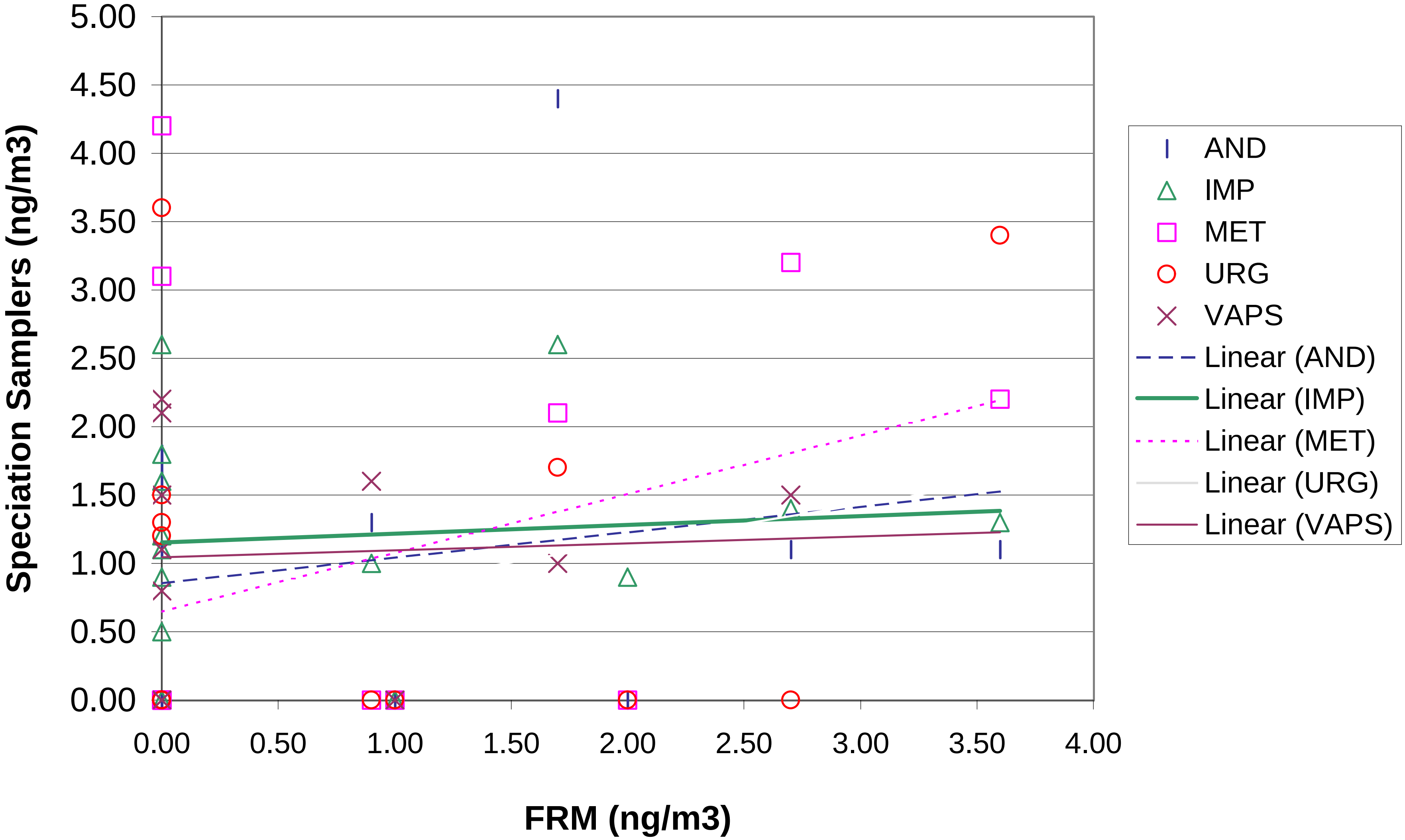
FRM vs Speciation Samplers for Cu at Philadelphia

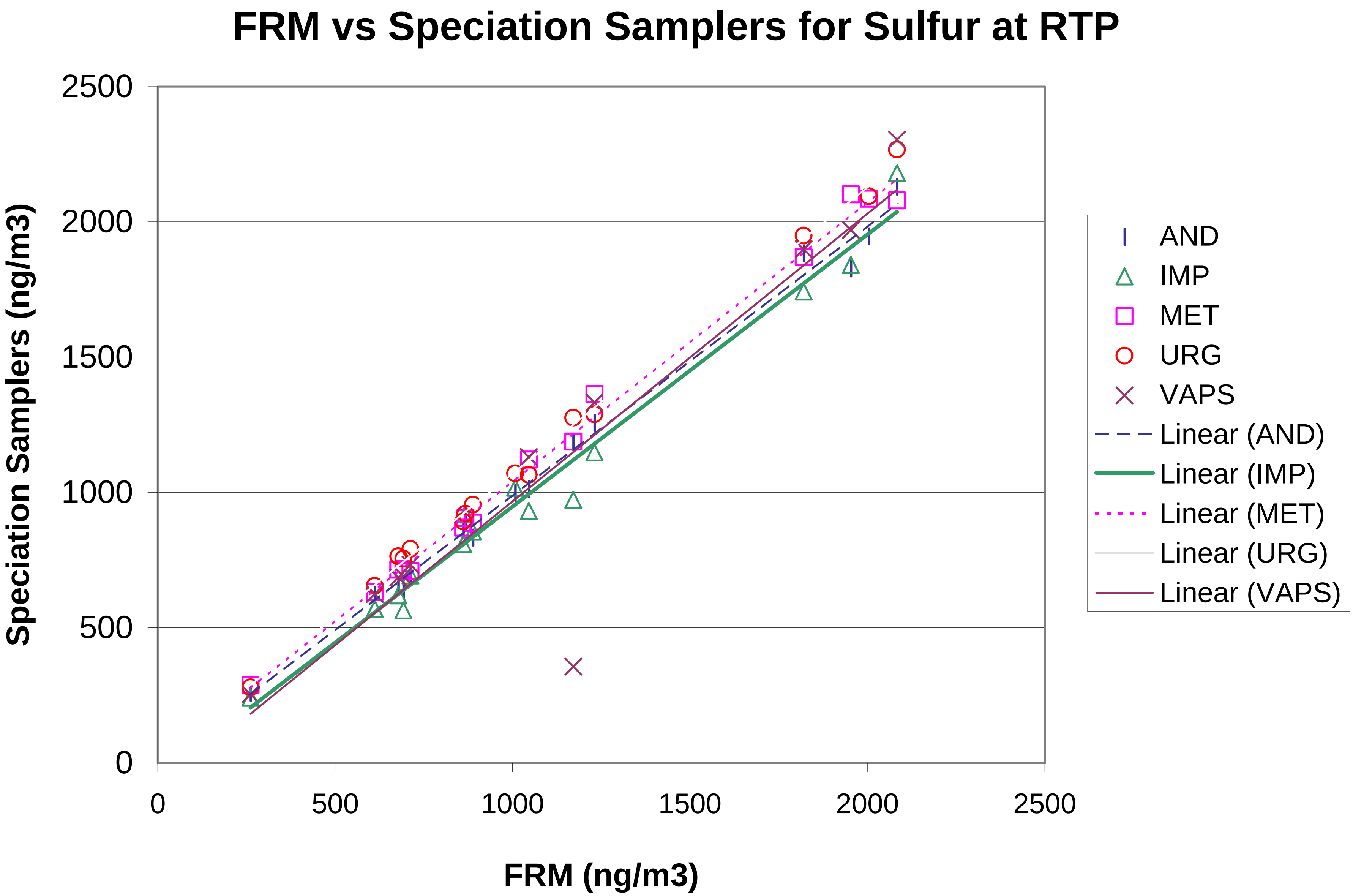


FRM vs Speciation Samplers for Pb at Philadelphia

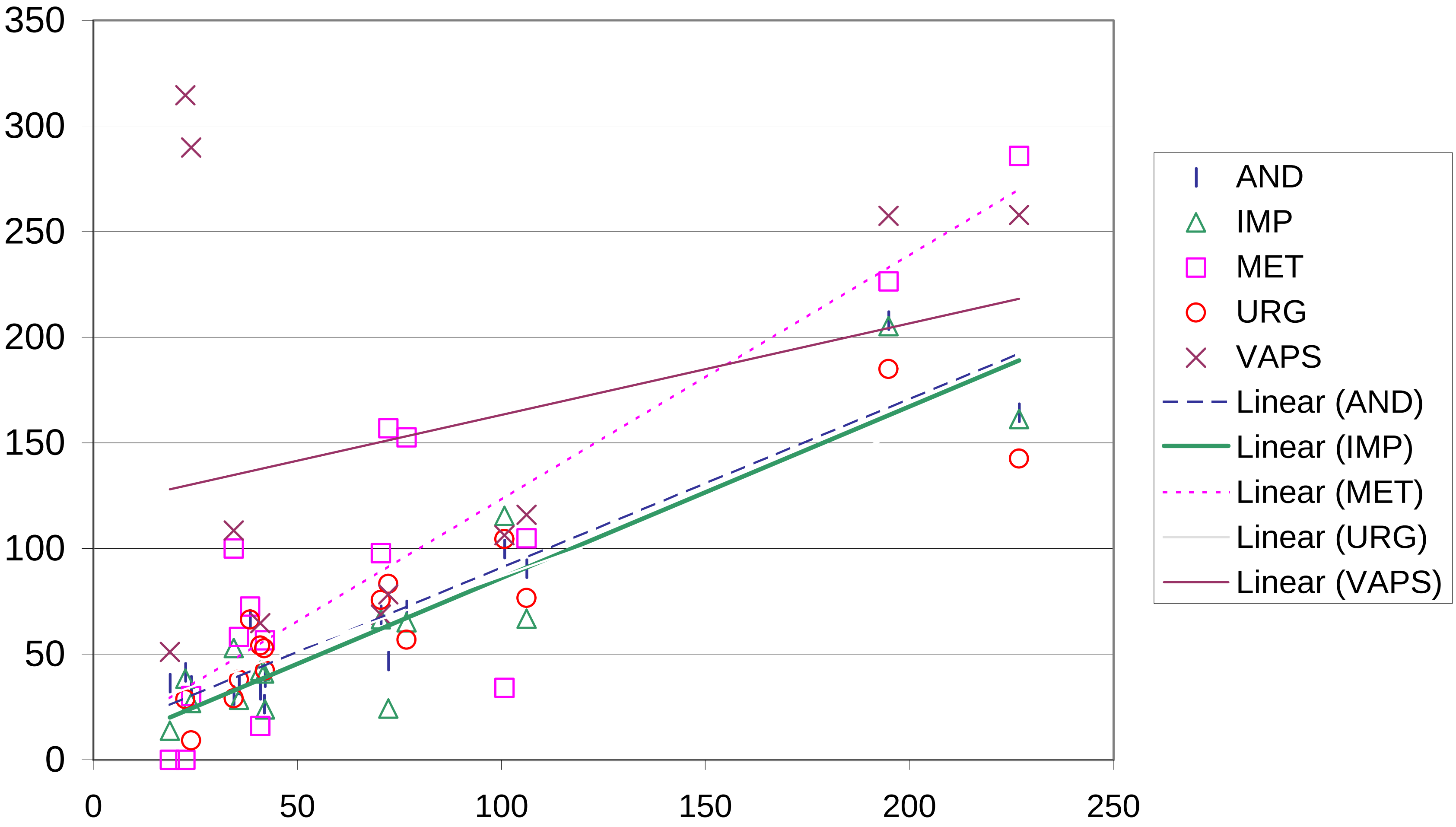


FRM vs Speciation Samplers for As at Philadelphia

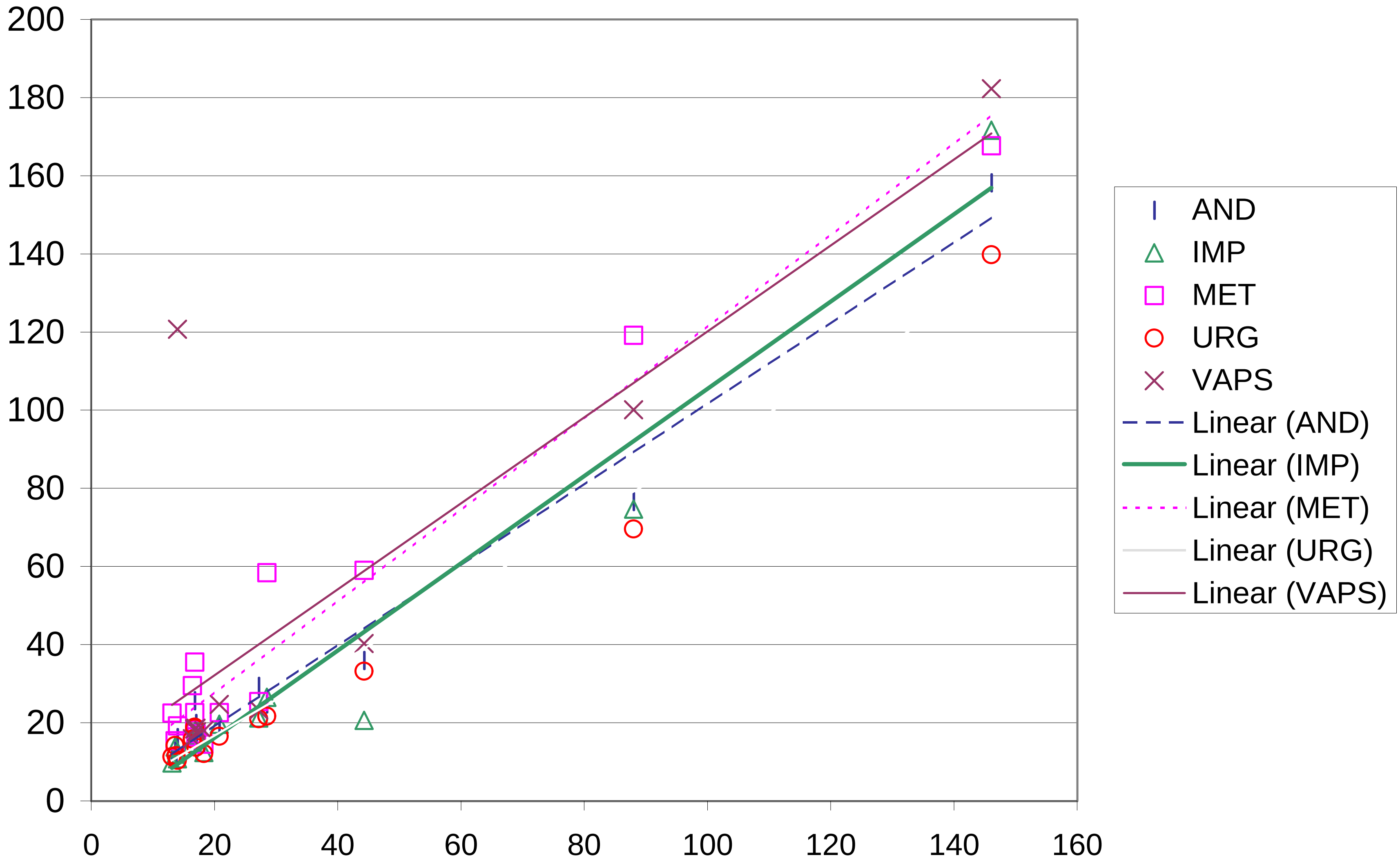



FRM vs Speciation Samplers for Sulfur at RTP
Speciation Samplers (ng/m3)
FRM (ng/m3)
0
500
1000
1500
2000
2500
0
500
1000
1500
2000
2500
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

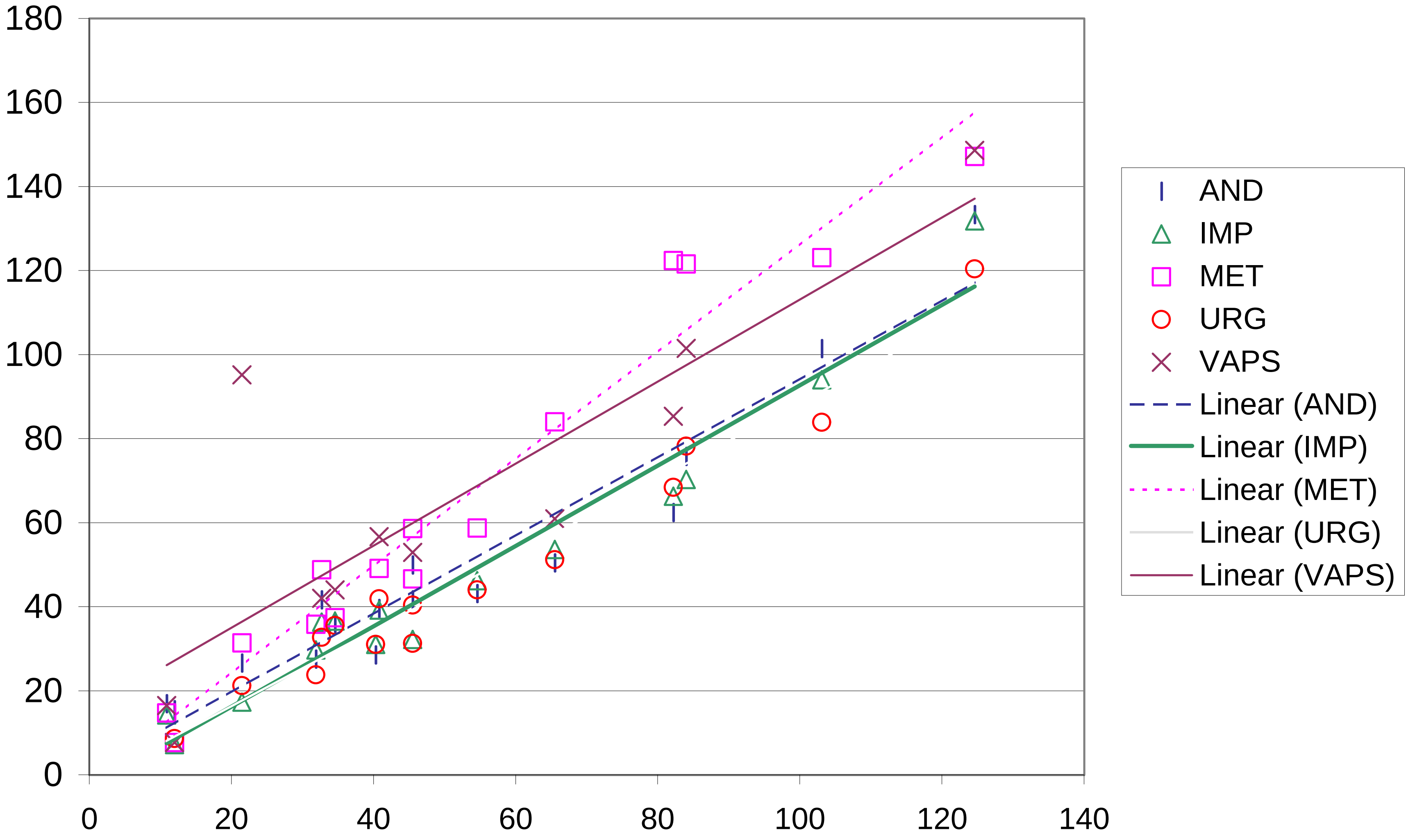
FRM vs Speciation Samplers for Si at RTP



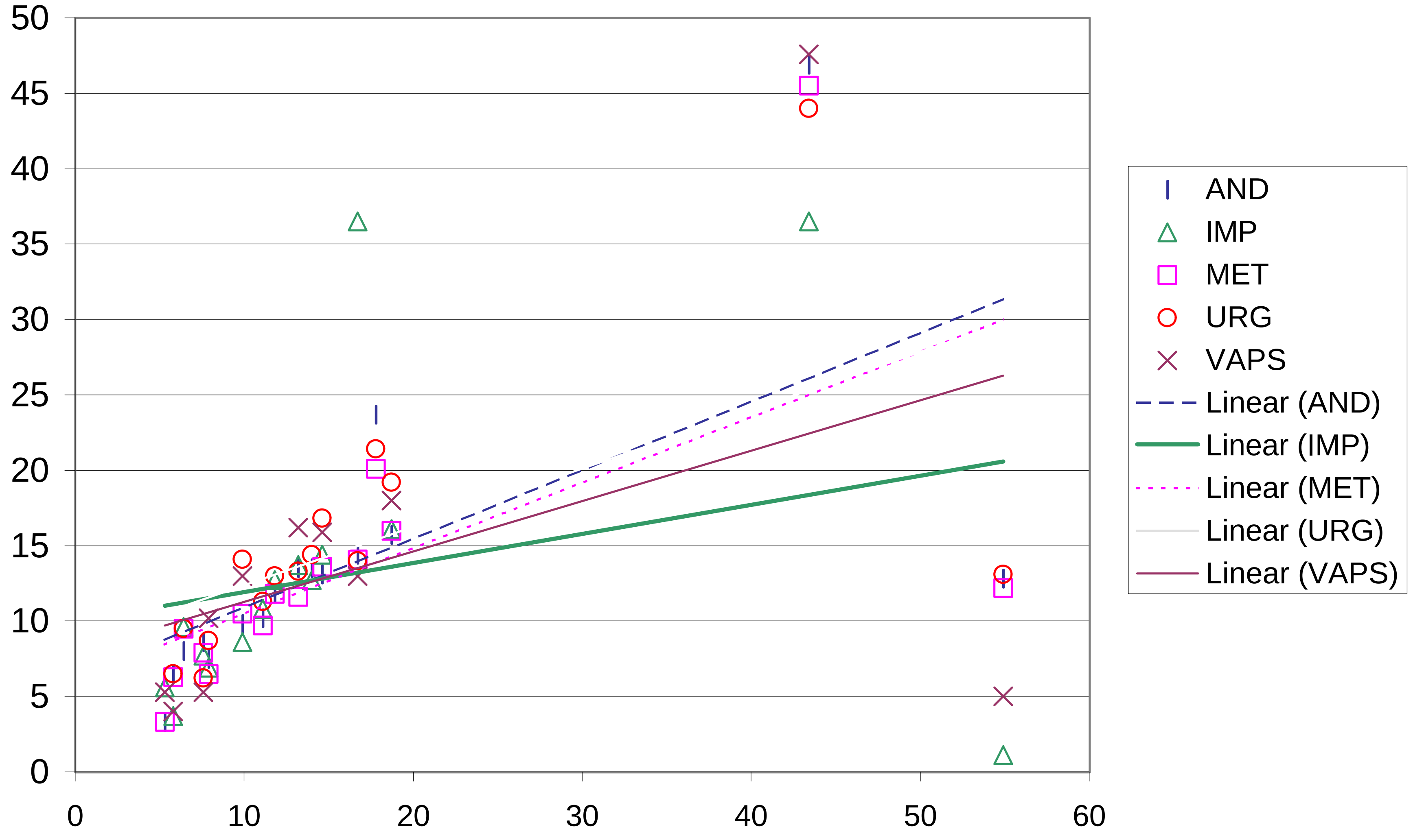
FRM vs Speciation Samplers for Ca at RTP



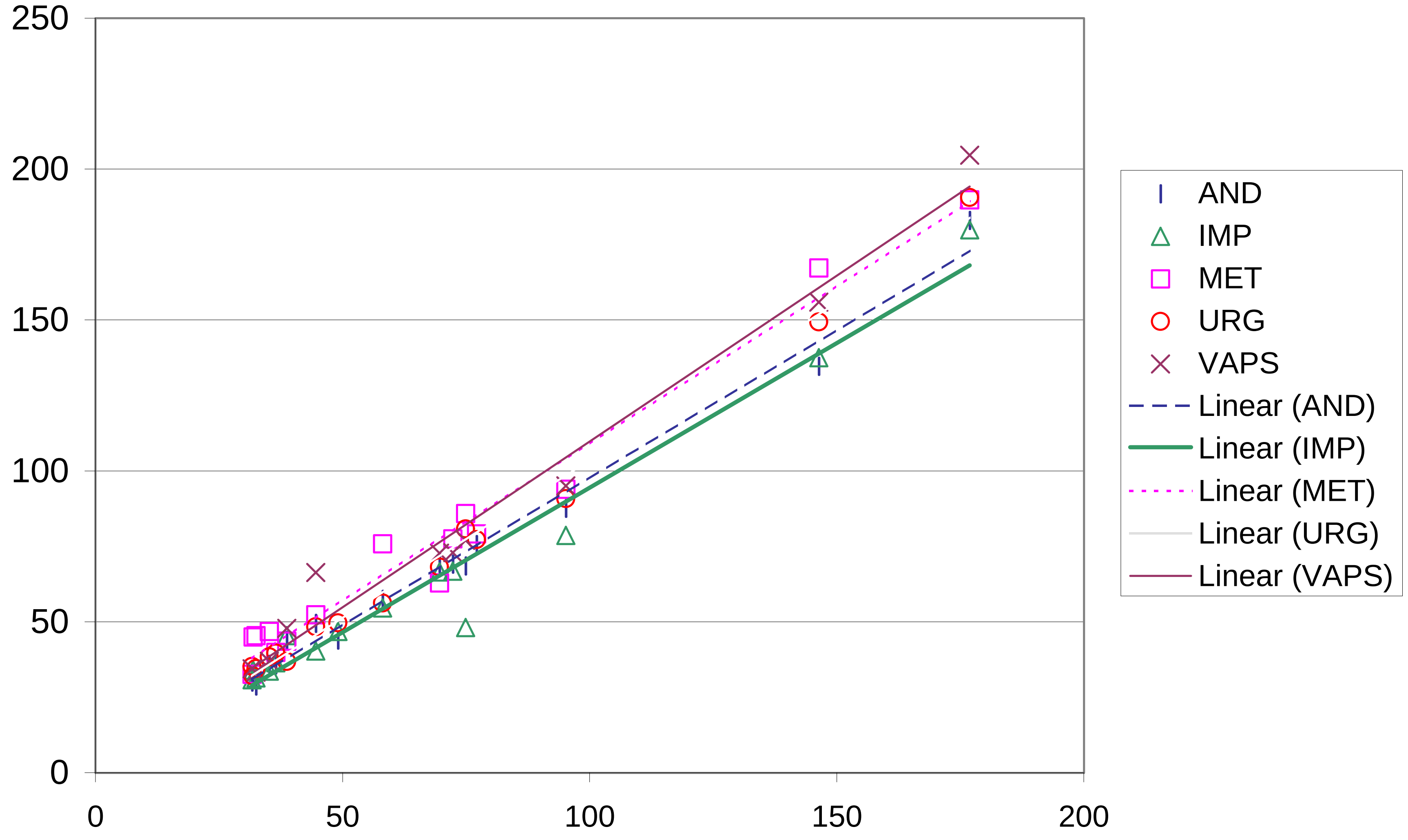
FRM vs Speciation Samplers for Fe at RTP



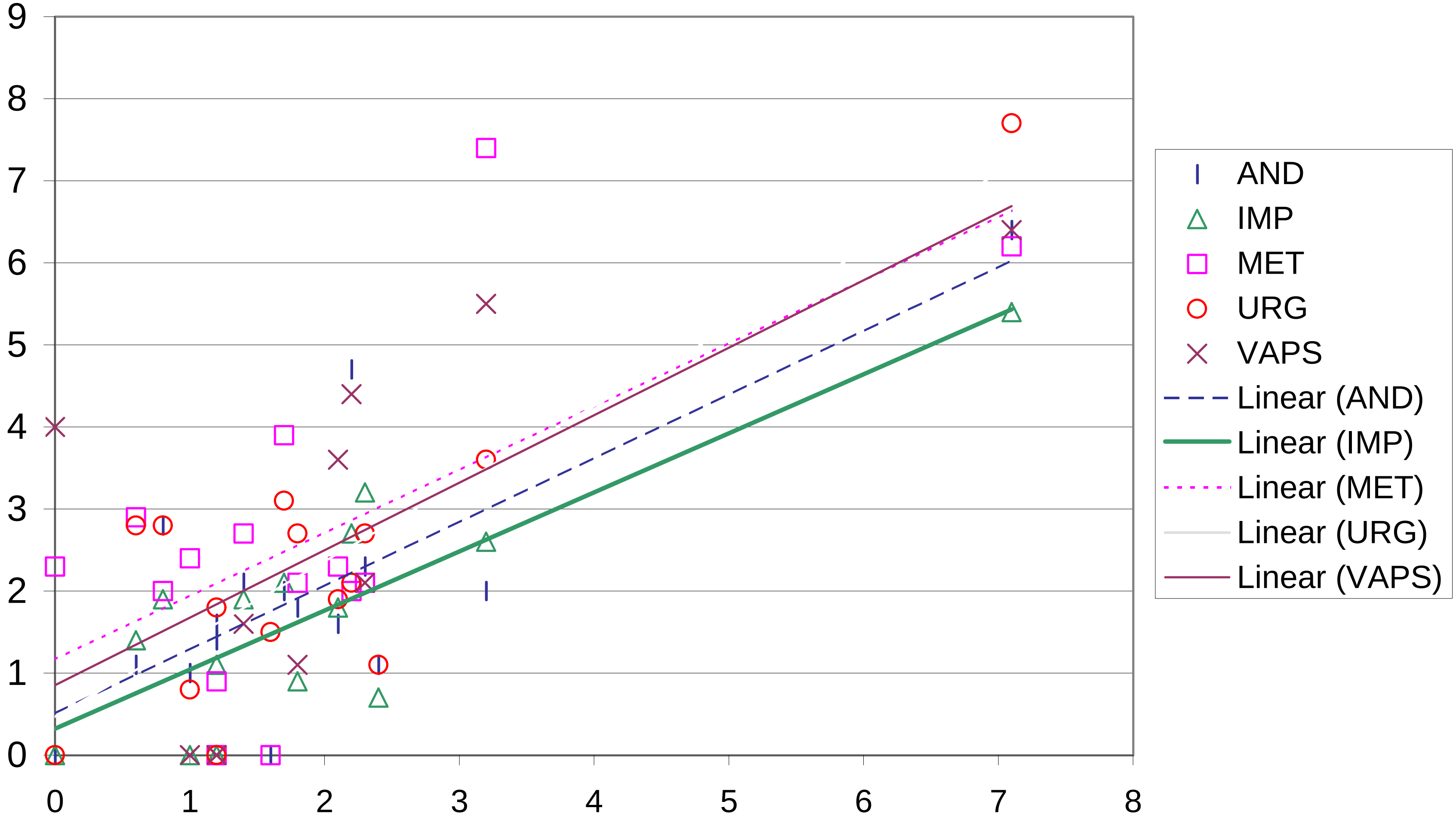
FRM vs Speciation Samplers for Zn at RTP



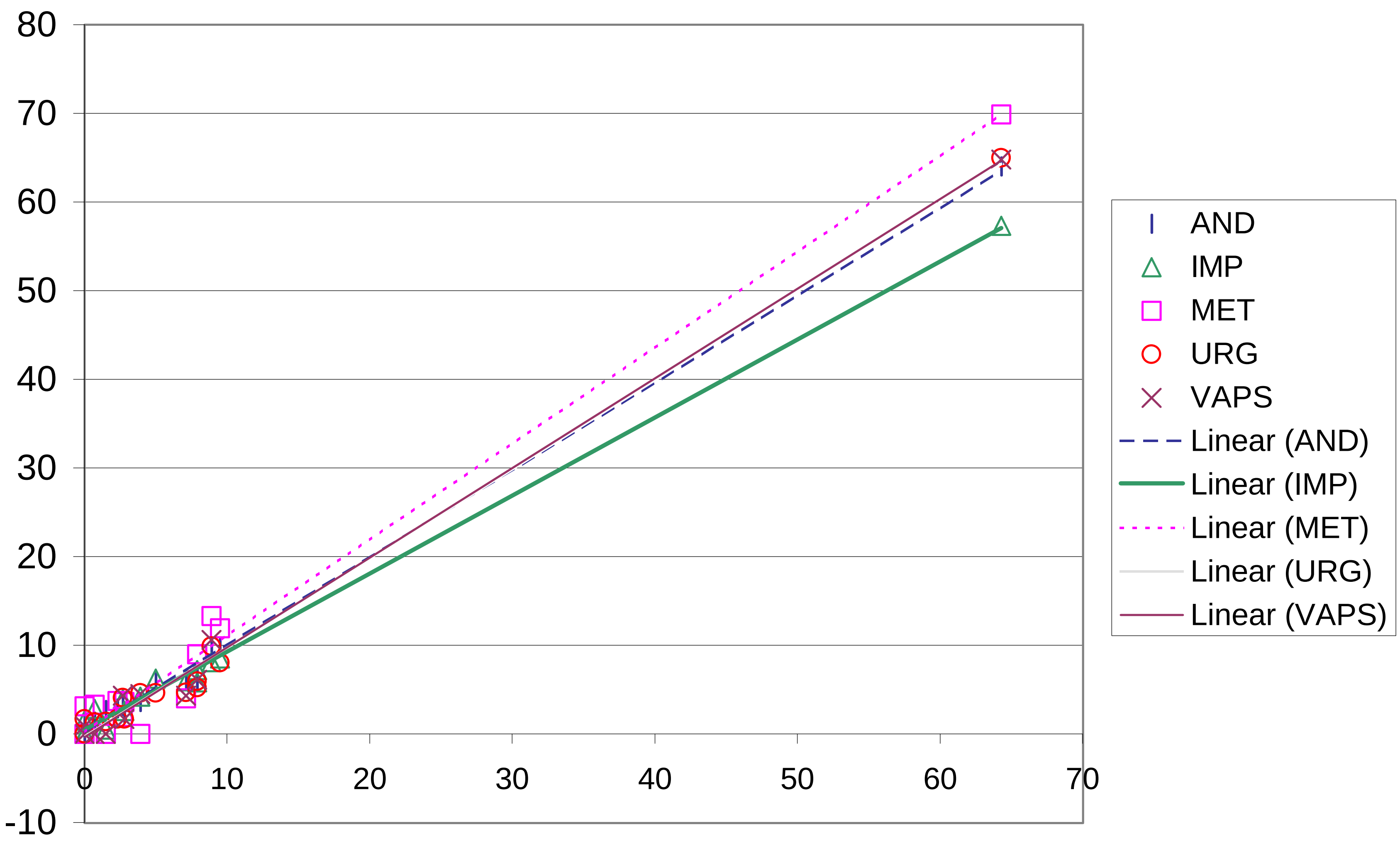
FRM vs Speciation Samplers for K at RTP



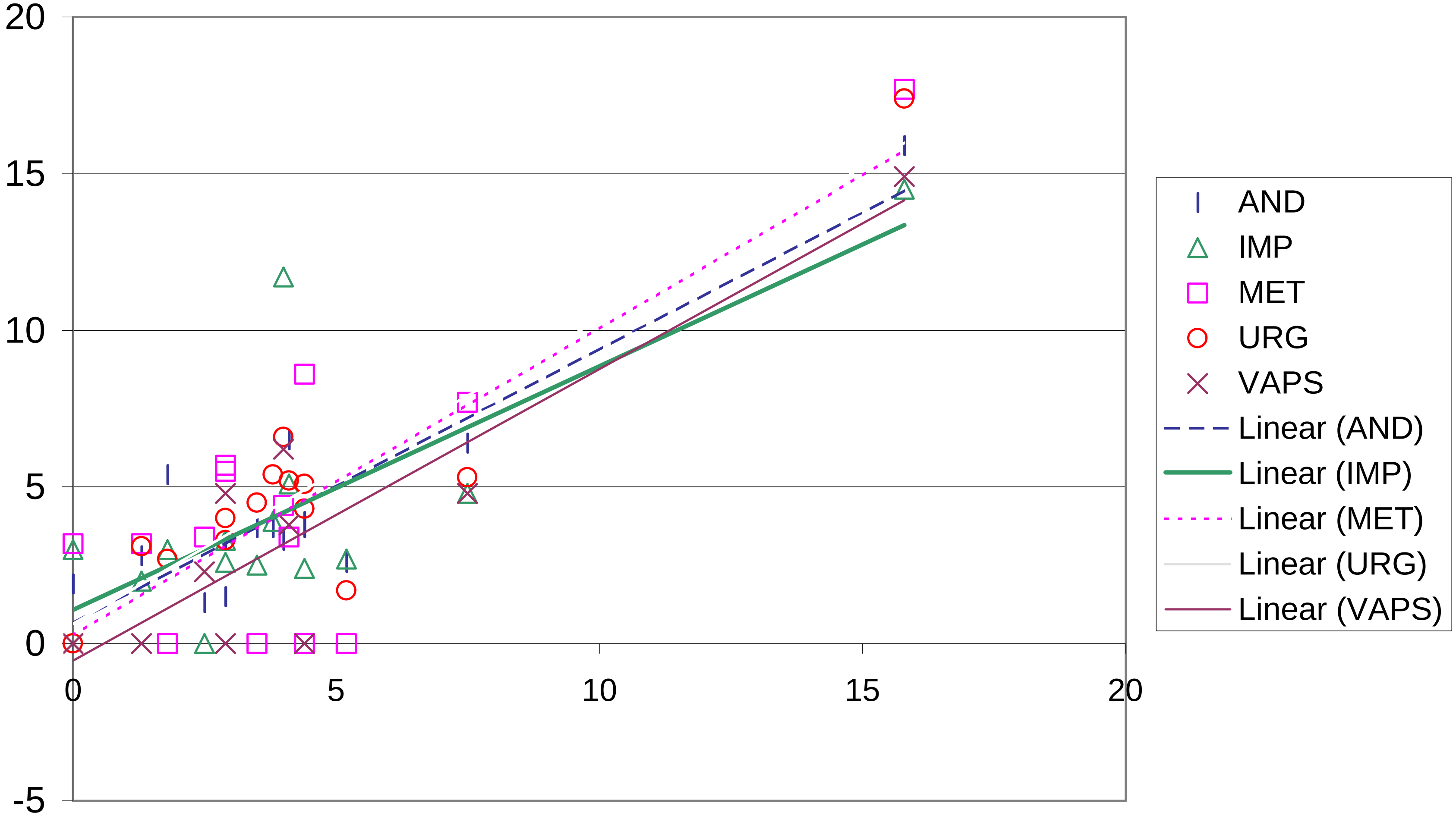
FRM vs Speciation Samplers for Mn at RTP

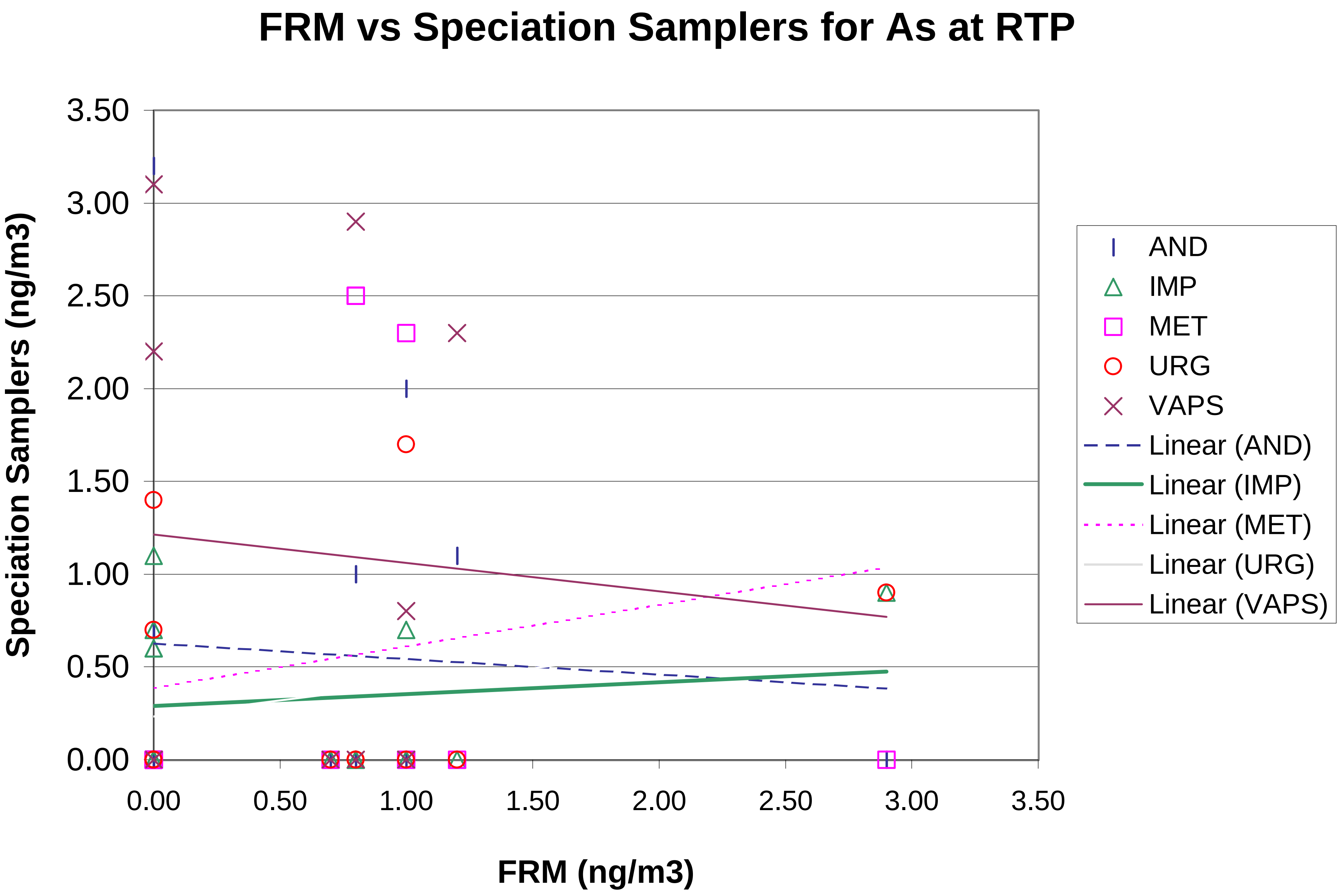


FRM vs Speciation Samplers for Cu at RTP



FRM vs Speciation Samplers for Pb at RTP




FRM vs Speciation Samplers for As at RTP
Speciation Samplers (ng/m3)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
FRM (ng/m3)
AND
IMP
MET
URG
VAPS
Linear (AND)
Linear (IMP)
Linear (MET)
Linear (URG)
Linear (VAPS)

APPENDIX G-1

Absolute Differences Between the FRM, (Reference Sampler), and the Speciation Samplers by Site and by Sampling Period

(Manganese, Copper, Lead and Arsenic Excluded Because of Too Few Samples)

DIFFERENCES FROM FRM FOR PM-2.5 (micrograms/m3)

SITE	DATE	FRM Mass	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	28.57	1.78	2.31	-37.58	-4.37	.
1	1/18/1999	74.28	-10.85	-13.25	-18.76	-30.82	.
1	1/21/1999	14.88	1.59	1.64	1.55	-1.89	-17.65
1	1/24/1999	29.36	-0.73	2.39	-4.07	-9.32	-28.18
1	1/27/1999	2.96	0.29	0.2	-0.08	-0.13	-1.95
1	1/30/1999	29.46	7.45	13.06	-3.95	.	-20.26
1	2/2/1999	5.58	0.15	-0.09	-8.65	0.46	-7
1	2/5/1999	21.02	3.01	1.33	1.7	.	-5.21
1	2/11/1999	2.21	-0.03	-0.43	-7.25	-0.33	-6.87
1	2/14/1999	35.62	1.42	1.42	-5.97	-17.84	-39.18
1	2/17/1999	59.01	0	0.35	-6.71	-21.53	.
1	2/20/1999	29.13	-2.08	-3.69	-9.72	-10.62	-25.08
1	2/23/1999	17.56	0.2	1.53	-14.42	-4.78	-18.85
1	2/26/1999	23.6	1.05	1.04	-1.63	-11.45	-39.84
2	1/14/1999	22.04	0.16	6.38	-15.96	3.08	.
2	1/16/1999	25.33	-0.22	4.12	-21.46	0.79	.
2	1/18/1999	24.38	-0.19	1.78	-19.29	0.88	-1.87
2	1/20/1999	12.71	-0.22	2.05	-13.99	1.13	.
2	1/22/1999	9.04	-0.1	0.18	-11.53	.	-0.08
2	1/24/1999	19.83	-0.74	5.17	-18.16	0.29	-1.84
2	1/26/1999	7.58	-0.81	0.68	-2.22	-0.54	-2.64
2	1/28/1999	4.12	-0.28	0	.	0.16	0.05
2	2/3/1999	17.29	0.24	1.77	-16.95	1.24	-0.19
2	2/5/1999	11.46	0.48	1.39	-0.63	-1.21	.
2	2/7/1999	23.33	1.07	5.17	-5.33	.	-8.93
2	2/9/1999	13.79	0.24	1.8	-7.29	.	0.16
2	2/11/1999	3.92	-0.23	-0.02	-2.43	0.54	0.15
2	2/13/1999	12.42	0.12	-0.82	-12.79	.	.
2	2/15/1999	12.75	0.16	0.53	-13.25	1.07	0.57
2	2/17/1999	20.29	0.08	2.87	-15.91	-0.53	-1.17
2	2/19/1999	13.42	-0.09	1.07	-15.49	-0.09	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	25.76	0.43	-0.91	0.77	0.73	-7.45
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	19.35	0.03	0.57	-1.09	-1.84	.
3	1/27/1999	37.58	-0.93	-0.98	-3.15	-3.33	-9.83
3	1/29/1999	15.03	0.05	0.31	-0.42	-0.39	-1.52
3	1/31/1999	12.36	0.58	0.7	1.45	0.06	-1.18
3	2/2/1999	13.77	-0.08	0.2	0.48	-0.27	-2.4
3	2/4/1999	25.84	0.05	0.14	0.75	-0.52	-8.77
3	2/8/1999	16.52	-0.39	-0.04	0.13	0.01	-2.05
3	2/10/1999	11.86	0.02	0.45	-0.92	0.14	-3.05
3	2/12/1999	15.56	0.04	.	0.01	0.26	.
3	2/14/1999	5.16	0.11	-0.2	-0.38	-0.01	1.65
3	2/16/1999	32.17	-0.36	1.84	-6.38	0.55	-9.35
3	2/18/1999	24.85	-0.08	-0.25	0.46	0.44	-0.54
3	2/20/1999	10.45	-0.52	-0.02	-1.86	-0.89	-2.77
3	2/22/1999	5	-0.25	-0.72	-1.5	-0.86	.
3	2/24/1999	10.78	-0.06	-0.06	.	-0.89	.
3	2/26/1999	14.36	-0.42	-0.05	-1.55	-0.66	-2.63
4	1/19/1999	4.38	0.14	-0.64	-0.57	0.17	-0.19
4	1/21/1999	23.75	0.67	0.77	-0.66	-0.88	-1.69
4	1/23/1999	6.54	0.3	0.83	0.55	0.37	-1.69
4	1/25/1999	8.25	-0.27	-0.22	-1.32	-0.1	-1.15
4	1/27/1999	15.25	-0.46	.	-0.64	-0.88	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	8.71	-2.01	1.53	0.41	-0.38	-1.8
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	10.42	0.98	1.29	-0.53	0.54	-2.12
4	2/8/1999	6.58	0.51	0.39	-0.17	-0.59	.
4	2/10/1999	11.5	0.46	0.33	-1.4	-0.47	.
4	2/12/1999	12.83	0.48	0.27	-0.73	.	-3.45
4	2/14/1999	6.5	0.8	0.28	-0.21	-0.71	.
4	2/16/1999	20.54	0.86	0.18	-3.18	-0.76	-3.91
4	2/18/1999	9.75	0.21	-0.1	.	-1.22	.
4	2/20/1999	13.87	-0.06	-0.34	-1.48	-1.31	-2.22
4	2/22/1999	5.21	0.21	0.19	-0.42	-0.33	-0.21
4	2/24/1999	12	0.1	0.62	-0.28	-1.1	-3.13

DIFFERENCES FROM FRM FOR SULFATE BY IC (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	0.57	0.08	0.12	-0.4	0.04	-0.34
1	1/18/1999	5.98	-0.08	0.56	-0.04	-0.66	-0.73
1	1/21/1999	1.62	-0.02	-0.02	-0.04	-0.11	-0.3
1	1/24/1999	1.89	0.14	0.2	0.11	-0.07	-0.14
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	0.59	0.06	0.06	-0.07	-0.06	-0.07
1	2/2/1999	0.34	0.08	0.07	-0.06	-0.05	-0.07
1	2/5/1999	1.16	0.42	0.47	0.41	0.42	0.36
1	2/11/1999	0.39	0.05	0.06	-0.04	0	-0.04
1	2/14/1999	1.79	0.1	0.19	0.06	-0.06	-0.02
1	2/17/1999	3.69	-0.09	0.12	0.05	-0.06	-0.05
1	2/20/1999	1.61	-0.62	-0.39	-0.5	-0.33	-0.65
1	2/23/1999	0.43	-0.02	0.01	-0.38	-0.03	-0.28
1	2/26/1999	1.98	-0.08	0.1	0.06	-0.06	-0.14
2	1/14/1999	0.75	0.05	0.05	-0.24	0.01	.
2	1/16/1999	1.02	0.08	0.11	-0.17	0.04	.
2	1/18/1999	1.78	0.12	0.14	-0.11	-0.06	0.06
2	1/20/1999	1.16	0.11	0.1	-0.11	0.06	.
2	1/22/1999	0.24	0.05	0.06	-0.13	0	0.02
2	1/24/1999	0.63	0.08	0.09	-0.15	0.03	0.05
2	1/26/1999	0.33	0.04	0.04	-0.11	-0.02	0.03
2	1/28/1999	0.47	0.08	0.09	.	0.04	0.05
2	2/3/1999	0.7	0.14	0.12	-0.11	0.04	0.04
2	2/5/1999	0.44	0.08	0.07	-0.02	0.02	0.04
2	2/7/1999	0.71	0.11	0.1	-0.03	0	0.03
2	2/9/1999	1.19	0.15	0.1	-0.08	-0.06	0.09
2	2/11/1999	0.28	0.08	0.07	-0.04	-0.05	0.02
2	2/13/1999	0.7	0.1	0.09	-0.17	-0.03	0
2	2/15/1999	1.13	0.15	0.13	-0.1	0.05	0.1
2	2/17/1999	1.57	0.42	0.44	0.1	0.33	0.48
2	2/19/1999	1.15	0.12	0.12	-0.11	0	0.08
2	2/21/1999	1.2	0.08	0.07	.	-0.12	0.01
3	1/21/1999	3.96	-0.08	-0.26	-0.32	-0.13	0.33
3	1/23/1999	2.62	1.32	-0.21	0.09	0.34	0.29
3	1/25/1999	6.66	0	-0.06	-0.12	-0.15	.
3	1/27/1999	8.42	0.21	0.34	0.07	0.06	0.96
3	1/29/1999	4.42	0.44	0.4	0.43	0.24	0.94
3	1/31/1999	2.03	0.37	0.33	0.27	0.28	0.65
3	2/2/1999	3.03	0.11	0.08	0.01	0.28	0.46
3	2/4/1999	5.68	0.3	0.28	0.33	-0.19	0.77
3	2/8/1999	4.01	-0.09	-0.12	-0.17	0.08	0.63
3	2/10/1999	2.68	0.26	0.21	0.18	0.11	0.42
3	2/12/1999	4.14	-0.01	-0.02	-0.26	0.13	0.61
3	2/14/1999	1.54	0.31	0.32	0.26	0.19	0.34
3	2/16/1999	6.54	0.28	0.47	0.07	-0.02	0.7
3	2/18/1999	7.33	0.25	0.45	0.31	0.52	0.86
3	2/20/1999	3.74	0.1	0.16	0.15	-0.11	0.43
3	2/22/1999	1.46	0.37	0.39	0.31	0.02	0.25
3	2/24/1999	2.01	0.33	0.36	.	0.04	0.27
3	2/26/1999	2.74	0.12	0.28	0.22	0.2	0.15
4	1/19/1999	0.71	0.06	0.03	-0.01	0.05	-0.02
4	1/21/1999	5.24	-0.06	-0.06	0.1	0.27	0.38
4	1/23/1999	1.7	-0.1	.	-0.07	-0.06	-0.12
4	1/25/1999	3.51	0.1	.	0.01	-0.17	0.18
4	1/27/1999	5.38	-0.16	.	-0.3	-0.25	.
4	1/29/1999	6.2	0.09	0.01	-0.01	-0.19	-0.35
4	1/31/1999	3.32	0.18	0.06	0.07	0.11	-0.1
4	2/2/1999	2.84	0.09	0.11	0.06	0.19	0.01
4	2/6/1999	2.03	0.21	0.23	0.2	0.16	0.14
4	2/8/1999	2.57	0.1	0.02	0.07	0.07	.
4	2/10/1999	2.25	-0.07	-0.12	-0.16	-0.18	-0.01
4	2/12/1999	5.51	-0.1	0.19	-0.11	-0.02	0.14
4	2/14/1999	2.63	0.16	0.19	0.1	-0.06	0.51
4	2/16/1999	2.24	0.23	0.33	0.77	-0.18	0.15
4	2/18/1999	2.75	-0.05	0.08	.	-0.11	.
4	2/20/1999	5.86	-0.31	-0.2	-0.24	-0.23	-0.34
4	2/22/1999	1.97	0.1	0.35	0.06	-0.29	0.24
4	2/24/1999	2.88	0.1	0.1	0.05	0.32	-0.15

DIFFERENCES FROM FRM FOR PARTICLE NITRATE (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	9.64	1.36	1.88	-0.55	0.11	.
1	1/18/1999	38.03	3.38	3.45	-2.39	-3.75	-4.31
1	1/21/1999	3.06	-0.16	-0.45	-0.76	-3.46	-1.1
1	1/24/1999	12.13	1.21	0.51	-0.34	-0.46	-1.18
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	9.69	1.71	1.32	-0.02	.	.
1	2/2/1999	0.44	0.05	0.03	-0.05	.	-0.18
1	2/5/1999	9.52	2.57	1.64	1.2	.	0.94
1	2/11/1999	0.13	0.03	0.05	-0.04	-0.02	-0.03
1	2/14/1999	16.71	2.47	1.32	-0.23	-1.15	-0.72
1	2/17/1999	25.83	1.69	-0.02	-1.46	-0.88	-1.21
1	2/20/1999	12.22	-1.82	-2.61	-4.05	-5.69	-8.03
1	2/23/1999	6.2	1.06	0.17	-0.32	.	-0.61
1	2/26/1999	9.7	0.56	0.02	-0.8	-0.83	-1.43
2	1/14/1999	3.46	-0.72	0.81	-1.17	-2.54	.
2	1/16/1999	5.33	0.27	0.91	-0.42	-2.01	.
2	1/18/1999	2.55	-0.95	-0.19	-1.42	-1.91	-1.74
2	1/20/1999	3.71	0.1	0.81	.	-1.56	.
2	1/22/1999	0.45	0.05	0.04	-0.1	.	-0.08
2	1/24/1999	1.37	0.08	0.12	-0.22	-0.49	-0.38
2	1/26/1999	1.99	0.06	0.08	0.44	-1.1	-0.58
2	1/28/1999	0.44	0.03	0.07	.	-0.23	-0.18
2	2/3/1999	4.42	0.34	0.9	-0.14	-1.53	-1.54
2	2/5/1999	2.23	0.09	0.13	-0.01	-0.84	-2.03
2	2/7/1999	7.43	0.41	1.15	0.01	.	-1.68
2	2/9/1999	4.24	0.06	0.73	0.17	.	-0.35
2	2/11/1999	0.2	0.04	0.06	0.01	-0.04	0
2	2/13/1999	0.29	0.01	0.04	-0.08	-0.23	.
2	2/15/1999	2.36	0	0.53	-0.21	-1.42	-1.49
2	2/17/1999	6.81	0.37	2.38	-0.03	-2.49	-1.96
2	2/19/1999	5.47	0.08	1.96	-0.35	-3.26	.
2	2/21/1999	2.42	-0.09	0.43	-0.4	-1.92	-1.87
3	1/21/1999	5.46	0.15	-0.45	-0.23	-0.27	-0.85
3	1/23/1999	1.63	-2.36	-0.28	-0.08	-0.31	-1.6
3	1/25/1999	4.62	0.3	-0.16	-0.05	-0.41	.
3	1/27/1999	8.64	0.69	0.34	0.07	-0.2	0.57
3	1/29/1999	3.39	0.49	0.27	0.21	-0.28	0.39
3	1/31/1999	3.46	0.66	0.4	0.32	0.34	1.06
3	2/2/1999	2.71	0.07	-0.08	-0.06	0.13	-0.59
3	2/4/1999	6.53	0.63	0.23	0.19	-0.44	-0.33
3	2/8/1999	3.14	0.11	-0.19	-0.22	-0.09	-0.08
3	2/10/1999	2.18	0.21	0.11	0.03	-0.43	0.19
3	2/12/1999	2.62	0.02	-0.06	-0.11	-0.45	-0.16
3	2/14/1999	0.92	0.27	0.24	0.19	0.18	0.19
3	2/16/1999	6.14	-0.18	0.63	-0.77	-2.14	-1.79
3	2/18/1999	3.86	0.36	0.12	1.52	0.11	.
3	2/20/1999	1.59	0.23	0.17	0.08	-0.25	-0.14
3	2/22/1999	1.07	0.54	0.53	0.46	0.34	0.45
3	2/24/1999	3.84	0.99	0.81	.	0.49	0.31
3	2/26/1999	6.09	0.96	0.77	0.49	0.07	-0.31
4	1/19/1999	0.13	-0.01	0.01	-0.11	-0.04	-0.07
4	1/21/1999	1	-0.1	-0.08	0.28	-0.58	-0.34
4	1/23/1999	0.25	-0.19	.	-0.24	-0.06	-0.17
4	1/25/1999	0.23	-0.04	.	-0.11	-0.16	-0.17
4	1/27/1999	1.01	-0.32	.	-0.56	-1.06	.
4	1/29/1999	1.07	0	-0.02	-0.29	-0.55	-0.69
4	1/31/1999	1.47	-0.07	-0.15	-0.22	-0.83	-1.21
4	2/2/1999	0.67	0.01	-0.02	-0.09	-0.28	-0.35
4	2/6/1999	0.25	-0.19	-0.15	-0.26	-0.45	-0.55
4	2/8/1999	0.17	0.01	0.03	-0.02	-0.04	.
4	2/10/1999	0.29	-0.28	-0.3	-0.42	-0.32	.
4	2/12/1999	0.11	-0.24	-0.22	-0.28	.	-0.3
4	2/14/1999	0.34	-0.18	-0.21	-0.3	-0.39	.
4	2/16/1999	1.75	0.15	0.47	1.47	-1.38	-1.07
4	2/18/1999	0.73	-0.03	0.01	.	-0.28	.
4	2/20/1999	1.14	-0.53	-0.45	-0.78	-1.35	-2.11
4	2/22/1999	0.4	-0.13	-0.18	-0.24	-0.36	-0.46
4	2/24/1999	2.25	-0.05	-0.15	-0.51	-0.83	-0.43

DIFFERENCES FROM FRM FOR AMMONIUM (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	3	0.55	1.15	0.35	0.04	1.71
1	1/18/1999	13.2	0	2.6	-0.28	-1.14	-0.11
1	1/21/1999	1.49	0.36	0.57	0.18	-0.09	0.03
1	1/24/1999	4.56	0.56	1.13	0.13	-0.3	0.21
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	3.04	0.59	0.94	0.1	-0.41	0.2
1	2/2/1999	0.26	0.15	0.2	0.18	-0.11	0.11
1	2/5/1999	2.76	0.32	0.57	0.1	-0.23	0.21
1	2/11/1999	0.14	0.02	0.04	0.06	-0.03	0.08
1	2/14/1999	5.41	0.51	1.17	0.1	-0.57	0.62
1	2/17/1999	9.34	0.34	1.51	0.07	-0.08	0.95
1	2/20/1999	4.24	0.06	-0.11	-0.45	-1.08	-0.67
1	2/23/1999	1.81	0.12	0.33	0.23	-0.28	0.24
1	2/26/1999	3.21	0.33	0.52	-0.18	-0.64	-0.27
2	1/14/1999	1.19	0.21	0.83	0.1	-0.06	.
2	1/16/1999	1.87	0.5	0.83	0.21	0.16	.
2	1/18/1999	1.31	0.29	0.48	0	0.17	-0.18
2	1/20/1999	1.5	0.71	0.81	0.53	0.14	.
2	1/22/1999	0.2	0.14	0.14	0.1	0.18	0.03
2	1/24/1999	0.51	0.27	0.26	0.19	0.14	0.01
2	1/26/1999	0.7	0.37	0.31	0.32	0.06	0
2	1/28/1999	0.23	0.07	0.08	.	0.03	-0.02
2	2/3/1999	1.55	0.66	0.85	0.32	0.37	-0.04
2	2/5/1999	0.86	0.39	0.46	0.33	0.07	0
2	2/7/1999	2.52	1.04	0.96	0.58	0.28	0.1
2	2/9/1999	1.69	0.95	0.74	0.7	0.88	0.84
2	2/11/1999	0.13	0.08	0.07	0.05	-0.07	0.01
2	2/13/1999	0.26	0.05	0.06	0.01	-0.01	-0.01
2	2/15/1999	1.12	0.55	0.63	0.45	0.04	0.01
2	2/17/1999	2.44	1.02	1.45	0.88	0.2	0.3
2	2/19/1999	1.93	1.16	1.28	0.71	-0.08	0.02
2	2/21/1999	1.13	0.61	0.61	.	-0.05	0.08
3	1/21/1999	3.1	-0.12	0.03	-0.46	-0.3	0.47
3	1/23/1999	1.38	0.2	0.3	0.04	0.08	0.14
3	1/25/1999	3.66	-0.1	0.13	-0.43	-0.37	.
3	1/27/1999	5.78	0.25	0.78	0.14	-0.05	0.87
3	1/29/1999	2.59	0.24	0.45	0.06	-0.02	0.5
3	1/31/1999	1.8	0.24	0.4	0.05	0.23	0.63
3	2/2/1999	2.05	0.09	0.42	-0.08	0.22	0.5
3	2/4/1999	4.03	0.21	0.47	0.07	-0.23	0.58
3	2/8/1999	2.43	-0.12	0.11	-0.32	-0.01	0.45
3	2/10/1999	1.72	0.22	0.36	0.14	0.04	0.37
3	2/12/1999	2.38	0.29	0.42	0.27	0.03	0.48
3	2/14/1999	0.78	0.19	0.27	0.12	0.15	0.21
3	2/16/1999	4.02	0.05	0.98	-0.22	-0.47	0.18
3	2/18/1999	3.86	0.18	0.52	0.06	0.22	0.44
3	2/20/1999	1.83	0.11	0.31	-0.06	0	0.37
3	2/22/1999	0.89	0.34	0.4	0.22	0.2	0.36
3	2/24/1999	1.97	0.5	0.68	.	0.31	0.55
3	2/26/1999	2.82	0.3	0.74	0.38	0.36	0.37
4	1/19/1999	0.23	-0.01	0.11	0	-0.05	-0.04
4	1/21/1999	1.88	0.06	0.29	-0.01	-0.05	0.08
4	1/23/1999	0.42	-0.07	.	-0.11	-0.03	-0.04
4	1/25/1999	1.21	-0.09	.	-0.07	-0.29	-0.08
4	1/27/1999	1.99	-0.04	.	-0.15	-0.38	.
4	1/29/1999	2.26	-0.05	0.1	-0.16	-0.33	-0.52
4	1/31/1999	1.45	0.11	0.22	0.19	-0.11	-0.19
4	2/2/1999	1.15	0.07	0.2	0.16	-0.08	-0.21
4	2/6/1999	0.64	-0.06	0.02	0.06	-0.18	-0.17
4	2/8/1999	0.85	-0.04	-0.04	-0.01	-0.09	.
4	2/10/1999	0.86	-0.1	-0.02	-0.03	-0.14	-0.21
4	2/12/1999	1.5	-0.12	0.06	0.03	-0.25	-0.42
4	2/14/1999	0.91	0.01	0.07	0.01	-0.11	0.01
4	2/16/1999	1.26	0.33	0.46	0.46	-0.26	-0.02
4	2/18/1999	1.13	-0.03	0.15	.	-0.27	.
4	2/20/1999	2.3	-0.08	0	0.01	-0.24	-0.55
4	2/22/1999	0.77	-0.02	0.02	0.05	-0.21	-0.05
4	2/24/1999	1.78	0.28	0.44	0.37	0.08	-0.01

DIFFERNCES FROM FRM FOR ORGANIC CARBON (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	7.72	-2.32	3.56	-1.65	0.91	-7.27
1	1/18/1999	10.01	-4.2	4.75	-0.41	-1.48	-4.49
1	1/21/1999	2.98	-1.3	1.23	-0.45	-0.1	-0.59
1	1/24/1999	6.89	-1.24	3.92	-0.71	1.17	-0.76
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	7.78	0.07	4.5	0	1.39	.
1	2/2/1999	4.58	-0.21	2.02	0.79	1.34	2.07
1	2/5/1999	4.65	-1.24	0.67	0.36	0.82	1.03
1	2/11/1999	2.05	0.09	0.47	-0.3	0.39	0.89
1	2/14/1999	5.53	-1.44	-0.33	-2.04	-0.33	-0.15
1	2/17/1999	5.69	-2.65	-0.76	0.23	-0.71	-1.01
1	2/20/1999	6.93	-1.33	1.02	-0.89	0.61	0.7
1	2/23/1999	5.5	-1.17	0.92	-1.88	0.33	0.68
1	2/26/1999	4.19	1.19	0.36	-0.45	0.25	-1.26
2	1/14/1999	9.48	-2.55	2.76	7.84	1.84	.
2	1/16/1999	11.79	-2.84	2.37	-0.92	3.46	.
2	1/18/1999	10.14	-1.99	-0.07	-3.18	1.51	1.82
2	1/20/1999	5.6	-2	1.56	0.09	1.55	.
2	1/22/1999	6.23	-0.64	0.78	0.81	2.02	2.95
2	1/24/1999	12.51	-2.2	2.4	0.4	3.32	4.67
2	1/26/1999	4.34	-1.44	0.38	-0.51	0.65	1.4
2	1/28/1999	3.96	-0.77	0.71	.	1.8	2.24
2	2/3/1999	8.98	-1.39	0.88	-1.79	-0.25	3.47
2	2/5/1999	5.6	-1.63	1.15	-0.12	-0.01	1.56
2	2/7/1999	9.67	-1.11	2.06	-0.68	-0.05	2.57
2	2/9/1999	7.69	-1.52	1.11	-1.61	2.78	3.15
2	2/11/1999	3.99	-1.55	0.48	-0.53	0.27	2.18
2	2/13/1999	7.29	-1.21	1.5	-3.12	1.65	2.61
2	2/15/1999	7.34	-1.19	1.25	-0.3	0.39	3.26
2	2/17/1999	8.34	-1.91	0.84	-1.25	1.13	4.13
2	2/19/1999	6.45	-1.8	0.81	5.04	-0.11	3.49
2	2/21/1999	7.75	-1.07	1.63	-0.74	1.37	3.77
3	1/21/1999	5.17	-1.19	-0.65	2.53	0.45	1.05
3	1/23/1999	2.31	-0.82	0.38	-0.23	0.34	0.32
3	1/25/1999	2.8	-0.75	0.51	-0.06	0.7	.
3	1/27/1999	9.57	0.43	1.74	1.57	2	3.51
3	1/29/1999	4.05	-1.63	0.23	0.07	0.57	1.71
3	1/31/1999	4.13	-0.47	0.18	0.18	0.49	2.25
3	2/2/1999	3.1	-3.01	0.36	-0.14	0.17	0.84
3	2/4/1999	5.32	-1.44	0.78	0.88	0.84	1.48
3	2/8/1999	3.4	-0.64	0.16	-0.35	0.33	0.95
3	2/10/1999	4.46	-0.33	0.72	0.32	1.1	2.04
3	2/12/1999	4.6	-1.96	0.89	0.37	0.96	2.14
3	2/14/1999	2.31	-1.31	0.39	0.29	0.78	1
3	2/16/1999	8.54	-2.47	0.71	-1.6	0.25	2.89
3	2/18/1999	4.41	-2.41	-0.3	0.02	0.21	1.11
3	2/20/1999	2.78	-0.32	0.39	2.39	0.62	1.16
3	2/22/1999	2.77	-0.95	-0.21	0.38	0.57	1.53
3	2/24/1999	3.66	-1.03	-0.05	.	0.6	1.59
3	2/26/1999	3.3	-0.65	0.2	0.23	0.09	0.97
4	1/19/1999	2.79	0.12	0.78	0.14	1.07	1.33
4	1/21/1999	7.27	-0.16	1.28	0.07	1.05	1.71
4	1/23/1999	2.49	0.17	0.7	-0.31	1.6	0.47
4	1/25/1999	2.4	-0.05	0.57	-0.43	0.66	0.76
4	1/27/1999	3.78	-0.22	.	-0.05	-0.44	.
4	1/29/1999	4.66	-0.93	0.69	-0.67	0.62	-2.19
4	1/31/1999	2.39	-0.72	0.61	.	0.33	0.53
4	2/2/1999	2	-0.96	0.28	-0.86	0.05	0.2
4	2/6/1999	3.75	-0.1	0.92	-0.26	0.79	0.69
4	2/8/1999	2.21	0.51	0.92	-0.23	0.53	.
4	2/10/1999	.	.	.	.	.	.
4	2/12/1999	3.32	-0.64	0.85	-0.83	0.63	0.33
4	2/14/1999	1.81	-0.73	0.19	-0.46	0.3	0.64
4	2/16/1999	8.51	-1.56	1	-1.82	0.56	1.17
4	2/18/1999	3.37	0.06	1.12	.	0.65	.
4	2/20/1999	3.11	0.35	0.8	0.05	1.02	0.86
4	2/22/1999	1.46	-0.56	-0.12	-0.31	-0.01	0.27
4	2/24/1999	3.24	-0.51	0.55	-0.38	0.37	.

DIFFERENCES FROM FRM FOR ELEMENTAL CARBON (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	5.22	0.45	3.73	0.27	1.05	-0.26
1	1/18/1999	7.7	2.01	5.85	0.47	0.97	1.98
1	1/21/1999	1.61	-0.03	1.24	0.05	0.11	0.06
1	1/24/1999	3.22	0.17	2.49	0.46	0.44	0.27
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	4.44	0.84	3.31	1.45	0.67	.
1	2/2/1999	1.59	0.14	0.74	0.13	0.28	0.2
1	2/5/1999	2.5	0.42	0.05	-0.17	0.06	-0.13
1	2/11/1999	0.56	0.35	0.1	0.05	0.02	0.17
1	2/14/1999	2.86	0.57	0.39	-0.13	-0.42	0.31
1	2/17/1999	5.43	0.89	1.19	1.4	0.46	0.9
1	2/20/1999	3.08	-0.43	0.22	-0.3	-0.9	-0.11
1	2/23/1999	2.64	-0.67	0.26	-0.37	-0.73	-0.46
1	2/26/1999	1.9	0.94	0.22	0.26	-0.13	-0.02
2	1/14/1999	4.56	-0.16	0.64	4.46	0.3	.
2	1/16/1999	4.82	-0.34	0.05	0.32	0.35	.
2	1/18/1999	5.71	0.28	1.45	0.78	0.34	0.52
2	1/20/1999	2.29	0.31	0.8	0.26	0.24	.
2	1/22/1999	2.37	0.16	0.41	0.26	-0.24	0.35
2	1/24/1999	5.03	0.94	1.25	1.13	0.14	0.71
2	1/26/1999	1.86	0.48	0.45	0.32	-0.06	0.2
2	1/28/1999	1.53	0.27	0.41	.	0.23	0.33
2	2/3/1999	4.56	1.58	1.02	0.24	0.6	1.07
2	2/5/1999	3.26	0.94	0.6	0.3	-0.1	0.5
2	2/7/1999	4.28	1.08	0.47	-0.08	0.05	0.37
2	2/9/1999	3.28	0.87	0.35	-0.05	0.34	0.6
2	2/11/1999	1.47	0.48	0.06	-0.2	-0.06	0.34
2	2/13/1999	2.7	0.77	0.44	-0.14	0.31	0.47
2	2/15/1999	2.99	0.26	0.5	0.23	0.12	0.58
2	2/17/1999	3.98	0.21	0.65	-0.16	0.37	0.76
2	2/19/1999	2.37	-0.23	0.4	2.25	0.02	0.42
2	2/21/1999	2.64	-0.01	0.19	-0.21	0.18	0.38
3	1/21/1999	3.54	1.95	1.22	2.07	-0.06	0.69
3	1/23/1999	0.82	-4.53	0.05	0.03	0.05	0.18
3	1/25/1999	1.64	-0.49	0.21	-0.03	-0.04	.
3	1/27/1999	5.21	3.66	0.5	0.28	0.65	0.48
3	1/29/1999	2.07	-0.06	0.06	-0.06	-0.02	0.35
3	1/31/1999	1.73	0.2	-0.09	-0.07	-0.07	0.8
3	2/2/1999	1.91	-0.34	0.12	0.11	-0.29	0.31
3	2/4/1999	3.35	-0.15	0.4	0.22	-0.12	0.55
3	2/8/1999	2.45	0.51	0.35	0.69	0.38	0.95
3	2/10/1999	2.42	0.51	0.45	0.36	0.27	0.61
3	2/12/1999	2.71	0.36	0.63	0.54	0.63	0.67
3	2/14/1999	1.16	0.05	0.05	0.25	0.18	-0.06
3	2/16/1999	5.73	0.45	1.28	-0.52	0.25	0.4
3	2/18/1999	3.43	0.15	0.05	0.66	0.09	0.34
3	2/20/1999	1.63	0.18	-0.07	1.63	0.22	0.1
3	2/22/1999	1.71	0.25	-0.12	0.34	0.32	0.11
3	2/24/1999	1.91	0.4	0.31	.	0.45	0.57
3	2/26/1999	1.57	-0.02	0.15	0.23	0.07	0.54
4	1/19/1999	1.41	0.54	0.45	0.29	0.21	0.32
4	1/21/1999	3.7	0.74	1.49	0.58	0.34	0.12
4	1/23/1999	0.76	0.38	0.4	0.24	0.39	0.38
4	1/25/1999	1.16	0.28	0.28	0.15	-0.04	0.22
4	1/27/1999	2.51	0.43	.	0.31	0.29	.
4	1/29/1999	2.84	0.43	0.6	0.14	0.14	-1.68
4	1/31/1999	0.9	0.22	0.26	.	0.09	0.22
4	2/2/1999	0.96	0.06	0.2	-0.03	0.03	0.15
4	2/6/1999	1.6	-0.23	0.18	0	-0.44	-0.31
4	2/8/1999	0.78	-0.05	0.13	0.05	-0.14	.
4	2/10/1999	.	.	.	.	.	.
4	2/12/1999	0.82	-0.17	0.02	0.07	-0.14	0.16
4	2/14/1999	0.55	-0.02	-0.01	0.13	-0.04	0.14
4	2/16/1999	3.06	0.4	0.66	0.35	0.12	0.69
4	2/18/1999	1.2	0.04	0.2	.	0	.
4	2/20/1999	1.06	-0.15	-0.02	-0.07	-0.19	-0.01
4	2/22/1999	0.65	0.03	-0.11	-0.1	-0.18	-0.1
4	2/24/1999	1.43	0.18	0.22	0.26	0.41	.

DIFFERENCES FROM FRM FOR SULFUR BY XRF (micrograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM-IMP	FRM-MET	FRM-URG	FRM-VAPS
1	1/15/1999	204.7	-3.1	5.8	-125.8	-0.3	.
1	1/18/1999	1928.3	-306.4	-190.8	-359.6	-381.8	.
1	1/21/1999	605.9	-17.7	35.9	-58.1	.	-66.4
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	242.3	32	95.6	-49.2	.	-26.8
1	2/2/1999	111	6.7	22.4	-40.9	.	-18.8
1	2/5/1999	310.6	-4.2	4.3	-42.7	.	-33.6
1	2/11/1999	120.6	1.6	7.8	-7.3	-10.8	-25.3
1	2/14/1999	644.8	8.7	40.2	-59.5	-19.8	-5.7
1	2/17/1999	1391.7	-81.4	32.5	-46.8	-65.3	.
1	2/20/1999	645.7	-156.3	-113.8	-190.4	-171.8	-216.5
1	2/23/1999	174.7	.	32.2	-111.3	.	12.4
1	2/26/1999	787.5	36.3	69.3	-19.1	-10.6	-51.6
2	1/14/1999	299.6	-1.6	-28.5	-59.4	1.8	.
2	1/16/1999	365.5	8.9	64.2	-88.8	7.7	.
2	1/18/1999	642.8	11.4	-237.6	-141.2	-10.7	63.7
2	1/20/1999	385.5	-17.5	23.8	-45.7	1.5	.
2	1/22/1999	71.2	-13.1	-2	-55.7	.	-79.9
2	1/24/1999	237.9	15.9	78.6	-58.2	17.2	19.5
2	1/26/1999	122.3	-6.5	-1.7	-52.3	-4.1	1.8
2	1/28/1999	161.9	13.7	18.8	.	18.9	24.1
2	2/3/1999	226.6	-10.1	-7.2	-86.2	-11.6	-0.4
2	2/5/1999	176.7	11	7.2	27.9	19	.
2	2/7/1999	285.2	17.2	17.3	-29.8	.	20.5
2	2/9/1999	402.3	1.6	38.4	-44.8	.	-21.8
2	2/11/1999	85.3	5	13.1	-6.8	8	8.6
2	2/13/1999	237.1	0	7.7	-46.8	.	.
2	2/15/1999	407	4.8	29.7	-53.9	15.5	61.4
2	2/17/1999	479.5	20.5	54.1	32	16.7	43.7
2	2/19/1999	434.9	35.7	40.9	-55.2	23	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	1322.8	-218.2	-177.6	-342.2	-157.5	-244.6
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	2232.9	-130.2	109.3	-290.4	-270.1	.
3	1/27/1999	2794	-158.9	38.4	-344.3	-445.4	-239.9
3	1/29/1999	1429.6	-24.1	103.4	-34	-90.7	14
3	1/31/1999	640.2	12.3	23.1	-33.5	-53.4	-40.6
3	2/2/1999	1033.4	-39	74.8	-80	-68.2	2.2
3	2/4/1999	2026.7	84.5	274.5	-21.9	-44.2	26.9
3	2/8/1999	1480.9	19.5	868.6	-155.2	-27.9	-137.9
3	2/10/1999	900.1	24.1	63	-60.7	-27.3	33.3
3	2/12/1999	1474.4	20.3	.	-83.5	-17.5	.
3	2/14/1999	440.7	7.1	34.2	-19.8	0.9	106
3	2/16/1999	2202.8	49.1	208.3	-84.3	21.1	33
3	2/18/1999	2411.2	-55.9	185.1	-108.2	-71.2	.
3	2/20/1999	1289.9	20.2	.	-49.3	-47.2	32.9
3	2/22/1999	394.2	-1.1	-2.9	-56.6	-38	.
3	2/24/1999	589.7	11.8	33.2	.	-73.6	.
3	2/26/1999	891.5	-49.5	21.3	-95.4	-77.8	-23.1
4	1/19/1999	261.7	2.5	20.9	-27	-18.1	8.1
4	1/21/1999	1820.8	-63.1	78.6	-48.8	-128.4	-78.4
4	1/23/1999	611.7	-9.9	41.8	-20.3	-42.8	-12.7
4	1/25/1999	1231	-26.6	83.1	-132.8	-57.9	-101.4
4	1/27/1999	2004.1	57.9	.	-82	-90.3	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	1171.4	-12.2	199.4	-16.7	-104.3	815.5
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	692.4	54.5	129	-24.7	-62.6	2.6
4	2/8/1999	867.2	-22.4	-53.1	-37.6	-53.7	.
4	2/10/1999	861.3	-3.9	52.4	-8.2	-31	.
4	2/12/1999	1953.4	125.4	112.6	-148.5	.	-16
4	2/14/1999	888.5	55.7	33.7	0.5	-65.7	.
4	2/16/1999	712.1	23.5	19.5	3	-78.3	-19.9
4	2/18/1999	1007.4	8.7	-9.7	.	-62.6	.
4	2/20/1999	2083.7	-45.8	-96.3	4.7	-183.7	-220.6
4	2/22/1999	677.9	21.3	58.6	-36.9	-86.3	-7.7
4	2/24/1999	1046.2	34.4	114.8	-75.3	-19	-84.3

DIFFERENCES FROM FRM FOR SILICON (nanograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM_IMP	FRM_MET	FRM_URG	FRM_VAPS
1	1/15/1999	377.8	-70.7	-231.6	-2031.5	39.1	.
1	1/18/1999	216.5	50.1	10.8	-292.9	100.9	.
1	1/21/1999	16.2	-50.7	-8	-113.3	.	-325
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	150.1	10.3	33.7	-544	.	-875.1
1	2/2/1999	145.7	-20.5	-20.5	-769.4	.	-742.2
1	2/5/1999	43	-22.2	5.9	-33.5	.	-147.9
1	2/11/1999	101.1	-78.2	-48.7	-691.1	-9.1	-887.2
1	2/14/1999	121.4	-52.1	-49.8	-550.1	-4.1	-672.7
1	2/17/1999	235.9	-95.6	-47.8	-406.5	-8.3	.
1	2/20/1999	118.7	-51.2	-16	-494	12.8	-797.2
1	2/23/1999	280.1	.	-60.8	-1346.9	.	-1990
1	2/26/1999	71.7	-41.3	-9	-62.1	-11.4	-513.3
2	1/14/1999	467.1	-1.5	-92.6	-1284.4	126.5	.
2	1/16/1999	475.4	-25.3	3.3	-2442.4	98.8	.
2	1/18/1999	403.3	-47.1	-228.5	-2169.5	108.3	-88.1
2	1/20/1999	416.5	-55.2	10.8	-819.8	115.6	.
2	1/22/1999	211.5	-62.2	-45.1	-1197.6	.	-3746.9
2	1/24/1999	444.2	-30	91.5	-1304.3	130.4	-140.4
2	1/26/1999	133.1	-46.1	-28.6	-537.7	42.8	-62.6
2	1/28/1999	75.1	-13.3	-39.7	.	32.3	-37.7
2	2/3/1999	333.6	-116.4	-130.4	-2013.8	18.2	-146.7
2	2/5/1999	55.7	-4	-71.4	-48.1	13.6	.
2	2/7/1999	94	-1.4	-8.5	-484.3	.	-63.3
2	2/9/1999	172	-53.4	-41	-358.2	.	-93.6
2	2/11/1999	49.9	-22.1	-43.8	-321.3	2.7	-19.8
2	2/13/1999	395.3	-79.7	-56.4	-1241	.	.
2	2/15/1999	312.2	-77.9	-98.7	-1028.6	45.1	-77.4
2	2/17/1999	374.7	-100.3	-54.8	-1090.8	80.3	-92.8
2	2/19/1999	320.4	-125.1	-166.5	-1252.4	20.4	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	51.8	-15.2	-30.8	-40.9	-8.9	0.4
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	48.5	14.4	1	-28.8	9.9	.
3	1/27/1999	96.5	12.6	25.2	-95.8	11.9	-15
3	1/29/1999	40.5	-19.6	5.1	-42.3	-3.3	-6.1
3	1/31/1999	31.2	-3.9	-13.8	-32.4	-9.6	15.6
3	2/2/1999	25	-20.7	-19.5	25	-22.6	-32.2
3	2/4/1999	59.1	-30.3	-4.7	-115.5	-31.2	-11.2
3	2/8/1999	40.3	11.4	-30.9	-21.7	36.7	6
3	2/10/1999	23.7	-8	-17.5	-51.6	-10.3	-20.8
3	2/12/1999	19.3	-20.6	.	-129.2	-12.7	.
3	2/14/1999	25.9	16.4	12	-12.2	25.9	22.5
3	2/16/1999	132.8	6.5	-19.9	-185.2	2.1	-10
3	2/18/1999	24.7	-39.4	-39	-41.1	-25.1	.
3	2/20/1999	22.1	-25.4	.	-44.5	-8.8	9.4
3	2/22/1999	31.8	-3.9	-17.6	-203.3	6.1	.
3	2/24/1999	61.3	-10	16.5	.	15.7	.
3	2/26/1999	71.6	-3.9	-9.8	-136.7	-14.4	-25.1
4	1/19/1999	70.5	1.9	4	-27.3	-5.1	1.8
4	1/21/1999	194.9	-13	-10.3	-31.5	9.9	-62.6
4	1/23/1999	22.6	-18.7	-15.7	22.6	-6.1	-291.9
4	1/25/1999	34.4	4	-18.5	-65.6	5.3	-74.1
4	1/27/1999	38.4	-28.2	.	-34.1	-28	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	24	-11.2	-2.8	-6.2	14.8	-265.8
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	72.3	25.6	48.1	-84.6	-11	-6
4	2/8/1999	35.7	0.4	7.3	-22.4	-2.3	.
4	2/10/1999	76.8	5.8	11.8	-75.8	20	.
4	2/12/1999	18.8	-17.4	5.1	18.8	.	-32.3
4	2/14/1999	42.1	3.2	18.3	-14.5	-0.2	.
4	2/16/1999	226.9	62.6	65.7	-58.9	84.4	-31
4	2/18/1999	41.9	15.6	1	.	-10.9	.
4	2/20/1999	100.8	1	-14.7	66.8	-3.6	-5.5
4	2/22/1999	40.9	8.1	-1.2	24.9	-13.2	-23.7
4	2/24/1999	106.2	15.7	39.4	1.3	29.6	-9.8

DIFFERENCES FROM FRM FOR POTASSIUM (nanograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM_IMP	FRM_MET	FRM_URG	FRM_VAPS
1	1/15/1999	121	-14.8	-22.8	-352.9	-4.9	.
1	1/18/1999	122.5	-39.4	-39.8	-109	-41.5	.
1	1/21/1999	40.1	-13.8	-13.6	-25.6	.	-76.6
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	124.7	19.9	52	-75.7	.	-122.2
1	2/2/1999	48.4	-3.7	4.7	-118.7	.	-99.3
1	2/5/1999	62.5	-1.3	1.7	1.8	.	-23.7
1	2/11/1999	23.5	-7.3	-6.7	-107.3	-1.1	-126
1	2/14/1999	93.4	-6.3	-1.7	-93.4	-1.2	-106.8
1	2/17/1999	112	-20.3	-3	-63.7	-2.4	.
1	2/20/1999	77.1	-13.8	-5.8	-93.2	-8.4	-141.3
1	2/23/1999	80.7	.	1	-240.2	.	-293.7
1	2/26/1999	49.9	-8.5	-6.1	-21.3	2.7	-134.7
2	1/14/1999	194.5	0.5	-16.7	-184.8	16.7	.
2	1/16/1999	225.6	0.4	31.1	-402.7	12.1	.
2	1/18/1999	237.2	4.3	-90.2	-324.1	10.4	-0.9
2	1/20/1999	181.1	-11	7.6	-144	15.2	.
2	1/22/1999	81.9	-5.3	-4.7	-186.3	.	-528.2
2	1/24/1999	244.8	7.7	72	-205.7	15.7	-19.8
2	1/26/1999	62.4	-8.2	-6.4	-87.4	3.8	-7.3
2	1/28/1999	29.5	-0.8	-4.8	.	4.8	-3.4
2	2/3/1999	124.2	-14.5	-14	-312.1	-0.3	-21.7
2	2/5/1999	58.8	-1.1	-6.5	-1.6	3.5	.
2	2/7/1999	123.6	7.1	6.3	-72.6	.	6
2	2/9/1999	83.5	-7.6	-3.8	-64.8	.	-12.3
2	2/11/1999	31.5	-0.8	-6.8	-50.4	0.2	-3.7
2	2/13/1999	134.6	-10.1	-2.7	-203	.	.
2	2/15/1999	127.2	-5.8	-9.4	-165.7	5.1	-3
2	2/17/1999	159.7	-3.6	6.5	-166.7	16.1	-6.4
2	2/19/1999	188.2	-5	-3.1	-188.5	10.8	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	53.9	-7.6	-8.8	-3.8	-14.8	-12.6
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	35.7	-2.7	-0.1	-10.9	0.4	.
3	1/27/1999	111.9	-7.2	0.5	-25.8	-13.7	-16.5
3	1/29/1999	44.2	-2.6	0.8	-15.9	-5.4	-0.6
3	1/31/1999	58.6	1	-0.3	-6.8	-7.3	-3.5
3	2/2/1999	36.1	-1.8	-0.7	0.1	-2.2	-0.2
3	2/4/1999	71	4.7	12.4	-4.1	5.3	2.1
3	2/8/1999	48.5	3.5	-22	-7.1	2.6	-4.1
3	2/10/1999	45.5	-4	-1.2	-13.6	-1.3	-3.5
3	2/12/1999	57.4	0.5	.	-6.8	-0.9	.
3	2/14/1999	31.1	2.2	2.7	-4.5	2.1	12.1
3	2/16/1999	115.1	-1.3	10.1	-32	-0.2	-7.7
3	2/18/1999	63.9	-4.1	1.4	-4.9	-7.3	.
3	2/20/1999	40.2	-1.9	.	-11.6	-3.1	1
3	2/22/1999	28.5	-5.3	-5.6	-34.4	-6.1	.
3	2/24/1999	37.5	-0.8	2.5	.	-1	.
3	2/26/1999	51.9	-2.4	-0.7	-21.8	-2.6	-1.8
4	1/19/1999	32.5	3.8	1.1	-12.9	-2	-0.8
4	1/21/1999	176.9	-6.1	-3	-12.9	-13.7	-27.7
4	1/23/1999	38.7	-5.1	-6.7	-4.9	1.9	-9.1
4	1/25/1999	35.2	-0.7	1.6	-11.6	-3.2	-1.7
4	1/27/1999	77.1	1.5	.	-2	-0.1	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	44.6	-4.9	4.3	-7.7	-3.7	-21.7
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	74.9	6.4	26.8	-11	-5.9	-2.1
4	2/8/1999	31.9	-0.8	-2.1	-13.1	-0.1	.
4	2/10/1999	58.1	0.7	3.5	-17.7	1.9	.
4	2/12/1999	72.3	3.2	5.5	-5.2	.	-0.6
4	2/14/1999	36.5	0.8	0.1	-3.4	-3.1	.
4	2/16/1999	146.4	11.8	8.9	-20.8	-2.9	-9.5
4	2/18/1999	49.1	5.2	2.3	.	-0.5	.
4	2/20/1999	69.6	0.4	3.1	6.7	1.5	-3.1
4	2/22/1999	31.7	1.7	0.9	-0.9	-3.5	-2.7
4	2/24/1999	95.2	7.6	16.6	1.3	4.4	0.2

DIFFERENCES FROM FRM FOR CALCIUM (nanograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM_IMP	FRM_MET	FRM_URG	FRM_VAPS
1	1/15/1999	360.3	-113	-206.2	-2046.9	36.3	.
1	1/18/1999	343.1	82.3	60.8	-408.1	187.8	.
1	1/21/1999	33.6	-22.8	-22.9	-55.2	.	-173.1
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	140.4	-0.6	39	-562.5	.	-780.8
1	2/2/1999	246.1	-47.1	-38	-1450.4	.	-1319
1	2/5/1999	52.3	-23.3	-12.1	-14.1	.	-277.6
1	2/11/1999	63.7	-21.8	-23.4	-321.9	-0.5	-401.5
1	2/14/1999	112.4	-64.7	-53.9	-615.1	0.3	-633.7
1	2/17/1999	124.5	-62.5	-34.2	-196.3	2.3	.
1	2/20/1999	80.1	-84.3	-58.1	-631.2	-18	-672.8
1	2/23/1999	243.1	.	-42.1	-1540.6	.	-1592.8
1	2/26/1999	60.6	-16.1	-18.5	-28.5	11.8	-283.1
2	1/14/1999	218.6	-14.7	-37.2	-596.6	48.2	.
2	1/16/1999	187.9	-24.6	3.3	-1073.7	39.5	.
2	1/18/1999	159.4	-24.8	-102.6	-927.4	40.9	-53.1
2	1/20/1999	150.8	-26.9	-16.6	-407.8	41	.
2	1/22/1999	88.8	-29.2	-32.7	-551.6	.	-1657.8
2	1/24/1999	167.1	-26.9	28.7	-530.2	40.4	-69.4
2	1/26/1999	40	-22.6	-17.7	-272	6.5	-31.8
2	1/28/1999	25.6	-12.9	-24.4	.	2	-13.2
2	2/3/1999	148.9	-58	-64.8	-965.6	9.1	-76
2	2/5/1999	29.1	-8.5	-39.2	-22	1.4	.
2	2/7/1999	38.9	-13.3	-10.1	-198.7	.	-12.1
2	2/9/1999	65.4	-21.9	-21.8	-159	.	-30.9
2	2/11/1999	32.7	-11.3	-29.9	-187.9	3	-20.4
2	2/13/1999	123.9	-19.4	-20.5	-382.2	.	.
2	2/15/1999	129.6	-34.4	-43.2	-480.6	15.7	-34.9
2	2/17/1999	157.8	-48.2	-32.3	-498	35.2	-38.3
2	2/19/1999	116.3	-50.4	-60.2	-520.3	13.5	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	53	-14.4	5.5	2.5	6.9	-1.6
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	24.1	-0.1	1.3	-16.4	6.1	.
3	1/27/1999	58.9	-13.8	-7.6	-77.5	-6.5	-10.3
3	1/29/1999	23.8	-1.9	-0.4	-41.8	1.4	-0.6
3	1/31/1999	26.7	1.9	1.4	-23.9	0.7	8.2
3	2/2/1999	24.8	-6.6	-2.5	1.6	2.1	0.3
3	2/4/1999	47.7	4.7	9.6	-56.7	14	5.6
3	2/8/1999	16.7	0.4	-19.1	-25	3.4	0.4
3	2/10/1999	27.7	-5.5	-3.4	-32.5	3.8	2.2
3	2/12/1999	65.5	20.4	.	-17.8	28.1	.
3	2/14/1999	12.6	-0.3	-0.4	-3.2	2.3	8.6
3	2/16/1999	106.9	-19.6	-17.3	-209	5.3	-15.2
3	2/18/1999	22.5	-4.9	-2.4	-4.7	-0.5	.
3	2/20/1999	13.7	-4.9	.	-27	-2.2	-3
3	2/22/1999	20.3	-5.1	-6	-72	0.5	.
3	2/24/1999	28.1	-3.4	-1.8	.	-1.1	.
3	2/26/1999	23.4	-9.6	-8.8	-39.4	1.2	-3.6
4	1/19/1999	16.8	1.7	0.1	-18.7	-2.1	-1.6
4	1/21/1999	146.1	-12.1	-25.5	-21.6	6.3	-36.2
4	1/23/1999	27.2	-2.1	6	1.8	6.2	3.9
4	1/25/1999	16.4	-0.4	1.6	-13.1	0.6	0.5
4	1/27/1999	16.8	-8.8	.	-5.8	-1.8	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	14	-2.2	3.2	-5.2	3.6	-106.7
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	44.3	8.4	23.7	-14.7	11.1	4
4	2/8/1999	13.1	2.2	3.4	-9.4	1.8	.
4	2/10/1999	28.5	3.7	2	-29.9	6.8	.
4	2/12/1999	17.1	2	-1.6	0.7	.	-0.6
4	2/14/1999	13.6	0.8	-0.2	-1.8	-0.6	.
4	2/16/1999	88	11.4	13.3	-31.2	18.4	-12.1
4	2/18/1999	13.8	2.3	1.8	.	2.2	.
4	2/20/1999	17	-2.8	0.1	-0.2	3.3	-1.6
4	2/22/1999	20.8	1.6	1.2	-1.8	4.3	-3.9
4	2/24/1999	18.3	3.5	5.9	3.8	6.2	0.3

DIFFERENCES FROM FRM FOR IRON (nanograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM_IMP	FRM_MET	FRM_URG	FRM_VAPS
1	1/15/1999	385.9	-96.2	-100.4	-950.1	22.9	.
1	1/18/1999	239.4	-52.8	-84.8	-161.6	11.3	.
1	1/21/1999	54.6	-18.9	-12.2	-55.6	.	-198.9
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	220.1	15.2	69.4	-284.1	.	-567.8
1	2/2/1999	113.8	-10.9	-7	-312.9	.	-356.9
1	2/5/1999	72.2	-8.1	-2.9	4.7	.	-123
1	2/11/1999	58	-10.2	-10.9	-252.8	6.5	-348.3
1	2/14/1999	166.2	-75.2	-37.2	-332.7	-5.5	-429.8
1	2/17/1999	209.9	-72.2	-23.6	-152.9	-3.7	.
1	2/20/1999	125.7	-67.3	-64.6	-287.5	-33.4	-492.9
1	2/23/1999	276.6	.	-14.8	-652.1	.	-860.4
1	2/26/1999	92.5	-18.2	-9.4	-39.7	6.9	-298.2
2	1/14/1999	420.6	-33	-52.6	-450.7	58	.
2	1/16/1999	337.6	-22.5	27.5	-848.7	58.5	.
2	1/18/1999	330.3	-10.6	-155.3	-833.9	70.7	-71.7
2	1/20/1999	186	-22.8	0.8	-294.8	47.6	.
2	1/22/1999	173.7	-38.8	-31.3	-424	.	-1444.8
2	1/24/1999	304.8	-37.9	77.1	-473.1	46.5	-93.9
2	1/26/1999	94.5	-33.6	-15.1	-197.7	19.8	-40.3
2	1/28/1999	57.1	-12.6	-19.9	.	13	-19.6
2	2/3/1999	270.3	-54.6	-53.1	-701.1	11.2	-79.9
2	2/5/1999	73.3	-21.6	-52.1	-27	7.8	.
2	2/7/1999	141.5	-29.9	-19.3	-197.3	.	-19.9
2	2/9/1999	174	-44	-40.1	-142.3	.	-75.8
2	2/11/1999	59.8	-18.1	-63	-182.1	-7.7	-18.2
2	2/13/1999	257.3	-29.5	-26.6	-386.3	.	.
2	2/15/1999	200.8	-43.3	-48.4	-358.8	20.7	-21.9
2	2/17/1999	298.4	-74.2	-32.6	-374	50.4	-45.7
2	2/19/1999	190.2	-44.2	-61.3	-388.1	18.7	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	101.8	-56.2	-42.3	-67.8	-31.7	-57.7
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	69.4	-5.2	1.7	-0.6	1.9	.
3	1/27/1999	256.3	-30	-30.7	-96.4	-16	-30.1
3	1/29/1999	67.1	-7.5	-3.2	-35.3	-0.7	-3.5
3	1/31/1999	69.3	5.2	6.7	-13.7	11	43.3
3	2/2/1999	89.3	5.6	4.7	15.2	11.4	15.7
3	2/4/1999	221.5	14.8	27.4	-57.4	3.9	11.8
3	2/8/1999	68.8	-15.4	-5.3	-23.5	10.4	-8.8
3	2/10/1999	92.3	-22.5	-4.5	-61	-11.6	-12.8
3	2/12/1999	138	-2.4	.	-51.6	5.6	.
3	2/14/1999	18.1	-1	1.5	-6.1	2.2	8.2
3	2/16/1999	303.3	-14.5	-7	-205.8	20.9	-8.4
3	2/18/1999	76.4	-13.8	1.3	-9.3	1.8	.
3	2/20/1999	24	-11.9	.	-36.7	-6.4	-7.5
3	2/22/1999	34	-5.4	-10.9	-49.5	-1	.
3	2/24/1999	56.2	-1	1.7	.	-2.9	.
3	2/26/1999	53.2	-18.4	-13.3	-49	-0.4	-4
4	1/19/1999	65.5	15.1	11.9	-18.5	14.3	4.6
4	1/21/1999	124.6	-8.7	-7.2	-22.6	4.2	-24
4	1/23/1999	12	-3.5	4.8	4.3	3.4	4.3
4	1/25/1999	32.7	-8.9	-3.6	-16.1	0	-9.3
4	1/27/1999	45.5	-4.4	.	-13.1	5.1	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	21.5	-5.1	4.2	-9.9	0.3	-73.7
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	84	8.2	13.7	-37.6	5.8	-17.5
4	2/8/1999	54.6	11.5	8.4	-4.1	10.6	.
4	2/10/1999	103.1	1.7	9.1	-20	19.2	.
4	2/12/1999	10.9	-6	-3.3	-3.8	.	-5.6
4	2/14/1999	31.9	4.4	2.2	-3.9	8.1	.
4	2/16/1999	82.2	19.8	15.9	-40.2	13.8	-3.1
4	2/18/1999	40.3	11.8	9.3	.	9.3	.
4	2/20/1999	34.6	-1.4	-2	-2.8	-0.9	-9.4
4	2/22/1999	40.8	1.2	1.6	-8.3	-1.1	-15.9
4	2/24/1999	45.5	3.9	13.3	-1.1	14.2	-7.4

DIFFERENCES FROM FRM FOR ZINC (nanograms/m3)

SITE	DATE	FRM MEAN	FRM-AND	FRM_IMP	FRM_MET	FRM_URG	FRM_VAPS
1	1/15/1999	254.8	3.1	8.5	-10.7	-15.2	.
1	1/18/1999	85.4	-74.1	-77.5	-77.8	-88.6	.
1	1/21/1999	8.2	0.1	-0.9	-3.7	.	-4.5
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	25.5	1.1	6.6	-16.2	.	-7.4
1	2/2/1999	139.2	2.3	23.8	-0.8	.	5.7
1	2/5/1999	78.8	3.8	7.2	5.6	.	-1
1	2/11/1999	3.9	-0.6	-0.4	-1.9	1.6	-5.9
1	2/14/1999	17.4	0	1.1	-43.8	1	-4.4
1	2/17/1999	47.1	-6.8	2.7	-8.6	-7.1	.
1	2/20/1999	15.9	-3.6	-0.6	-6.1	-3.6	-8.7
1	2/23/1999	156.1	.	39.2	-24	.	93.6
1	2/26/1999	12	-0.1	1	-0.7	-1.2	-5.8
2	1/14/1999	47.5	17	19.1	5.1	18.5	.
2	1/16/1999	25.8	1.4	5.7	-19.7	0.2	.
2	1/18/1999	25.1	-2.7	-14.7	-28.3	0	-2.9
2	1/20/1999	25	-3.4	-0.6	-5.2	-0.1	.
2	1/22/1999	11.4	0.4	1.5	-7.3	.	-21.2
2	1/24/1999	24.8	0.4	6.3	-13.1	0.6	0.2
2	1/26/1999	15.7	-1.4	-1.3	-4.2	-0.2	-1.2
2	1/28/1999	1.5	-2.2	-2.6	.	-0.4	-2.7
2	2/3/1999	19.2	1.2	0.2	-18.9	-1	-0.6
2	2/5/1999	11.8	3.5	1.5	0.7	3.3	.
2	2/7/1999	10.1	-2.5	-0.7	-7.9	.	-0.3
2	2/9/1999	15.7	-1.6	1.4	-2.7	.	-4.6
2	2/11/1999	3.8	-0.6	-0.8	-2.6	0.5	1.8
2	2/13/1999	16.5	-0.6	0	-9.7	.	.
2	2/15/1999	15	-2.2	-1.1	-9.3	-0.4	4.4
2	2/17/1999	22.9	2.8	6	-4	4	3.9
2	2/19/1999	14.9	-1.8	0.2	-12.1	1.5	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	65.1	-15.1	-14.5	-10.4	-11.8	-21.7
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	21.2	-3.8	1.6	-0.5	-0.3	.
3	1/27/1999	83.3	-12	-7.3	-14.9	-18	-15.6
3	1/29/1999	19.8	0.7	3.8	1.4	0.3	2.4
3	1/31/1999	16.8	1.2	-0.1	2.3	-0.9	1.3
3	2/2/1999	22.4	-1.2	2.1	-3.4	-1.6	2.5
3	2/4/1999	48.7	4.8	9.5	-2.6	0.5	2.8
3	2/8/1999	30.4	-2.2	18	-3.3	-3.5	-5.8
3	2/10/1999	22.9	-3	1.2	-1	-0.4	-2.6
3	2/12/1999	35.4	15.4	.	11	13.5	.
3	2/14/1999	5.2	0.3	0.3	0.3	0.2	2.2
3	2/16/1999	67.8	3.4	4.5	3	4.7	6.1
3	2/18/1999	35.6	-2.2	0.2	4.3	-6.4	.
3	2/20/1999	10.6	0.8	.	1	-0.8	1.5
3	2/22/1999	6.7	-1.9	-2	-3.9	-1.8	.
3	2/24/1999	30.8	1.1	-0.1	.	-2.3	.
3	2/26/1999	15.4	0.5	0	2.5	0.8	0.6
4	1/19/1999	18.7	3	2.6	2.7	-0.5	0.7
4	1/21/1999	43.4	-3.5	6.9	-2.1	-0.6	-4.2
4	1/23/1999	5.8	-0.7	2.1	-0.5	-0.7	1.8
4	1/25/1999	7.6	-1	-0.1	-0.3	1.4	2.3
4	1/27/1999	17.8	-5.9	.	-2.3	-3.6	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	54.9	42.1	53.8	42.7	41.8	49.9
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	16.7	2.3	-19.8	2.6	2.7	3.7
4	2/8/1999	6.4	-1.6	-3.2	-3.1	-3.1	.
4	2/10/1999	11.8	0	-0.9	0	-1.2	.
4	2/12/1999	5.3	2	-0.3	2	.	0
4	2/14/1999	11.1	0.9	0.3	1.4	-0.2	.
4	2/16/1999	14.6	1.5	0.2	1	-2.2	-1.3
4	2/18/1999	14	0.5	1.3	.	-0.4	.
4	2/20/1999	13.2	-0.3	-0.5	1.6	-0.1	-3
4	2/22/1999	7.9	0.4	1	1.4	-0.8	-2.3
4	2/24/1999	9.9	0.1	1.3	-0.6	-4.2	-3.1

APPENDIX G-2

Percent Differences Between the FRM, (Reference Sampler), and the Speciation Samplers by Site and by Sampling Period

(Manganese, Copper, Lead and Arsenic Excluded Because of Too Few Samples)

Percent Differences From FRM For PM-2.5

% Difference = [(FRM Conc- Sampler Conc)/FRM]*100

SITE	DATE	FRM (ug/m3) AND % Difference		IMP % Difference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	28.6	6.2	8.1	-131.5	-15.3	.
1	1/18/1999	74.3	-14.6	-17.8	-25.3	-41.5	.
1	1/21/1999	14.9	10.7	11.0	10.4	-12.7	-118.6
1	1/24/1999	29.4	-2.5	8.1	-13.9	-31.7	-96.0
1	1/27/1999	3.0	9.8	6.8	-2.7	-4.4	-65.9
1	1/30/1999	29.5	25.3	44.3	-13.4	.	-68.8
1	2/2/1999	5.6	2.7	-1.6	-155.0	8.2	-125.5
1	2/5/1999	21.0	14.3	6.3	8.1	.	-24.8
1	2/11/1999	2.2	-1.4	-19.5	-328.1	-14.9	-310.9
1	2/14/1999	35.6	4.0	4.0	-16.8	-50.1	-110.0
1	2/17/1999	59.0	0.0	0.6	-11.4	-36.5	.
1	2/20/1999	29.1	-7.1	-12.7	-33.4	-36.5	-86.1
1	2/23/1999	17.6	1.1	8.7	-82.1	-27.2	-107.4
1	2/26/1999	23.6	4.5	4.4	-6.9	-48.5	-168.8
2	1/14/1999	22.0	0.7	29.0	-72.4	14.0	.
2	1/16/1999	25.3	-0.9	16.3	-84.7	3.1	.
2	1/18/1999	24.4	-0.8	7.3	-79.1	3.6	-7.7
2	1/20/1999	12.7	-1.7	16.1	-110.1	8.9	.
2	1/22/1999	9.0	-1.1	2.0	-127.5	.	-0.9
2	1/24/1999	19.8	-3.7	26.1	-91.6	1.5	-9.3
2	1/26/1999	7.6	-10.7	9.0	-29.3	-7.1	-34.8
2	1/28/1999	4.1	-6.8	0.0	.	3.9	1.2
2	2/3/1999	17.3	1.4	10.2	-98.0	7.2	-1.1
2	2/5/1999	11.5	4.2	12.1	-5.5	-10.6	.
2	2/7/1999	23.3	4.6	22.2	-22.9	.	-38.3
2	2/9/1999	13.8	1.7	13.1	-52.9	.	1.2
2	2/11/1999	3.9	-5.9	-0.5	-62.0	13.8	3.8
2	2/13/1999	12.4	1.0	-6.6	-103.0	.	.
2	2/15/1999	12.8	1.3	4.2	-103.9	8.4	4.5
2	2/17/1999	20.3	0.4	14.1	-78.4	-2.6	-5.8
2	2/19/1999	13.4	-0.7	8.0	-115.4	-0.7	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	25.8	1.7	-3.5	3.0	2.8	-28.9
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	19.4	0.2	3.0	-5.6	-9.5	.
3	1/27/1999	37.6	-2.5	-2.6	-8.4	-8.9	-26.2
3	1/29/1999	15.0	0.3	2.1	-2.8	-2.6	-10.1
3	1/31/1999	12.4	4.7	5.7	11.7	0.5	-9.6
3	2/2/1999	13.8	-0.6	1.5	3.5	-2.0	-17.4
3	2/4/1999	25.8	0.2	0.5	2.9	-2.0	-33.9
3	2/8/1999	16.5	-2.4	-0.2	0.8	0.1	-12.4
3	2/10/1999	11.9	0.2	3.8	-7.8	1.2	-25.7
3	2/12/1999	15.6	0.3	.	0.1	1.7	.
3	2/14/1999	5.2	2.1	-3.9	-7.4	-0.2	32.0
3	2/16/1999	32.2	-1.1	5.7	-19.8	1.7	-29.1
3	2/18/1999	24.9	-0.3	-1.0	1.9	1.8	-2.2
3	2/20/1999	10.5	-5.0	-0.2	-17.8	-8.5	-26.5
3	2/22/1999	5.0	-5.0	-14.4	-30.0	-17.2	.
3	2/24/1999	10.8	-0.6	-0.6	.	-8.3	.
3	2/26/1999	14.4	-2.9	-0.4	-10.8	-4.6	-18.3
4	1/19/1999	4.4	3.2	-14.6	-13.0	3.9	-4.3
4	1/21/1999	23.8	2.8	3.2	-2.8	-3.7	-7.1
4	1/23/1999	6.5	4.6	12.7	8.4	5.7	-25.8
4	1/25/1999	8.3	-3.3	-2.7	-16.0	-1.2	-13.9
4	1/27/1999	15.3	-3.0	.	-4.2	-5.8	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	8.7	-23.1	17.6	4.7	-4.4	-20.7
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	10.4	9.4	12.4	-5.1	5.2	-20.4
4	2/8/1999	6.6	7.8	5.9	-2.6	-9.0	.
4	2/10/1999	11.5	4.0	2.9	-12.2	-4.1	.
4	2/12/1999	12.8	3.7	2.1	-5.7	.	-26.9
4	2/14/1999	6.5	12.3	4.3	-3.2	-10.9	.
4	2/16/1999	20.5	4.2	0.9	-15.5	-3.7	-19.0
4	2/18/1999	9.8	2.2	-1.0	.	-12.5	.
4	2/20/1999	13.9	-0.4	-2.5	-10.7	-9.4	-16.0
4	2/22/1999	5.2	4.0	3.7	-8.1	-6.3	-4.0
4	2/24/1999	12.0	0.8	5.2	-2.3	-9.2	-26.1

Percent Differences From FRM For Sulfate by IC

% Difference = [FRM Conc- Sampler Conc)/FRM]*100

SITE	DATE	FRM (ug/m3)	AND % DIfference	IMP Percent Difference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	0.6	14.0	21.1	-70.2	7.0	-59.7
1	1/18/1999	6.0	-1.3	9.4	-0.7	-11.0	-12.2
1	1/21/1999	1.6	-1.2	-1.2	-2.5	-6.8	-18.5
1	1/24/1999	1.9	7.4	10.6	5.8	-3.7	-7.4
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	0.6	10.2	10.2	-11.9	-10.2	-11.9
1	2/2/1999	0.3	23.5	20.6	-17.7	-14.7	-20.6
1	2/5/1999	1.2	36.2	40.5	35.3	36.2	31.0
1	2/11/1999	0.4	12.8	15.4	-10.3	0.0	-10.3
1	2/14/1999	1.8	5.6	10.6	3.4	-3.4	-1.1
1	2/17/1999	3.7	-2.4	3.3	1.4	-1.6	-1.4
1	2/20/1999	1.6	-38.5	-24.2	-31.1	-20.5	-40.4
1	2/23/1999	0.4	-4.7	2.3	-88.4	-7.0	-65.1
1	2/26/1999	2.0	-4.0	5.1	3.0	-3.0	-7.1
2	1/14/1999	0.8	6.7	6.7	-32.0	1.3	.
2	1/16/1999	1.0	7.8	10.8	-16.7	3.9	.
2	1/18/1999	1.8	6.7	7.9	-6.2	-3.4	3.4
2	1/20/1999	1.2	9.5	8.6	-9.5	5.2	.
2	1/22/1999	0.2	20.8	25.0	-54.2	0.0	8.3
2	1/24/1999	0.6	12.7	14.3	-23.8	4.8	7.9
2	1/26/1999	0.3	12.1	12.1	-33.3	-6.1	9.1
2	1/28/1999	0.5	17.0	19.2	.	8.5	10.6
2	2/3/1999	0.7	20.0	17.1	-15.7	5.7	5.7
2	2/5/1999	0.4	18.2	15.9	-4.6	4.6	9.1
2	2/7/1999	0.7	15.5	14.1	-4.2	0.0	4.2
2	2/9/1999	1.2	12.6	8.4	-6.7	-5.0	7.6
2	2/11/1999	0.3	28.6	25.0	-14.3	-17.9	7.1
2	2/13/1999	0.7	14.3	12.9	-24.3	-4.3	0.0
2	2/15/1999	1.1	13.3	11.5	-8.9	4.4	8.9
2	2/17/1999	1.6	26.8	28.0	6.4	21.0	30.6
2	2/19/1999	1.2	10.4	10.4	-9.6	0.0	7.0
2	2/21/1999	1.2	6.7	5.8	.	-10.0	0.8
3	1/21/1999	4.0	-2.0	-6.6	-8.1	-3.3	8.3
3	1/23/1999	2.6	50.4	-8.0	3.4	13.0	11.1
3	1/25/1999	6.7	0.0	-0.9	-1.8	-2.3	.
3	1/27/1999	8.4	2.5	4.0	0.8	0.7	11.4
3	1/29/1999	4.4	10.0	9.1	9.7	5.4	21.3
3	1/31/1999	2.0	18.2	16.3	13.3	13.8	32.0
3	2/2/1999	3.0	3.6	2.6	0.3	9.2	15.2
3	2/4/1999	5.7	5.3	4.9	5.8	-3.4	13.6
3	2/8/1999	4.0	-2.2	-3.0	-4.2	2.0	15.7
3	2/10/1999	2.7	9.7	7.8	6.7	4.1	15.7
3	2/12/1999	4.1	-0.2	-0.5	-6.3	3.1	14.7
3	2/14/1999	1.5	20.1	20.8	16.9	12.3	22.1
3	2/16/1999	6.5	4.3	7.2	1.1	-0.3	10.7
3	2/18/1999	7.3	3.4	6.1	4.2	7.1	11.7
3	2/20/1999	3.7	2.7	4.3	4.0	-2.9	11.5
3	2/22/1999	1.5	25.3	26.7	21.2	1.4	17.1
3	2/24/1999	2.0	16.4	17.9	.	2.0	13.4
3	2/26/1999	2.7	4.4	10.2	8.0	7.3	5.5
4	1/19/1999	0.7	8.5	4.2	-1.4	7.0	-2.8
4	1/21/1999	5.2	-1.2	-1.2	1.9	5.2	7.3
4	1/23/1999	1.7	-5.9	.	-4.1	-3.5	-7.1
4	1/25/1999	3.5	2.9	.	0.3	-4.8	5.1
4	1/27/1999	5.4	-3.0	.	-5.6	-4.7	.
4	1/29/1999	6.2	1.5	0.2	-0.2	-3.1	-5.7
4	1/31/1999	3.3	5.4	1.8	2.1	3.3	-3.0
4	2/2/1999	2.8	3.2	3.9	2.1	6.7	0.4
4	2/6/1999	2.0	10.3	11.3	9.9	7.9	6.9
4	2/8/1999	2.6	3.9	0.8	2.7	2.7	.
4	2/10/1999	2.3	-3.1	-5.3	-7.1	-8.0	-0.4
4	2/12/1999	5.5	-1.8	3.5	-2.0	-0.4	2.5
4	2/14/1999	2.6	6.1	7.2	3.8	-2.3	19.4
4	2/16/1999	2.2	10.3	14.7	34.4	-8.0	6.7
4	2/18/1999	2.8	-1.8	2.9	.	-4.0	.
4	2/20/1999	5.9	-5.3	-3.4	-4.1	-3.9	-5.8
4	2/22/1999	2.0	5.1	17.8	3.1	-14.7	12.2
4	2/24/1999	2.9	3.5	3.5	1.7	11.1	-5.2

Percent Differences From FRM for Particle Nitrate

% Difference = [FRM Conc- Sampler Conc)/FRM]*100

SITE	DATE	FRM (ug/m3) AND % Difference		IMP % Difference	MET % Difference	URG % DIfference	VAPS % Difference
1	1/15/1999	9.6	14.1	19.5	-5.7	1.1	.
1	1/18/1999	38.0	8.9	9.1	-6.3	-9.9	-11.3
1	1/21/1999	3.1	-5.2	-14.7	-24.8	-113.1	-36.0
1	1/24/1999	12.1	10.0	4.2	-2.8	-3.8	-9.7
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	9.7	17.7	13.6	-0.2	.	.
1	2/2/1999	0.4	11.4	6.8	-11.4	.	-40.9
1	2/5/1999	9.5	27.0	17.2	12.6	.	9.9
1	2/11/1999	0.1	23.1	38.5	-30.8	-15.4	-23.1
1	2/14/1999	16.7	14.8	7.9	-1.4	-6.9	-4.3
1	2/17/1999	25.8	6.5	-0.1	-5.7	-3.4	-4.7
1	2/20/1999	12.2	-14.9	-21.4	-33.1	-46.6	-65.7
1	2/23/1999	6.2	17.1	2.7	-5.2	.	-9.8
1	2/26/1999	9.7	5.8	0.2	-8.3	-8.6	-14.7
2	1/14/1999	3.5	-20.8	23.4	-33.8	-73.4	.
2	1/16/1999	5.3	5.1	17.1	-7.9	-37.7	.
2	1/18/1999	2.6	-37.3	-7.5	-55.7	-74.9	-68.2
2	1/20/1999	3.7	2.7	21.8	.	-42.1	.
2	1/22/1999	0.5	11.1	8.9	-22.2	.	-17.8
2	1/24/1999	1.4	5.8	8.8	-16.1	-35.8	-27.7
2	1/26/1999	2.0	3.0	4.0	22.1	-55.3	-29.2
2	1/28/1999	0.4	6.8	15.9	.	-52.3	-40.9
2	2/3/1999	4.4	7.7	20.4	-3.2	-34.6	-34.8
2	2/5/1999	2.2	4.0	5.8	-0.5	-37.7	-91.0
2	2/7/1999	7.4	5.5	15.5	0.1	.	-22.6
2	2/9/1999	4.2	1.4	17.2	4.0	.	-8.3
2	2/11/1999	0.2	20.0	30.0	5.0	-20.0	0.0
2	2/13/1999	0.3	3.5	13.8	-27.6	-79.3	.
2	2/15/1999	2.4	0.0	22.5	-8.9	-60.2	-63.1
2	2/17/1999	6.8	5.4	35.0	-0.4	-36.6	-28.8
2	2/19/1999	5.5	1.5	35.8	-6.4	-59.6	.
2	2/21/1999	2.4	-3.7	17.8	-16.5	-79.3	-77.3
3	1/21/1999	5.5	2.8	-8.2	-4.2	-5.0	-15.6
3	1/23/1999	1.6	-144.8	-17.2	-4.9	-19.0	-98.2
3	1/25/1999	4.6	6.5	-3.5	-1.1	-8.9	.
3	1/27/1999	8.6	8.0	3.9	0.8	-2.3	6.6
3	1/29/1999	3.4	14.5	8.0	6.2	-8.3	11.5
3	1/31/1999	3.5	19.1	11.6	9.3	9.8	30.6
3	2/2/1999	2.7	2.6	-3.0	-2.2	4.8	-21.8
3	2/4/1999	6.5	9.7	3.5	2.9	-6.7	-5.1
3	2/8/1999	3.1	3.5	-6.1	-7.0	-2.9	-2.6
3	2/10/1999	2.2	9.6	5.1	1.4	-19.7	8.7
3	2/12/1999	2.6	0.8	-2.3	-4.2	-17.2	-6.1
3	2/14/1999	0.9	29.4	26.1	20.7	19.6	20.7
3	2/16/1999	6.1	-2.9	10.3	-12.5	-34.9	-29.2
3	2/18/1999	3.9	9.3	3.1	39.4	2.9	.
3	2/20/1999	1.6	14.5	10.7	5.0	-15.7	-8.8
3	2/22/1999	1.1	50.5	49.5	43.0	31.8	42.1
3	2/24/1999	3.8	25.8	21.1	.	12.8	8.1
3	2/26/1999	6.1	15.8	12.6	8.1	1.2	-5.1
4	1/19/1999	0.1	-7.7	7.7	-84.6	-30.8	-53.9
4	1/21/1999	1.0	-10.0	-8.0	28.0	-58.0	-34.0
4	1/23/1999	0.3	-76.0	.	-96.0	-24.0	-68.0
4	1/25/1999	0.2	-17.4	.	-47.8	-69.6	-73.9
4	1/27/1999	1.0	-31.7	.	-55.5	-105.0	.
4	1/29/1999	1.1	0.0	-1.9	-27.1	-51.4	-64.5
4	1/31/1999	1.5	-4.8	-10.2	-15.0	-56.5	-82.3
4	2/2/1999	0.7	1.5	-3.0	-13.4	-41.8	-52.2
4	2/6/1999	0.3	-76.0	-60.0	-104.0	-180.0	-220.0
4	2/8/1999	0.2	5.9	17.7	-11.8	-23.5	.
4	2/10/1999	0.3	-96.6	-103.5	-144.8	-110.3	.
4	2/12/1999	0.1	-218.2	-200.0	-254.6	.	-272.7
4	2/14/1999	0.3	-52.9	-61.8	-88.2	-114.7	.
4	2/16/1999	1.8	8.6	26.9	84.0	-78.9	-61.1
4	2/18/1999	0.7	-4.1	1.4	.	-38.4	.
4	2/20/1999	1.1	-46.5	-39.5	-68.4	-118.4	-185.1
4	2/22/1999	0.4	-32.5	-45.0	-60.0	-90.0	-115.0
4	2/24/1999	2.3	-2.2	-6.7	-22.7	-36.9	-19.1

Percent Difference From FRM For Ammonium

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM AND % Difference		IMP % Difference	MET % DIfference	URG % Difference	VAPS % Difference
1	1/15/1999	3.0	18.3	38.3	11.7	1.3	57.0
1	1/18/1999	13.2	0.0	19.7	-2.1	-8.6	-0.8
1	1/21/1999	1.5	24.2	38.3	12.1	-6.0	2.0
1	1/24/1999	4.6	12.3	24.8	2.9	-6.6	4.6
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	3.0	19.4	30.9	3.3	-13.5	6.6
1	2/2/1999	0.3	57.7	76.9	69.2	-42.3	42.3
1	2/5/1999	2.8	11.6	20.7	3.6	-8.3	7.6
1	2/11/1999	0.1	14.3	28.6	42.9	-21.4	57.1
1	2/14/1999	5.4	9.4	21.6	1.9	-10.5	11.5
1	2/17/1999	9.3	3.6	16.2	0.8	-0.9	10.2
1	2/20/1999	4.2	1.4	-2.6	-10.6	-25.5	-15.8
1	2/23/1999	1.8	6.6	18.2	12.7	-15.5	13.3
1	2/26/1999	3.2	10.3	16.2	-5.6	-19.9	-8.4
2	1/14/1999	1.2	17.7	69.8	8.4	-5.0	.
2	1/16/1999	1.9	26.7	44.4	11.2	8.6	.
2	1/18/1999	1.3	22.1	36.6	0.0	13.0	-13.7
2	1/20/1999	1.5	47.3	54.0	35.3	9.3	.
2	1/22/1999	0.2	70.0	70.0	50.0	90.0	15.0
2	1/24/1999	0.5	52.9	51.0	37.3	27.5	2.0
2	1/26/1999	0.7	52.9	44.3	45.7	8.6	0.0
2	1/28/1999	0.2	30.4	34.8	.	13.0	-8.7
2	2/3/1999	1.6	42.6	54.8	20.7	23.9	-2.6
2	2/5/1999	0.9	45.4	53.5	38.4	8.1	0.0
2	2/7/1999	2.5	41.3	38.1	23.0	11.1	4.0
2	2/9/1999	1.7	56.2	43.8	41.4	52.1	49.7
2	2/11/1999	0.1	61.5	53.9	38.5	-53.9	7.7
2	2/13/1999	0.3	19.2	23.1	3.9	-3.9	-3.9
2	2/15/1999	1.1	49.1	56.3	40.2	3.6	0.9
2	2/17/1999	2.4	41.8	59.4	36.1	8.2	12.3
2	2/19/1999	1.9	60.1	66.3	36.8	-4.2	1.0
2	2/21/1999	1.1	54.0	54.0	.	-4.4	7.1
3	1/21/1999	3.1	-3.9	1.0	-14.8	-9.7	15.2
3	1/23/1999	1.4	14.5	21.7	2.9	5.8	10.1
3	1/25/1999	3.7	-2.7	3.6	-11.8	-10.1	.
3	1/27/1999	5.8	4.3	13.5	2.4	-0.9	15.1
3	1/29/1999	2.6	9.3	17.4	2.3	-0.8	19.3
3	1/31/1999	1.8	13.3	22.2	2.8	12.8	35.0
3	2/2/1999	2.1	4.4	20.5	-3.9	10.7	24.4
3	2/4/1999	4.0	5.2	11.7	1.7	-5.7	14.4
3	2/8/1999	2.4	-4.9	4.5	-13.2	-0.4	18.5
3	2/10/1999	1.7	12.8	20.9	8.1	2.3	21.5
3	2/12/1999	2.4	12.2	17.7	11.3	1.3	20.2
3	2/14/1999	0.8	24.4	34.6	15.4	19.2	26.9
3	2/16/1999	4.0	1.2	24.4	-5.5	-11.7	4.5
3	2/18/1999	3.9	4.7	13.5	1.6	5.7	11.4
3	2/20/1999	1.8	6.0	16.9	-3.3	0.0	20.2
3	2/22/1999	0.9	38.2	44.9	24.7	22.5	40.5
3	2/24/1999	2.0	25.4	34.5	.	15.7	27.9
3	2/26/1999	2.8	10.6	26.2	13.5	12.8	13.1
4	1/19/1999	0.2	-4.4	47.8	0.0	-21.7	-17.4
4	1/21/1999	1.9	3.2	15.4	-0.5	-2.7	4.3
4	1/23/1999	0.4	-16.7	.	-26.2	-7.1	-9.5
4	1/25/1999	1.2	-7.4	.	-5.8	-24.0	-6.6
4	1/27/1999	2.0	-2.0	.	-7.5	-19.1	.
4	1/29/1999	2.3	-2.2	4.4	-7.1	-14.6	-23.0
4	1/31/1999	1.5	7.6	15.2	13.1	-7.6	-13.1
4	2/2/1999	1.2	6.1	17.4	13.9	-7.0	-18.3
4	2/6/1999	0.6	-9.4	3.1	9.4	-28.1	-26.6
4	2/8/1999	0.9	-4.7	-4.7	-1.2	-10.6	.
4	2/10/1999	0.9	-11.6	-2.3	-3.5	-16.3	-24.4
4	2/12/1999	1.5	-8.0	4.0	2.0	-16.7	-28.0
4	2/14/1999	0.9	1.1	7.7	1.1	-12.1	1.1
4	2/16/1999	1.3	26.2	36.5	36.5	-20.6	-1.6
4	2/18/1999	1.1	-2.7	13.3	.	-23.9	.
4	2/20/1999	2.3	-3.5	0.0	0.4	-10.4	-23.9
4	2/22/1999	0.8	-2.6	2.6	6.5	-27.3	-6.5
4	2/24/1999	1.8	15.7	24.7	20.8	4.5	-0.6

Percent Differences from FRM For Organic Carbon

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM AND % Difference		IMP % DIfference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	7.7	-30.1	46.1	-21.4	11.8	-94.2
1	1/18/1999	10.0	-42.0	47.5	-4.1	-14.8	-44.9
1	1/21/1999	3.0	-43.6	41.3	-15.1	-3.4	-19.8
1	1/24/1999	6.9	-18.0	56.9	-10.3	17.0	-11.0
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	7.8	0.9	57.8	0.0	17.9	.
1	2/2/1999	4.6	-4.6	44.1	17.3	29.3	45.2
1	2/5/1999	4.7	-26.7	14.4	7.7	17.6	22.2
1	2/11/1999	2.1	4.4	22.9	-14.6	19.0	43.4
1	2/14/1999	5.5	-26.0	-6.0	-36.9	-6.0	-2.7
1	2/17/1999	5.7	-46.6	-13.4	4.0	-12.5	-17.8
1	2/20/1999	6.9	-19.2	14.7	-12.8	8.8	10.1
1	2/23/1999	5.5	-21.3	16.7	-34.2	6.0	12.4
1	2/26/1999	4.2	28.4	8.6	-10.7	6.0	-30.1
2	1/14/1999	9.5	-26.9	29.1	82.7	19.4	.
2	1/16/1999	11.8	-24.1	20.1	-7.8	29.4	.
2	1/18/1999	10.1	-19.6	-0.7	-31.4	14.9	18.0
2	1/20/1999	5.6	-35.7	27.9	1.6	27.7	.
2	1/22/1999	6.2	-10.3	12.5	13.0	32.4	47.4
2	1/24/1999	12.5	-17.6	19.2	3.2	26.5	37.3
2	1/26/1999	4.3	-33.2	8.8	-11.8	15.0	32.3
2	1/28/1999	4.0	-19.4	17.9	.	45.5	56.6
2	2/3/1999	9.0	-15.5	9.8	-19.9	-2.8	38.6
2	2/5/1999	5.6	-29.1	20.5	-2.1	-0.2	27.9
2	2/7/1999	9.7	-11.5	21.3	-7.0	-0.5	26.6
2	2/9/1999	7.7	-19.8	14.4	-20.9	36.2	41.0
2	2/11/1999	4.0	-38.9	12.0	-13.3	6.8	54.6
2	2/13/1999	7.3	-16.6	20.6	-42.8	22.6	35.8
2	2/15/1999	7.3	-16.2	17.0	-4.1	5.3	44.4
2	2/17/1999	8.3	-22.9	10.1	-15.0	13.6	49.5
2	2/19/1999	6.5	-27.9	12.6	78.1	-1.7	54.1
2	2/21/1999	7.8	-13.8	21.0	-9.6	17.7	48.7
3	1/21/1999	5.2	-23.0	-12.6	48.9	8.7	20.3
3	1/23/1999	2.3	-35.5	16.5	-10.0	14.7	13.9
3	1/25/1999	2.8	-26.8	18.2	-2.1	25.0	.
3	1/27/1999	9.6	4.5	18.2	16.4	20.9	36.7
3	1/29/1999	4.1	-40.3	5.7	1.7	14.1	42.2
3	1/31/1999	4.1	-11.4	4.4	4.4	11.9	54.5
3	2/2/1999	3.1	-97.1	11.6	-4.5	5.5	27.1
3	2/4/1999	5.3	-27.1	14.7	16.5	15.8	27.8
3	2/8/1999	3.4	-18.8	4.7	-10.3	9.7	27.9
3	2/10/1999	4.5	-7.4	16.1	7.2	24.7	45.7
3	2/12/1999	4.6	-42.6	19.4	8.0	20.9	46.5
3	2/14/1999	2.3	-56.7	16.9	12.6	33.8	43.3
3	2/16/1999	8.5	-28.9	8.3	-18.7	2.9	33.8
3	2/18/1999	4.4	-54.7	-6.8	0.5	4.8	25.2
3	2/20/1999	2.8	-11.5	14.0	86.0	22.3	41.7
3	2/22/1999	2.8	-34.3	-7.6	13.7	20.6	55.2
3	2/24/1999	3.7	-28.1	-1.4	.	16.4	43.4
3	2/26/1999	3.3	-19.7	6.1	7.0	2.7	29.4
4	1/19/1999	2.8	4.3	28.0	5.0	38.4	47.7
4	1/21/1999	7.3	-2.2	17.6	1.0	14.4	23.5
4	1/23/1999	2.5	6.8	28.1	-12.5	64.3	18.9
4	1/25/1999	2.4	-2.1	23.8	-17.9	27.5	31.7
4	1/27/1999	3.8	-5.8	.	-1.3	-11.6	.
4	1/29/1999	4.7	-20.0	14.8	-14.4	13.3	-47.0
4	1/31/1999	2.4	-30.1	25.5	.	13.8	22.2
4	2/2/1999	2.0	-48.0	14.0	-43.0	2.5	10.0
4	2/6/1999	3.8	-2.7	24.5	-6.9	21.1	18.4
4	2/8/1999	2.2	23.1	41.6	-10.4	24.0	.
4	2/10/1999	.	.	.	.	.	.
4	2/12/1999	3.3	-19.3	25.6	-25.0	19.0	9.9
4	2/14/1999	1.8	-40.3	10.5	-25.4	16.6	35.4
4	2/16/1999	8.5	-18.3	11.8	-21.4	6.6	13.8
4	2/18/1999	3.4	1.8	33.2	.	19.3	.
4	2/20/1999	3.1	11.3	25.7	1.6	32.8	27.7
4	2/22/1999	1.5	-38.4	-8.2	-21.2	-0.7	18.5
4	2/24/1999	3.2	-15.7	17.0	-11.7	11.4	.

Percent Differences From FRM For Elemental Carbon

% Difference = [(FRM COnc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM AND % Difference		IMP % DIfference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	5.2	8.6	71.5	5.2	20.1	-5.0
1	1/18/1999	7.7	26.1	76.0	6.1	12.6	25.7
1	1/21/1999	1.6	-1.9	77.0	3.1	6.8	3.7
1	1/24/1999	3.2	5.3	77.3	14.3	13.7	8.4
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	4.4	18.9	74.6	32.7	15.1	.
1	2/2/1999	1.6	8.8	46.5	8.2	17.6	12.6
1	2/5/1999	2.5	16.8	2.0	-6.8	2.4	-5.2
1	2/11/1999	0.6	62.5	17.9	8.9	3.6	30.4
1	2/14/1999	2.9	19.9	13.6	-4.6	-14.7	10.8
1	2/17/1999	5.4	16.4	21.9	25.8	8.5	16.6
1	2/20/1999	3.1	-14.0	7.1	-9.7	-29.2	-3.6
1	2/23/1999	2.6	-25.4	9.9	-14.0	-27.7	-17.4
1	2/26/1999	1.9	49.5	11.6	13.7	-6.8	-1.1
2	1/14/1999	4.6	-3.5	14.0	97.8	6.6	.
2	1/16/1999	4.8	-7.1	1.0	6.6	7.3	.
2	1/18/1999	5.7	4.9	25.4	13.7	6.0	9.1
2	1/20/1999	2.3	13.5	34.9	11.4	10.5	.
2	1/22/1999	2.4	6.8	17.3	11.0	-10.1	14.8
2	1/24/1999	5.0	18.7	24.9	22.5	2.8	14.1
2	1/26/1999	1.9	25.8	24.2	17.2	-3.2	10.8
2	1/28/1999	1.5	17.7	26.8	.	15.0	21.6
2	2/3/1999	4.6	34.7	22.4	5.3	13.2	23.5
2	2/5/1999	3.3	28.8	18.4	9.2	-3.1	15.3
2	2/7/1999	4.3	25.2	11.0	-1.9	1.2	8.6
2	2/9/1999	3.3	26.5	10.7	-1.5	10.4	18.3
2	2/11/1999	1.5	32.7	4.1	-13.6	-4.1	23.1
2	2/13/1999	2.7	28.5	16.3	-5.2	11.5	17.4
2	2/15/1999	3.0	8.7	16.7	7.7	4.0	19.4
2	2/17/1999	4.0	5.3	16.3	-4.0	9.3	19.1
2	2/19/1999	2.4	-9.7	16.9	94.9	0.8	17.7
2	2/21/1999	2.6	-0.4	7.2	-8.0	6.8	14.4
3	1/21/1999	3.5	55.1	34.5	58.5	-1.7	19.5
3	1/23/1999	0.8	-552.4	6.1	3.7	6.1	22.0
3	1/25/1999	1.6	-29.9	12.8	-1.8	-2.4	.
3	1/27/1999	5.2	70.3	9.6	5.4	12.5	9.2
3	1/29/1999	2.1	-2.9	2.9	-2.9	-1.0	16.9
3	1/31/1999	1.7	11.6	-5.2	-4.1	-4.1	46.2
3	2/2/1999	1.9	-17.8	6.3	5.8	-15.2	16.2
3	2/4/1999	3.4	-4.5	11.9	6.6	-3.6	16.4
3	2/8/1999	2.5	20.8	14.3	28.2	15.5	38.8
3	2/10/1999	2.4	21.1	18.6	14.9	11.2	25.2
3	2/12/1999	2.7	13.3	23.3	19.9	23.3	24.7
3	2/14/1999	1.2	4.3	4.3	21.6	15.5	-5.2
3	2/16/1999	5.7	7.9	22.3	-9.1	4.4	7.0
3	2/18/1999	3.4	4.4	1.5	19.2	2.6	9.9
3	2/20/1999	1.6	11.0	-4.3	100.0	13.5	6.1
3	2/22/1999	1.7	14.6	-7.0	19.9	18.7	6.4
3	2/24/1999	1.9	20.9	16.2	.	23.6	29.8
3	2/26/1999	1.6	-1.3	9.6	14.7	4.5	34.4
4	1/19/1999	1.4	38.3	31.9	20.6	14.9	22.7
4	1/21/1999	3.7	20.0	40.3	15.7	9.2	3.2
4	1/23/1999	0.8	50.0	52.6	31.6	51.3	50.0
4	1/25/1999	1.2	24.1	24.1	12.9	-3.5	19.0
4	1/27/1999	2.5	17.1	.	12.4	11.6	.
4	1/29/1999	2.8	15.1	21.1	4.9	4.9	-59.2
4	1/31/1999	0.9	24.4	28.9	.	10.0	24.4
4	2/2/1999	1.0	6.3	20.8	-3.1	3.1	15.6
4	2/6/1999	1.6	-14.4	11.3	0.0	-27.5	-19.4
4	2/8/1999	0.8	-6.4	16.7	6.4	-18.0	.
4	2/10/1999	.	.	.	.	.	.
4	2/12/1999	0.8	-20.7	2.4	8.5	-17.1	19.5
4	2/14/1999	0.6	-3.6	-1.8	23.6	-7.3	25.5
4	2/16/1999	3.1	13.1	21.6	11.4	3.9	22.6
4	2/18/1999	1.2	3.3	16.7	.	0.0	.
4	2/20/1999	1.1	-14.2	-1.9	-6.6	-17.9	-0.9
4	2/22/1999	0.7	4.6	-16.9	-15.4	-27.7	-15.4
4	2/24/1999	1.4	12.6	15.4	18.2	28.7	.

Differences From FRM For Sulfur By XRF

% Difference =[(FRM Conc - Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ug/m3)	AND % Difference	IMP % Difference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	204.7	-1.5	2.8	-61.5	-0.2	.
1	1/18/1999	1928.3	-15.9	-9.9	-18.7	-19.8	.
1	1/21/1999	605.9	-2.9	5.9	-9.6	.	-11.0
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	242.3	13.2	39.5	-20.3	.	-11.1
1	2/2/1999	111.0	6.0	20.2	-36.9	.	-16.9
1	2/5/1999	310.6	-1.4	1.4	-13.8	.	-10.8
1	2/11/1999	120.6	1.3	6.5	-6.1	-9.0	-21.0
1	2/14/1999	644.8	1.4	6.2	-9.2	-3.1	-0.9
1	2/17/1999	1391.7	-5.9	2.3	-3.4	-4.7	.
1	2/20/1999	645.7	-24.2	-17.6	-29.5	-26.6	-33.5
1	2/23/1999	174.7	.	18.4	-63.7	.	7.1
1	2/26/1999	787.5	4.6	8.8	-2.4	-1.4	-6.6
2	1/14/1999	299.6	-0.5	-9.5	-19.8	0.6	.
2	1/16/1999	365.5	2.4	17.6	-24.3	2.1	.
2	1/18/1999	642.8	1.8	-37.0	-22.0	-1.7	9.9
2	1/20/1999	385.5	-4.5	6.2	-11.9	0.4	.
2	1/22/1999	71.2	-18.4	-2.8	-78.2	.	-112.2
2	1/24/1999	237.9	6.7	33.0	-24.5	7.2	8.2
2	1/26/1999	122.3	-5.3	-1.4	-42.8	-3.4	1.5
2	1/28/1999	161.9	8.5	11.6	.	11.7	14.9
2	2/3/1999	226.6	-4.5	-3.2	-38.0	-5.1	-0.2
2	2/5/1999	176.7	6.2	4.1	15.8	10.8	.
2	2/7/1999	285.2	6.0	6.1	-10.5	.	7.2
2	2/9/1999	402.3	0.4	9.6	-11.1	.	-5.4
2	2/11/1999	85.3	5.9	15.4	-8.0	9.4	10.1
2	2/13/1999	237.1	0.0	3.3	-19.7	.	.
2	2/15/1999	407.0	1.2	7.3	-13.2	3.8	15.1
2	2/17/1999	479.5	4.3	11.3	6.7	3.5	9.1
2	2/19/1999	434.9	8.2	9.4	-12.7	5.3	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	1322.8	-16.5	-13.4	-25.9	-11.9	-18.5
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	2232.9	-5.8	4.9	-13.0	-12.1	.
3	1/27/1999	2794.0	-5.7	1.4	-12.3	-15.9	-8.6
3	1/29/1999	1429.6	-1.7	7.2	-2.4	-6.3	1.0
3	1/31/1999	640.2	1.9	3.6	-5.2	-8.3	-6.3
3	2/2/1999	1033.4	-3.8	7.2	-7.7	-6.6	0.2
3	2/4/1999	2026.7	4.2	13.5	-1.1	-2.2	1.3
3	2/8/1999	1480.9	1.3	58.7	-10.5	-1.9	-9.3
3	2/10/1999	900.1	2.7	7.0	-6.7	-3.0	3.7
3	2/12/1999	1474.4	1.4	.	-5.7	-1.2	.
3	2/14/1999	440.7	1.6	7.8	-4.5	0.2	24.1
3	2/16/1999	2202.8	2.2	9.5	-3.8	1.0	1.5
3	2/18/1999	2411.2	-2.3	7.7	-4.5	-3.0	.
3	2/20/1999	1289.9	1.6	.	-3.8	-3.7	2.6
3	2/22/1999	394.2	-0.3	-0.7	-14.4	-9.6	.
3	2/24/1999	589.7	2.0	5.6	.	-12.5	.
3	2/26/1999	891.5	-5.6	2.4	-10.7	-8.7	-2.6
4	1/19/1999	261.7	1.0	8.0	-10.3	-6.9	3.1
4	1/21/1999	1820.8	-3.5	4.3	-2.7	-7.1	-4.3
4	1/23/1999	611.7	-1.6	6.8	-3.3	-7.0	-2.1
4	1/25/1999	1231.0	-2.2	6.8	-10.8	-4.7	-8.2
4	1/27/1999	2004.1	2.9	.	-4.1	-4.5	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	1171.4	-1.0	17.0	-1.4	-8.9	69.6
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	692.4	7.9	18.6	-3.6	-9.0	0.4
4	2/8/1999	867.2	-2.6	-6.1	-4.3	-6.2	.
4	2/10/1999	861.3	-0.5	6.1	-1.0	-3.6	.
4	2/12/1999	1953.4	6.4	5.8	-7.6	.	-0.8
4	2/14/1999	888.5	6.3	3.8	0.1	-7.4	.
4	2/16/1999	712.1	3.3	2.7	0.4	-11.0	-2.8
4	2/18/1999	1007.4	0.9	-1.0	.	-6.2	.
4	2/20/1999	2083.7	-2.2	-4.6	0.2	-8.8	-10.6
4	2/22/1999	677.9	3.1	8.6	-5.4	-12.7	-1.1
4	2/24/1999	1046.2	3.3	11.0	-7.2	-1.8	-8.1

Percent Differences From FRM For Silicon

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ug/m3)	AND % Difference	IMP % Difference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	377.8	-18.7	-61.3	-537.7	10.4	.
1	1/18/1999	216.5	23.1	5.0	-135.3	46.6	.
1	1/21/1999	16.2	-313.0	-49.4	-699.4	.	-2006.2
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	150.1	6.9	22.5	-362.4	.	-583.0
1	2/2/1999	145.7	-14.1	-14.1	-528.1	.	-509.4
1	2/5/1999	43.0	-51.6	13.7	-77.9	.	-344.0
1	2/11/1999	101.1	-77.4	-48.2	-683.6	-9.0	-877.6
1	2/14/1999	121.4	-42.9	-41.0	-453.1	-3.4	-554.1
1	2/17/1999	235.9	-40.5	-20.3	-172.3	-3.5	.
1	2/20/1999	118.7	-43.1	-13.5	-416.2	10.8	-671.6
1	2/23/1999	280.1	.	-21.7	-480.9	.	-710.5
1	2/26/1999	71.7	-57.6	-12.6	-86.6	-15.9	-715.9
2	1/14/1999	467.1	-0.3	-19.8	-275.0	27.1	.
2	1/16/1999	475.4	-5.3	0.7	-513.8	20.8	.
2	1/18/1999	403.3	-11.7	-56.7	-537.9	26.9	-21.8
2	1/20/1999	416.5	-13.3	2.6	-196.8	27.8	.
2	1/22/1999	211.5	-29.4	-21.3	-566.2	.	-1771.6
2	1/24/1999	444.2	-6.8	20.6	-293.6	29.4	-31.6
2	1/26/1999	133.1	-34.6	-21.5	-404.0	32.2	-47.0
2	1/28/1999	75.1	-17.7	-52.9	.	43.0	-50.2
2	2/3/1999	333.6	-34.9	-39.1	-603.7	5.5	-44.0
2	2/5/1999	55.7	-7.2	-128.2	-86.4	24.4	.
2	2/7/1999	94.0	-1.5	-9.0	-515.2	.	-67.3
2	2/9/1999	172.0	-31.1	-23.8	-208.3	.	-54.4
2	2/11/1999	49.9	-44.3	-87.8	-643.9	5.4	-39.7
2	2/13/1999	395.3	-20.2	-14.3	-313.9	.	.
2	2/15/1999	312.2	-25.0	-31.6	-329.5	14.5	-24.8
2	2/17/1999	374.7	-26.8	-14.6	-291.1	21.4	-24.8
2	2/19/1999	320.4	-39.0	-52.0	-390.9	6.4	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	51.8	-29.3	-59.5	-79.0	-17.2	0.8
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	48.5	29.7	2.1	-59.4	20.4	.
3	1/27/1999	96.5	13.1	26.1	-99.3	12.3	-15.5
3	1/29/1999	40.5	-48.4	12.6	-104.4	-8.2	-15.1
3	1/31/1999	31.2	-12.5	-44.2	-103.9	-30.8	50.0
3	2/2/1999	25.0	-82.8	-78.0	100.0	-90.4	-128.8
3	2/4/1999	59.1	-51.3	-8.0	-195.4	-52.8	-19.0
3	2/8/1999	40.3	28.3	-76.7	-53.9	91.1	14.9
3	2/10/1999	23.7	-33.8	-73.8	-217.7	-43.5	-87.8
3	2/12/1999	19.3	-106.7	.	-669.4	-65.8	.
3	2/14/1999	25.9	63.3	46.3	-47.1	100.0	86.9
3	2/16/1999	132.8	4.9	-15.0	-139.5	1.6	-7.5
3	2/18/1999	24.7	-159.5	-157.9	-166.4	-101.6	.
3	2/20/1999	22.1	-114.9	.	-201.4	-39.8	42.5
3	2/22/1999	31.8	-12.3	-55.4	-639.3	19.2	.
3	2/24/1999	61.3	-16.3	26.9	.	25.6	.
3	2/26/1999	71.6	-5.5	-13.7	-190.9	-20.1	-35.1
4	1/19/1999	70.5	2.7	5.7	-38.7	-7.2	2.6
4	1/21/1999	194.9	-6.7	-5.3	-16.2	5.1	-32.1
4	1/23/1999	22.6	-82.7	-69.5	100.0	-27.0	-1291.6
4	1/25/1999	34.4	11.6	-53.8	-190.7	15.4	-215.4
4	1/27/1999	38.4	-73.4	.	-88.8	-72.9	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	24.0	-46.7	-11.7	-25.8	61.7	-1107.5
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	72.3	35.4	66.5	-117.0	-15.2	-8.3
4	2/8/1999	35.7	1.1	20.5	-62.8	-6.4	.
4	2/10/1999	76.8	7.6	15.4	-98.7	26.0	.
4	2/12/1999	18.8	-92.6	27.1	100.0	.	-171.8
4	2/14/1999	42.1	7.6	43.5	-34.4	-0.5	.
4	2/16/1999	226.9	27.6	29.0	-26.0	37.2	-13.7
4	2/18/1999	41.9	37.2	2.4	.	-26.0	.
4	2/20/1999	100.8	1.0	-14.6	66.3	-3.6	-5.5
4	2/22/1999	40.9	19.8	-2.9	60.9	-32.3	-58.0
4	2/24/1999	106.2	14.8	37.1	1.2	27.9	-9.2

Percent Differences From FRM For Potassium

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ng/m3)	AND % Difference	IMP % Difference	MET % Difference	URG % Difference	VAPS % Difference
1	1/15/1999	121.0	-12.2	-18.8	-291.7	-4.1	.
1	1/18/1999	122.5	-32.2	-32.5	-89.0	-33.9	.
1	1/21/1999	40.1	-34.4	-33.9	-63.8	.	-191.0
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	124.7	16.0	41.7	-60.7	.	-98.0
1	2/2/1999	48.4	-7.6	9.7	-245.3	.	-205.2
1	2/5/1999	62.5	-2.1	2.7	2.9	.	-37.9
1	2/11/1999	23.5	-31.1	-28.5	-456.6	-4.7	-536.2
1	2/14/1999	93.4	-6.8	-1.8	-100.0	-1.3	-114.4
1	2/17/1999	112.0	-18.1	-2.7	-56.9	-2.1	.
1	2/20/1999	77.1	-17.9	-7.5	-120.9	-10.9	-183.3
1	2/23/1999	80.7	.	1.2	-297.7	.	-363.9
1	2/26/1999	49.9	-17.0	-12.2	-42.7	5.4	-269.9
2	1/14/1999	194.5	0.3	-8.6	-95.0	8.6	.
2	1/16/1999	225.6	0.2	13.8	-178.5	5.4	.
2	1/18/1999	237.2	1.8	-38.0	-136.6	4.4	-0.4
2	1/20/1999	181.1	-6.1	4.2	-79.5	8.4	.
2	1/22/1999	81.9	-6.5	-5.7	-227.5	.	-644.9
2	1/24/1999	244.8	3.2	29.4	-84.0	6.4	-8.1
2	1/26/1999	62.4	-13.1	-10.3	-140.1	6.1	-11.7
2	1/28/1999	29.5	-2.7	-16.3	.	16.3	-11.5
2	2/3/1999	124.2	-11.7	-11.3	-251.3	-0.2	-17.5
2	2/5/1999	58.8	-1.9	-11.1	-2.7	6.0	.
2	2/7/1999	123.6	5.7	5.1	-58.7	.	4.9
2	2/9/1999	83.5	-9.1	-4.6	-77.6	.	-14.7
2	2/11/1999	31.5	-2.5	-21.6	-160.0	0.6	-11.8
2	2/13/1999	134.6	-7.5	-2.0	-150.8	.	.
2	2/15/1999	127.2	-4.6	-7.4	-130.3	4.0	-2.4
2	2/17/1999	159.7	-2.3	4.1	-104.4	10.1	-4.0
2	2/19/1999	188.2	-2.7	-1.7	-100.2	5.7	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	53.9	-14.1	-16.3	-7.1	-27.5	-23.4
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	35.7	-7.6	-0.3	-30.5	1.1	.
3	1/27/1999	111.9	-6.4	0.5	-23.1	-12.2	-14.8
3	1/29/1999	44.2	-5.9	1.8	-36.0	-12.2	-1.4
3	1/31/1999	58.6	1.7	-0.5	-11.6	-12.5	-6.0
3	2/2/1999	36.1	-5.0	-1.9	0.3	-6.1	-0.6
3	2/4/1999	71.0	6.6	17.5	-5.8	7.5	3.0
3	2/8/1999	48.5	7.2	-45.4	-14.6	5.4	-8.5
3	2/10/1999	45.5	-8.8	-2.6	-29.9	-2.9	-7.7
3	2/12/1999	57.4	0.9	.	-11.9	-1.6	.
3	2/14/1999	31.1	7.1	8.7	-14.5	6.8	38.9
3	2/16/1999	115.1	-1.1	8.8	-27.8	-0.2	-6.7
3	2/18/1999	63.9	-6.4	2.2	-7.7	-11.4	.
3	2/20/1999	40.2	-4.7	.	-28.9	-7.7	2.5
3	2/22/1999	28.5	-18.6	-19.7	-120.7	-21.4	.
3	2/24/1999	37.5	-2.1	6.7	.	-2.7	.
3	2/26/1999	51.9	-4.6	-1.4	-42.0	-5.0	-3.5
4	1/19/1999	32.5	11.7	3.4	-39.7	-6.2	-2.5
4	1/21/1999	176.9	-3.5	-1.7	-7.3	-7.7	-15.7
4	1/23/1999	38.7	-13.2	-17.3	-12.7	4.9	-23.5
4	1/25/1999	35.2	-2.0	4.6	-33.0	-9.1	-4.8
4	1/27/1999	77.1	2.0	.	-2.6	-0.1	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	44.6	-11.0	9.6	-17.3	-8.3	-48.7
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	74.9	8.5	35.8	-14.7	-7.9	-2.8
4	2/8/1999	31.9	-2.5	-6.6	-41.1	-0.3	.
4	2/10/1999	58.1	1.2	6.0	-30.5	3.3	.
4	2/12/1999	72.3	4.4	7.6	-7.2	.	-0.8
4	2/14/1999	36.5	2.2	0.3	-9.3	-8.5	.
4	2/16/1999	146.4	8.1	6.1	-14.2	-2.0	-6.5
4	2/18/1999	49.1	10.6	4.7	.	-1.0	.
4	2/20/1999	69.6	0.6	4.5	9.6	2.2	-4.5
4	2/22/1999	31.7	5.4	2.8	-2.8	-11.0	-8.5
4	2/24/1999	95.2	8.0	17.4	1.4	4.6	0.2

Percent Differences From FRM For Calcium

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ng/m3)	AND % DIfference	IMP % Difference	MET % DIfference	URG % DIfference	VAPS % DIfference
1	1/15/1999	360.3	-31.4	-57.2	-568.1	10.1	.
1	1/18/1999	343.1	24.0	17.7	-118.9	54.7	.
1	1/21/1999	33.6	-67.9	-68.2	-164.3	.	-515.2
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	140.4	-0.4	27.8	-400.6	.	-556.1
1	2/2/1999	246.1	-19.1	-15.4	-589.4	.	-536.0
1	2/5/1999	52.3	-44.6	-23.1	-27.0	.	-530.8
1	2/11/1999	63.7	-34.2	-36.7	-505.3	-0.8	-630.3
1	2/14/1999	112.4	-57.6	-48.0	-547.2	0.3	-563.8
1	2/17/1999	124.5	-50.2	-27.5	-157.7	1.9	.
1	2/20/1999	80.1	-105.2	-72.5	-788.0	-22.5	-840.0
1	2/23/1999	243.1	.	-17.3	-633.7	.	-655.2
1	2/26/1999	60.6	-26.6	-30.5	-47.0	19.5	-467.2
2	1/14/1999	218.6	-6.7	-17.0	-272.9	22.1	.
2	1/16/1999	187.9	-13.1	1.8	-571.4	21.0	.
2	1/18/1999	159.4	-15.6	-64.4	-581.8	25.7	-33.3
2	1/20/1999	150.8	-17.8	-11.0	-270.4	27.2	.
2	1/22/1999	88.8	-32.9	-36.8	-621.2	.	-1866.9
2	1/24/1999	167.1	-16.1	17.2	-317.3	24.2	-41.5
2	1/26/1999	40.0	-56.5	-44.3	-680.0	16.3	-79.5
2	1/28/1999	25.6	-50.4	-95.3	.	7.8	-51.6
2	2/3/1999	148.9	-39.0	-43.5	-648.5	6.1	-51.0
2	2/5/1999	29.1	-29.2	-134.7	-75.6	4.8	.
2	2/7/1999	38.9	-34.2	-26.0	-510.8	.	-31.1
2	2/9/1999	65.4	-33.5	-33.3	-243.1	.	-47.3
2	2/11/1999	32.7	-34.6	-91.4	-574.6	9.2	-62.4
2	2/13/1999	123.9	-15.7	-16.6	-308.5	.	.
2	2/15/1999	129.6	-26.5	-33.3	-370.8	12.1	-26.9
2	2/17/1999	157.8	-30.5	-20.5	-315.6	22.3	-24.3
2	2/19/1999	116.3	-43.3	-51.8	-447.4	11.6	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	53.0	-27.2	10.4	4.7	13.0	-3.0
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	24.1	-0.4	5.4	-68.1	25.3	.
3	1/27/1999	58.9	-23.4	-12.9	-131.6	-11.0	-17.5
3	1/29/1999	23.8	-8.0	-1.7	-175.6	5.9	-2.5
3	1/31/1999	26.7	7.1	5.2	-89.5	2.6	30.7
3	2/2/1999	24.8	-26.6	-10.1	6.5	8.5	1.2
3	2/4/1999	47.7	9.9	20.1	-118.9	29.4	11.7
3	2/8/1999	16.7	2.4	-114.4	-149.7	20.4	2.4
3	2/10/1999	27.7	-19.9	-12.3	-117.3	13.7	7.9
3	2/12/1999	65.5	31.2	.	-27.2	42.9	.
3	2/14/1999	12.6	-2.4	-3.2	-25.4	18.3	68.3
3	2/16/1999	106.9	-18.3	-16.2	-195.5	5.0	-14.2
3	2/18/1999	22.5	-21.8	-10.7	-20.9	-2.2	.
3	2/20/1999	13.7	-35.8	.	-197.1	-16.1	-21.9
3	2/22/1999	20.3	-25.1	-29.6	-354.7	2.5	.
3	2/24/1999	28.1	-12.1	-6.4	.	-3.9	.
3	2/26/1999	23.4	-41.0	-37.6	-168.4	5.1	-15.4
4	1/19/1999	16.8	10.1	0.6	-111.3	-12.5	-9.5
4	1/21/1999	146.1	-8.3	-17.5	-14.8	4.3	-24.8
4	1/23/1999	27.2	-7.7	22.1	6.6	22.8	14.3
4	1/25/1999	16.4	-2.4	9.8	-79.9	3.7	3.1
4	1/27/1999	16.8	-52.4	.	-34.5	-10.7	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	14.0	-15.7	22.9	-37.1	25.7	-762.1
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	44.3	19.0	53.5	-33.2	25.1	9.0
4	2/8/1999	13.1	16.8	26.0	-71.8	13.7	.
4	2/10/1999	28.5	13.0	7.0	-104.9	23.9	.
4	2/12/1999	17.1	11.7	-9.4	4.1	.	-3.5
4	2/14/1999	13.6	5.9	-1.5	-13.2	-4.4	.
4	2/16/1999	88.0	13.0	15.1	-35.5	20.9	-13.8
4	2/18/1999	13.8	16.7	13.0	.	15.9	.
4	2/20/1999	17.0	-16.5	0.6	-1.2	19.4	-9.4
4	2/22/1999	20.8	7.7	5.8	-8.7	20.7	-18.8
4	2/24/1999	18.3	19.1	32.2	20.8	33.9	1.6

Percent Differences From FRM For Iron

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ng/m3) AND % Difference		IMP % Difference	MET % Difference	URG % DIfference	VAPS % Difference
1	1/15/1999	385.9	-24.9	-26.0	-246.2	5.9	.
1	1/18/1999	239.4	-22.1	-35.4	-67.5	4.7	.
1	1/21/1999	54.6	-34.6	-22.3	-101.8	.	-364.3
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	220.1	6.9	31.5	-129.1	.	-258.0
1	2/2/1999	113.8	-9.6	-6.2	-275.0	.	-313.6
1	2/5/1999	72.2	-11.2	-4.0	6.5	.	-170.4
1	2/11/1999	58.0	-17.6	-18.8	-435.9	11.2	-600.5
1	2/14/1999	166.2	-45.3	-22.4	-200.2	-3.3	-258.6
1	2/17/1999	209.9	-34.4	-11.2	-72.8	-1.8	.
1	2/20/1999	125.7	-53.5	-51.4	-228.7	-26.6	-392.1
1	2/23/1999	276.6	.	-5.4	-235.8	.	-311.1
1	2/26/1999	92.5	-19.7	-10.2	-42.9	7.5	-322.4
2	1/14/1999	420.6	-7.9	-12.5	-107.2	13.8	.
2	1/16/1999	337.6	-6.7	8.2	-251.4	17.3	.
2	1/18/1999	330.3	-3.2	-47.0	-252.5	21.4	-21.7
2	1/20/1999	186.0	-12.3	0.4	-158.5	25.6	.
2	1/22/1999	173.7	-22.3	-18.0	-244.1	.	-831.8
2	1/24/1999	304.8	-12.4	25.3	-155.2	15.3	-30.8
2	1/26/1999	94.5	-35.6	-16.0	-209.2	21.0	-42.7
2	1/28/1999	57.1	-22.1	-34.9	.	22.8	-34.3
2	2/3/1999	270.3	-20.2	-19.6	-259.4	4.1	-29.6
2	2/5/1999	73.3	-29.5	-71.1	-36.8	10.6	.
2	2/7/1999	141.5	-21.1	-13.6	-139.4	.	-14.1
2	2/9/1999	174.0	-25.3	-23.1	-81.8	.	-43.6
2	2/11/1999	59.8	-30.3	-105.4	-304.5	-12.9	-30.4
2	2/13/1999	257.3	-11.5	-10.3	-150.1	.	.
2	2/15/1999	200.8	-21.6	-24.1	-178.7	10.3	-10.9
2	2/17/1999	298.4	-24.9	-10.9	-125.3	16.9	-15.3
2	2/19/1999	190.2	-23.2	-32.2	-204.1	9.8	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	101.8	-55.2	-41.6	-66.6	-31.1	-56.7
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	69.4	-7.5	2.5	-0.9	2.7	.
3	1/27/1999	256.3	-11.7	-12.0	-37.6	-6.2	-11.7
3	1/29/1999	67.1	-11.2	-4.8	-52.6	-1.0	-5.2
3	1/31/1999	69.3	7.5	9.7	-19.8	15.9	62.5
3	2/2/1999	89.3	6.3	5.3	17.0	12.8	17.6
3	2/4/1999	221.5	6.7	12.4	-25.9	1.8	5.3
3	2/8/1999	68.8	-22.4	-7.7	-34.2	15.1	-12.8
3	2/10/1999	92.3	-24.4	-4.9	-66.1	-12.6	-13.9
3	2/12/1999	138.0	-1.7	.	-37.4	4.1	.
3	2/14/1999	18.1	-5.5	8.3	-33.7	12.2	45.3
3	2/16/1999	303.3	-4.8	-2.3	-67.9	6.9	-2.8
3	2/18/1999	76.4	-18.1	1.7	-12.2	2.4	.
3	2/20/1999	24.0	-49.6	.	-152.9	-26.7	-31.3
3	2/22/1999	34.0	-15.9	-32.1	-145.6	-2.9	.
3	2/24/1999	56.2	-1.8	3.0	.	-5.2	.
3	2/26/1999	53.2	-34.6	-25.0	-92.1	-0.8	-7.5
4	1/19/1999	65.5	23.1	18.2	-28.2	21.8	7.0
4	1/21/1999	124.6	-7.0	-5.8	-18.1	3.4	-19.3
4	1/23/1999	12.0	-29.2	40.0	35.8	28.3	35.8
4	1/25/1999	32.7	-27.2	-11.0	-49.2	0.0	-28.4
4	1/27/1999	45.5	-9.7	.	-28.8	11.2	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	21.5	-23.7	19.5	-46.1	1.4	-342.8
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	84.0	9.8	16.3	-44.8	6.9	-20.8
4	2/8/1999	54.6	21.1	15.4	-7.5	19.4	.
4	2/10/1999	103.1	1.7	8.8	-19.4	18.6	.
4	2/12/1999	10.9	-55.1	-30.3	-34.9	.	-51.4
4	2/14/1999	31.9	13.8	6.9	-12.2	25.4	.
4	2/16/1999	82.2	24.1	19.3	-48.9	16.8	-3.8
4	2/18/1999	40.3	29.3	23.1	.	23.1	.
4	2/20/1999	34.6	-4.1	-5.8	-8.1	-2.6	-27.2
4	2/22/1999	40.8	2.9	3.9	-20.3	-2.7	-39.0
4	2/24/1999	45.5	8.6	29.2	-2.4	31.2	-16.3

Percent Differences From FRM For Zinc

% Difference = [(FRM Conc- Sampler Conc)/FRM Conc]*100

SITE	DATE	FRM (ng/m3) AND % Difference		IMP % Difference	MET % Difference	URG % DIfference	VAPS % Difference
1	1/15/1999	254.8	1.2	3.3	-4.2	-6.0	.
1	1/18/1999	85.4	-86.8	-90.8	-91.1	-103.8	.
1	1/21/1999	8.2	1.2	-11.0	-45.1	.	-54.9
1	1/24/1999	.	.	.	.	.	.
1	1/27/1999	.	.	.	.	.	.
1	1/30/1999	25.5	4.3	25.9	-63.5	.	-29.0
1	2/2/1999	139.2	1.7	17.1	-0.6	.	4.1
1	2/5/1999	78.8	4.8	9.1	7.1	.	-1.3
1	2/11/1999	3.9	-15.4	-10.3	-48.7	41.0	-151.3
1	2/14/1999	17.4	0.0	6.3	-251.7	5.8	-25.3
1	2/17/1999	47.1	-14.4	5.7	-18.3	-15.1	.
1	2/20/1999	15.9	-22.6	-3.8	-38.4	-22.6	-54.7
1	2/23/1999	156.1	.	25.1	-15.4	.	60.0
1	2/26/1999	12.0	-0.8	8.3	-5.8	-10.0	-48.3
2	1/14/1999	47.5	35.8	40.2	10.7	39.0	.
2	1/16/1999	25.8	5.4	22.1	-76.4	0.8	.
2	1/18/1999	25.1	-10.8	-58.6	-112.8	0.0	-11.6
2	1/20/1999	25.0	-13.6	-2.4	-20.8	-0.4	.
2	1/22/1999	11.4	3.5	13.2	-64.0	.	-186.0
2	1/24/1999	24.8	1.6	25.4	-52.8	2.4	0.8
2	1/26/1999	15.7	-8.9	-8.3	-26.8	-1.3	-7.6
2	1/28/1999	1.5	-146.7	-173.3	.	-26.7	-180.0
2	2/3/1999	19.2	6.3	1.0	-98.4	-5.2	-3.1
2	2/5/1999	11.8	29.7	12.7	5.9	28.0	.
2	2/7/1999	10.1	-24.8	-6.9	-78.2	.	-3.0
2	2/9/1999	15.7	-10.2	8.9	-17.2	.	-29.3
2	2/11/1999	3.8	-15.8	-21.1	-68.4	13.2	47.4
2	2/13/1999	16.5	-3.6	0.0	-58.8	.	.
2	2/15/1999	15.0	-14.7	-7.3	-62.0	-2.7	29.3
2	2/17/1999	22.9	12.2	26.2	-17.5	17.5	17.0
2	2/19/1999	14.9	-12.1	1.3	-81.2	10.1	.
2	2/21/1999	.	.	.	.	.	.
3	1/21/1999	65.1	-23.2	-22.3	-16.0	-18.1	-33.3
3	1/23/1999	.	.	.	.	.	.
3	1/25/1999	21.2	-17.9	7.6	-2.4	-1.4	.
3	1/27/1999	83.3	-14.4	-8.8	-17.9	-21.6	-18.7
3	1/29/1999	19.8	3.5	19.2	7.1	1.5	12.1
3	1/31/1999	16.8	7.1	-0.6	13.7	-5.4	7.7
3	2/2/1999	22.4	-5.4	9.4	-15.2	-7.1	11.2
3	2/4/1999	48.7	9.9	19.5	-5.3	1.0	5.8
3	2/8/1999	30.4	-7.2	59.2	-10.9	-11.5	-19.1
3	2/10/1999	22.9	-13.1	5.2	-4.4	-1.8	-11.4
3	2/12/1999	35.4	43.5	.	31.1	38.1	.
3	2/14/1999	5.2	5.8	5.8	5.8	3.9	42.3
3	2/16/1999	67.8	5.0	6.6	4.4	6.9	9.0
3	2/18/1999	35.6	-6.2	0.6	12.1	-18.0	.
3	2/20/1999	10.6	7.6	.	9.4	-7.6	14.2
3	2/22/1999	6.7	-28.4	-29.9	-58.2	-26.9	.
3	2/24/1999	30.8	3.6	-0.3	.	-7.5	.
3	2/26/1999	15.4	3.3	0.0	16.2	5.2	3.9
4	1/19/1999	18.7	16.0	13.9	14.4	-2.7	3.7
4	1/21/1999	43.4	-8.1	15.9	-4.8	-1.4	-9.7
4	1/23/1999	5.8	-12.1	36.2	-8.6	-12.1	31.0
4	1/25/1999	7.6	-13.2	-1.3	-4.0	18.4	30.3
4	1/27/1999	17.8	-33.2	.	-12.9	-20.2	.
4	1/29/1999	.	.	.	.	.	.
4	1/31/1999	54.9	76.7	98.0	77.8	76.1	90.9
4	2/2/1999	.	.	.	.	.	.
4	2/6/1999	16.7	13.8	-118.6	15.6	16.2	22.2
4	2/8/1999	6.4	-25.0	-50.0	-48.4	-48.4	.
4	2/10/1999	11.8	0.0	-7.6	0.0	-10.2	.
4	2/12/1999	5.3	37.7	-5.7	37.7	.	0.0
4	2/14/1999	11.1	8.1	2.7	12.6	-1.8	.
4	2/16/1999	14.6	10.3	1.4	6.9	-15.1	-8.9
4	2/18/1999	14.0	3.6	9.3	.	-2.9	.
4	2/20/1999	13.2	-2.3	-3.8	12.1	-0.8	-22.7
4	2/22/1999	7.9	5.1	12.7	17.7	-10.1	-29.1
4	2/24/1999	9.9	1.0	13.1	-6.1	-42.4	-31.3

Appendix H

Field Evaluation of a Spiral and Cyclonic $PM_{2.5}$ Size Selective Separators for The Met One Ambient Chemical Speciation Sampler-SASS

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Abstract

The collection efficiency of several commercial candidate ambient chemical speciation samplers were field tested during the winter of 1998 and spring of 1999 during the 4-City study. The separation characteristics of the Met One sampler using the $PM_{2.5}$ Spiral seperator of Aerosol Dynamics demonstrated a shallow and higher mass measurement compared to the FRM 2.5 sampler. Re-testing of the Met One sampler at two of the four cities in April/May 1999 using a new $PM_{2.5}$ Sharp Cut Cyclone separator (SCC) compared favorably with the WINS and FRM sampler.

Field Evaluation

The selected field sites for re-testing of the Met One-SASS were Phoenix, AZ (characterized as a western high PM mass, coarse particles and high organic carbon) and Research Triangle Park (RTP), NC (characterized as an eastern low PM mass site with mainly fine particles). Two SASS samplers were collocated with FRM samplers at both sites in March-April 1999. The Met One–SASS sampler is a five channel device so sampling with repetitive channels would minimize the number of repeat days of sampling. Channels 1, 2 and 3 were configured with a Sharp Cut Cyclone inlet Model 2.141 (indicating internal cyclone diameter in cm) followed by 47mm PTFE FRM filter holders for mass concentration measurement. Channel 4 and 5 were configured with the old Spiral Inlet to demonstrate the over-sampling problem still existed during the re-test.

Channel 4 was a Spiral inlet which was lightly greased and cleaned after every 24 hour sample event to reduce particle bounce or re-entertainment. Channel 5 was a Spiral inlet dry which represents the SASS configuration used in the 4-City study.

Results and Discussion

PTFE filter samples from the two SASS and FRM's were gravimetrically measured and results compared.

Table 1 presents the re-test field data and calculated precision from Phoenix, AZ from March 28 to April 1, 1999. Table 2 presents the re-test field data and calculated precision from RTP,NC from April 4 to 11, 1999.

Table 1 SASS Re-test Phoenix.

SCC-SASS/PQ200FRM Tests- Phoenix, AZ 28 March to 1 April 1999

Test No.	FRM PQ200 Conc. μg/m3	SCC SASSA1 Conc. μg/m3	SCC SASSA2 Conc. μg/m3	SCC SASSA3 Conc. μg/m3	G. Spiral SASSA4 Conc. μg/m3	Dry Spiral SASSA5 Conc. μg/m3
1	9.9	11.2	13.4	11.9	11.6	18.3
2	11.4	13.0	13.5	14.2	13.0	24.9
3	6.7	8.2	9.9	7.4	7.4	15.4
4	7.3	8.9	9.2	8.7	8.0	22.6
5	2.5	2.4	1.9	1.5	1.5	2.8

SASSB1	SASSB2	SASSB3	SASSB4	SASSB5
11.4	11.9	11.1	10.9	18.7
14.4	14.3	14.4	13.3	24.3
8.3	7.8	8.1	7.1	15.4
8.4	8.9	9.2	8.5	20.5
1.9	2.2	2.2	2.7	2.3

Precision Comparisons-mg/m3

Test No.	Six (6) SCC	Six (6) SCC+FRM	Two (2) Grease Spiral+FRM	Two (2) Dry Spiral+FRM
1	0.85	1.06	0.85	4.97
2	0.58	1.11	1.02	7.63
3	0.85	0.98	0.33	5.02
4	0.30	0.66	0.61	8.29
5	0.32	0.36	0.64	0.25

Table 2. SASS Re-test RTP

SCC-SASS/PQ200FRM Tests- RTP, NC 4 April to 11 April 1999

Test No.	FRM PQ200 Conc.	SCC SASSA1 Conc.	SCC SASSA2 Conc.	SCC SASSA3 Conc.	G. Spiral SASSA4 Conc.	Dry Spiral SASSA5 Conc.
1	18.3	19.4	18.7	19.0	19.7	20.9
2	13.3	12.9	13.7	13.5	13.2	17.0
3	16.4	20.1	17.4	17.9	16.6	19.1
4	11.0	9.4	9.8	9.5	9.3	10.7
5	12.1	12.5	12.5	13.1	14.4	12.1

SASSB1	SASSB2	SASSB3	SASSB4	SASSB5
19.2	18.2	19.5	18.8	22.1
13.6	13.4	13.7	17.8	17.8
17.8	18.1	17.0	17.8	20.0
9.6	9.5	8.6	10.5	11.8
12.3	12.5	12.4	13.0	13.9

Precision Comparison-μg/m3

Test No.	Six (6) SCC	Six(6) SCC+FRM	Two (2) Grease Spiral+FRM	Two (2) Dry Spiral+FRM
1	0.49	0.52	0.69	1.92
2	0.30	0.28	2.61	2.42
3	1.09	1.18	0.76	1.90
4	0.42	0.71	0.89	0.55
5	0.27	0.30	1.17	1.07

Appendix I

Evaluation of $PM_{2.5}$ Size Selectors Used in Speciation Samplers

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Evaluation of $PM_{2.5}$ Size Selectors Used in Speciation Samplers

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Abstract

The separation characteristics of the $PM_{2.5}$ aerosol size selectors used in speciation samplers developed for the U.S. EPA National $PM_{2.5}$ Chemical Speciation Trends Network were evaluated under clean conditions. Measurement of particle penetration versus aerodynamic diameter was conducted using an APS 3320 in conjunction with a polydisperse test dust. The resulting penetration curves were integrated with assumed ambient particle size distributions (40 CFR Part 53, Subpart F) to obtain an estimate of measured mass concentration and to predict bias relative to the $PM_{2.5}$ reference separator. The cut-point of two SCC cyclones, from the family of cyclones developed by Kenny and Gussman (1997), compares favorably with the WINS, although possessing a slight tail that extends into the coarse particle mode. A second cyclone used by the Andersen Corp., AN 3.68, demonstrated the sharpest cut characteristics of the devices tested; however, it possesses a D_{50} cut size of 2.7 µm at its design flow rate. The separation characteristics of the Spiral separator were observed to be the shallowest and greater than 2.5 µm when greased or ungreased. Estimated mass concentration bias relative to the FRM was within ± 5% for the idealized fine and typical assumed ambient distributions for all separators. For the idealized coarse distribution, estimated bias ranged between + 4% and + 8%. A comparison of these results with actual field measurements made by the samplers that employ these separators demonstrates that a laboratory evaluation under clean conditions, while useful for design purposes, is not sufficient to predict separator behavior in the "real-world".

1. Introduction

The U.S. EPA is in the process of establishing a new monitoring network, the National $PM_{2.5}$ Chemical Speciation Trends Network, designed to measure the chemical constituents of $PM_{2.5}$ at selected sites around the U.S. (Tolocka et al., 2000). To secure samplers for this network, the U.S. EPA solicited innovative designs via the National $PM_{2.5}$ Sampler Procurement Contract leading to the development of several new samplers, all of which aspirate, separate, and collect atmospheric $PM_{2.5}$ in slightly differing manners. An extensive method intercomparison, the 4-City

Study, was conducted from January through March 1999 to determine similarities and differences between $PM_{2.5}$ mass and speciated chemical concentrations measured with these new samplers and the designated reference method samplers based on the Federal Reference Method (FRM).

This study provides a laboratory evaluation of the collection characteristics of the final aerosol size selectors used in $PM_{2.5}$ speciation samplers that have not been documented in peer-reviewed literature. In addition, a comparison is provided between these laboratory results and the field measurements made with their respective samplers during the 4-City Study and similar tests conducted immediately following the 4-City Study. The laboratory work was carried out at the Health and Safety Laboratory in Sheffield, England to take advantage of their well-characterized and well-documented rapid particle size separator testing apparatus.

2 Materials and Methods

2.1 Size Selectors Tested

A photograph of each of the particle size separators tested is presented in Figure 1 (A) through (D). Figure 2 presents a schematic diagram that identifies the critical dimensions of each device. Further identification details are presented in Table 1.

Three of the separators tested comprise a form of round entry cyclones, shown in Figure 1 (A), (B), and (C) and in Figure 2 (A), originally presented by Smith et al. (1979). They are a developmental variation of the original round entry cyclones developed by Southern Research Institute (SRI) under U.S. EPA contract (Smith et al., 1979) and further refined by Kenny and Gussman (1997). Kenny and Gussman (2000) describes the model adopted for the design of the two sharp cut cyclones (SCC) presented in this research. The SCC 2.141 cyclone operated at 6.7 Lpm serves as the inlet and the final separator in the Met One Instruments SASS sampler. The SCC 1.829 is not currently associated with a speciation monitor, but R&P Corporation plans to include this design in their real-time sulfate and nitrate monitors (Meyer, 2000). Their respective companies manufacture these two cyclones.

The AN 3.68 cyclone, shown in Figure 1(C), is similar to the SRI II (Smith et al., 1979) and to the selector described by John and Reischl (1980). Table 2 provides a comparison of the SRI II cyclone dimensions and the AN 3.68 cyclone as manufactured by Andersen

Samplers Inc. The similarities lie in the majority of the cylindrical diameter dimensions but differ in the height of the cylinder and cone which are longer. Aspiration in the Andersen-RAAS speciation sampler is achieved using a $PM_{2.5}$ FRM design inlet with the interior PM_{10} impaction section removed and operated at a flow rate of 54 Lpm. A small portion of this flow, 6 Lpm, is used to maintain the interior components at near ambient temperatures. The remaining 48 Lpm bifurcates into two identical AN 3.68 cyclones operated at 24 Lpm and then passes to a manifold from which the airflow is directed to the sample collection filters.

The Spiral collector, originally developed by Yaffee et al. (1952), is presented in Figure 1(D) and Figure 2 (B). The operating principle of this device is based upon the selective removal of particles by centrifugal forces induced as the air passes through a spiral channel. Further development of this device was reported by Macher and First (1984). The revision tested in this work was developed by Aerosol Dynamics Inc. and Particle Science Inc. for the Met One Instruments SASS sampler (Met One User’s Manual, 1998). During the 4-City Study, the Met One-SASS used five parallel Spirals to aspirate and separate the fine mode aerosol from the environment. As a result of field measurements presented in this paper, Met One Instruments discontinued the use of the Spiral in their speciation sampler (April 1999) in favor of the SCC 2.141, as mentioned above.

The Met One SASS manual dated December, 1998 provided performance curves for 5 different Spiral inlets, each tested at 7.0 Lpm. Also shown is data from one of these inlets operated at a lower flow rate of 6.5 Lpm. The manual states that "within the range from 6.5 to 7.0 Lpm, small changes in flow rate do not measurably alter the cut-point." In this work, the Spiral separator was evaluated at 7.0 Lpm due to the fact that five of the six performance curves in the manual were determined at this flow rate.

These size selectors are compared in the results and discussion section with the Well Impactor Ninety-Six (WINS), described in the US Federal Register (40 CFR Part 50 Appendix L), because of its adoption by EPA as the descriptor penetration curve for $PM_{2.5}$. The WINS is an impactor with a non-standard impaction plate geometry that is used in all reference method samplers for $PM_{2.5}$. It has been described in detail and tested by several authors (Kenny et al., 2000, Peters et al., in press). The curve used for the analysis in this paper is presented in Peters et al. (in press).

2.2 Determination of Aerosol Penetration Curves

The experimental methods used to test the cyclones were similar to those described in detail by Maynard and Kenny (1995). The tests were carried out in an aerosol chamber with working cross section of 1 m^2. The test aerosol consisted of solid, spherical glass microspheres (Whitehouse Scientific) with physical diameters up to 25 µm, and density 2.45 g/cm^3. The aerosol was dispersed using a rotating brush generator into the separate mixing section at the top of the chamber. An aluminum honeycomb layer was used to remove eddies from the aerosol which was transferred into the working section by a slow (<2 cm sec^{-1}) steady downflow of air. The generated aerosol typically had a number median diameter around 1 µm and a mass median diameter around 4 µm. The number concentration was typically 100-200 particles per cubic centimeter, and was generally stable over the time scales necessary for the test (10 minutes per separator).

The test sampling lines were situated close to the center of the chamber's working section, connected to an Aerodynamic Particle Sizer (APS 3320, TSI, Incorporated, St. Paul, MN) via two 15 mm diameter vertical metal tubes. The APS was situated directly below the working section, outside the chamber. Access to the working section was gained through sealed glove ports in the side of the chamber, which allowed the flow through each cyclone to be measured accurately using a Gilibrator bubble flow meter placed inside the chamber. The flow through the system was maintained using a mass flow controller, calibrated and set before each test using the Gilibrator.

The test procedure involved placing a separator on one of the two sampling lines. Both sampling lines to the APS shared identical geometry and switching from one to the other was accomplished by means of ball valves. The size selection characteristics were measured by taking five 60-second samples of the polydisperse aerosol alternately from the two sampling lines. The ratio of the aerosol size distributions measured through each line gives the size selective aerosol penetration through the selector alone, all other effects (including any aspiration and transfer losses) being identical in both lines. The entire test sequence was (in most cases) repeated on two different days, in order to provide a true replicate result for each sampler. Note that earlier tests on the WINS were carried out using an APS 3310 system, otherwise the methods were identical.

2.3 Data Analysis

Files from the APS were exported and processed using an Excel spreadsheet to calculate the penetration curves, taking into account the appropriate corrections for particle density and phantom particle counts. The average particle number counted in each size bin of the APS with the selector present was divided that without the selector present to determine the aerosol penetration for that diameter range. The raw data were normalized so that the penetration values tended to unity for $d_{ae}= 0$, where necessary.

TableCurve 2D (Jandel Scientific Software, San Rafael, CA), a computer software program for fitting curves to experimental data, was used to model the discrete penetration measurements with a reverse asymmetric sigmoid equation (equation 8092 in TableCurve 2D). This equation is expressed as:

$$y = a + b[1 - [1 + \exp(\frac{(x + d\ln(2^{\frac{1}{e}} - 1) - c)}{d})]^{-e}] \qquad (1)$$

where, y is the penetration represented as a fraction of one, x is particle aerodynamic diameter, and a through e are curve parameters. This equation has been shown to fit cyclone and impactor penetration measurements with r^2 values of greater than 0.99 where symmetric equations demonstrate poorer fits. The aerodynamic diameter associated with 84%, 16%, and 50% penetration or D_{84}, D_{16}, and D_{50}, respectively, are then determined using the modeled curve. The curve is then summarized with the D_{50} value (cut-point diameter) and the GSD, which is equal to:

$$GSD = \sqrt{\frac{D_{16}}{D_{84}}} \qquad \mathbf{(5)}$$

The fitted curve was then integrated with assumed ambient particle size distributions, as specified for equivalent methods for $PM_{2.5}$ (40 CFR Part 53 Subpart F), using a Visual Basic (Microsoft Corporation, Redmond, WA) program specifically written for this purpose. For each separator, an estimate of mass concentration measurement was calculated for particle distributions that represent idealized fine, typical, and coarse ambient aerosols. The various separation devices were compared with one another by expressing each device's percent bias from the FRM in estimated measured mass concentration.

2.4 Field Performance

Four sites in the U. S. (namely Philadelphia, PA; Phoenix, AZ; Rubidoux, CA; and RTP, NC) were identified as appropriate sites to challenge methods of fine aerosol collection, owing to individual differences in chemical atmospheres (Tolocka et al., 2000). The prominent objective of the 4-City Study was to perform an intercomparison between a variety of prototype chemical speciation samplers and the $PM_{2.5}$ reference method samplers. This study was conducted during the period of January thru March, 1999.

Sample collection details and analysis methods were presented in detail by Tolocka et al., 2000. Briefly, teflon sample collection filters were analyzed for mass and energy dispersive x-ray fluorescence (EDXRF) analysis. Mass concentration was determined using FRM procedures found in 40 CFR Part 50 Appendix L. Crustal material was calculated using the EDXRF analysis of three elements: Si, Ca, and Fe by the methods presented by Malm, et al (1994). Sulfates were measured by ion chromatography.

Immediately following the 4-City Study, Met One Instruments conducted tests in Phoenix, AZ and RTP, NC to compare the mass concentration measured with a reference method sampler to their speciation sampler operated with alternative $PM_{2.5}$ separators (Merrifield, 2000). During these tests, a reference method sampler was collocated with two Met One speciation samplers. On each Met One sampler, three of the five channels were operated with SCC 2.141 cyclones. The remaining channels were operated with a Spiral greased with Apeizon M and a Spiral ungreased as operated in the 4-City Study. Teflon sample collection filters were used in all channels. The post sampling analysis was limited to determination mass concentration by gravimetric methods outlined in the FRM. The tests were conducted from March to April 1999.

3 Results and Discussion

3.1 Separator Penetration and Bias Estimates

The size-selection curves for each of the separators tested are presented in Figure 3, Figure 4, and Figure 5. Table 3 presents the descriptive parameters of the curve fitted to the penetration measurements for each separator. Further, this table presents the D_{50}, D_{84}, D_{16}, and GSD to summarize the separation characteristics of each device. Table 4 presents the predicted mass concentration, difference from the FRM ideal mass concentration, and percent bias for the idealized fine, idealized typical, and idealized coarse particle size distributions. In some instances, more than one flow rate was tested in order to aid in identifying the flow rate that provides a D_{50} cut-point of 2.5 µm.

Figure 3 displays the separation curves measured for the SCCs. The SCC 1.829 possesses a cut-point diameter of 2.44 µm with a GSD equal to 1.23. The SCC 2.141 has a D_{50} value of 2.52 µm and 2.35 µm for flow rates of 6.7 Lpm and 7.0 Lpm, respectively. The GSD of the SCC 2.141 was measured to be 1.24 at both flow rates. In comparison with the WINS, the SCCs are slightly sharper below the respective device's cut-point, but possess a tail that extends slightly into the coarse particle mode. This finding is reflected in the positive bias estimated when the SCCs are integrated with the idealized coarse particle distribution: +6.1%, +2.1%, and +4.2% for the SCC 2.141 operated at 6.7 Lpm, the SCC 2.141 operated at 7.0 Lpm, and the SCC 1.829 operated at 5.0 Lpm, respectively. The percent bias for the idealized fine and idealized typical distributions ranged from +0.1% to 2.3% for both SCC designs at all flow rates tested.

The D_{50} cut-point of the AN 3.68 cyclone, presented in Figure 4, was measured to be 2.72 µm at its design flow rate of 24.0 Lpm. This cyclone demonstrated a slightly sharper cutoff curve, GSD = 1.15, than the WINS (GSD = 1.18). Although the cutoff is sharp, the percent bias estimate for the typical coarse aerosol is estimated to be +7.4% greater than the ideal FRM because the cut-point is greater than 2.5 µm.

The AN 3.68 separation characteristics were again measured at a higher flow rate, 28.1 Lpm, to aid in identifying the D_{50} cut-size for 2.5 µm. At this flow rate, the cut-point was measured to be

2.33 µm with a slightly less sharp GSD, equal to 1.18, than that measured at 24 Lpm. Interpolation between these points, using the log-normal relationship presented in Kenny and Gussman (1997) provides an estimated D_{50} of 2.5 at a flow rate of 26.6 Lpm. The bias estimated for the coarse aerosol, presented in the previous paragraph, should be eliminated by operating the AN 3.68 at this larger flow rate; however, caution is recommended because of the tendency of cyclonic separators to become more efficient as they are loaded with particles (Kenny et al., 2000). Further tests should be conducted to determine the magnitude of cut-point shift after being loaded with coarse mode aerosol before committing to flow rate alterations or design modifications.

The size-selection characteristics of the Spiral at 7.0 Lpm showed significant variability in the measured cut-point diameter. For example, the cut-point of the ungreased Spiral was measured to be 2.7 µm, 2.2 µm, and 1.9 µm for three discrete tests. We conjecture that, as the unit is tightened, the gasket material deforms causing a slight, but important, dimensional change in the height of the spiral channel which serves to increase air velocity, increase collection of smaller particles, and, hence, shift the cutsize of the device to a lower size. The variability in separation characteristics of the Spiral from run to run was minimized by eliminating the gasket and lapping the joining surfaces. The tests presented in this paper are with this refined Spiral.

The performance of the ungreased Spiral demonstrated the least sharp cutoff characteristics of all the separators evaluated (GSD = 1.30) with a cut-point of 2.69 µm. The Spiral was also evaluated by greasing the spiral channel with a thin film of Apeizon M grease because of reports of coarse particle breakthrough (Tolocka et al., 2000). The grease coating did not change the D_{50} cut-size (2.67 µm), but it did serve to sharpen the characteristic performance curve slightly to yield a GSD of 1.24. The bias estimate for the coarse mode ambient aerosol was reduced by a small magnitude from +6.1% when ungreased to 5.5% when greased.

3.2 Field Performance

The mass, sulfate, and crustal material concentrations measured by the reference method sampler and by the other methods can be compared to draw conclusions about the ability of the FRM to separate fine mode aerosol from coarse mode aerosol. Furthermore, a valuable comparison between the predicted bias from the FRM and that actually measured at a variety of sites around the U.S. can be made. It must be kept in mind, however, that any observed differences between samplers may be attributed to any of the physical processes involved in the collection of a representative sample (aspiration, separation, and transport to the sample collection filter). Chemical analysis results from the FRM and the other samplers operated at the four sites indicated that the criteria for varied chemical atmospheres was satisfied: [Philadelphia, high sulfate; Phoenix, high carbon and crustal material; Rubidoux, high nitrate; and RTP, all low concentrations] (Tolocka et al., 2000).

Ammonium sulfate particles typically have an aerodynamic diameter between 0.1 µm and 1.0 µm (John et al., 1990 and Hering and Freidlander, 1982). Therefore, no difference, or very small differences, should be observed in the measured sulfate concentrations between methods if the characteristic separation allows particles of less than 1.0 µm to pass to the sample collection filter with unit efficiency. On the other hand, a predominant fraction of crustal material particles have aerodynamic diameters greater than 2.5 µm (Lundgren and Paulus, 1975); therefore, the crustal material concentration measured with the various samplers penetrating to the sample collection filter is a good indicator of large particle intrusion.

A summary of selected results from the 4-City Study, presented in Table 5, provides a comparison of $PM_{2.5}$ mean mass, sulfate, and crustal material concentrations measured by the FRM, the Andersen RAAS, and the Met One SASS (with the Spiral) at the four cities. The mass, sulfate, and crustal material concentrations measured with the FRM agree closely to those measured with the Andersen RAAS speciation sampler in all cities. This indicates that the WINS in the reference method sampler provides similar separation characteristics as the AN 3.68 cyclone in the Andersen RASS speciation sampler. The bias estimates for the AN 3.68 cyclone were positive for the fine, coarse, and typical assumed ambient size distributions; however, at all four sites, the mean mass concentration for the Andersen RAAS was slightly less than that measured by the FRM.

The mean sulfate concentration measured with the Met One SASS was similar to the other methods in all cases indicating proper aspiration and collection of the fine aerosol. In contrast, the mean mass concentration measured with the Met One SASS was greater than that measured by the FRM at all sites. In RTP and in Philadelphia, this difference, although slight, may be attributed to an increased magnitude of crustal material reaching the sample collection filter. This difference is observed to be markedly more pronounced at the Phoenix and Rubidoux sites where the mean mass concentration was 2.0 and 1.4 times greater than the FRM, respectively. A bias of this magnitude was not predicted based on the laboratory evaluation of the clean Spiral presented in the previous section.

The tests conducted by Met One immediately following the 4-City Study to resolve these coarse particle intrusion issues are summarized in Table 6. In both Phoenix and RTP, the mass concentration measured by the SASS channels employing the SCC 2.141 cyclone and the greased Spiral were observed to be very near, but slightly greater than, that measured by the reference method sampler. This slight positive bias is consistent with the predicted bias based on the performance characteristics of these separators. In Phoenix, the mass concentration measured by the SASS channels operated with the ungreased Spiral was a factor of two greater than the FRM indicating that there was sufficient coarse mode aerosol present to test for coarse particle intrusion. As a result of these tests, Met One incorporated the SCC 2.141 into the SASS design.

4 Conclusions

The final size-selection devices for several $PM_{2.5}$ chemical speciation monitors were evaluated under laboratory conditions. The cut-point of the SCC cyclones compare favorably with the WINS although possessing a slight tail that extends into the coarse particle mode. The AN 3.68 demonstrated the sharpest cut characteristics of the devices tested; however, it has a D_{50} cut size of 2.7 µm at its design flow rate. The Spiral impactor possesses the shallowest cutoff curve and has a cut-point size that is greater than 2.5 µm when greased or ungreased.

The measured penetration curves were integrated with assumed ambient particle size distributions (fine, typical, and coarse) to obtain an estimate of measured mass concentration and to predict bias relative to the $PM_{2.5}$ reference separator (following procedures specified in 40 CFR Part 53, Subpart F). For all of these separators, the bias in mass concentration relative to the FRM was estimated to be within ± 5% for the fine and typical distributions and to be within 4% and 8% for the coarse distribution.

These bias estimates were then compared to field measurements made with the speciation samplers carried out during the 4-Cities Study. The Andersen RASS, employing the AN 3.68 cyclone, compared well with the FRM for all cities; however, the bias was observed to be slightly negative rather than slightly positive as predicted. The laboratory-based bias predicted for the Met One SASS operated with the Spiral inlet was severely underestimated for the cities with high crustal material (Phoenix and Rubidoux). Subsequent tests carried out by Met One demonstrated that this problem could be eliminated by using a SCC 2.141 cyclone or by greasing the Spiral channel.

This evaluation, with the separators clean and only tested with solid aerosol, represents a single component of the overall understanding of the collection of ambient particulate matter with these samplers. The comparison of laboratory predicted bias and "real-world" observations demonstrates the necessity to evaluate performance of these separators after becoming dirty from field operation or with some variation of the loading tests described in 40 CFR Part 53, Subpart F. Additionally, evaluation of the inlet aspiration and aerosol transport through the sampler is needed to ensure that the collected sample is representative of the atmospheric aerosol.

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Table 1. Identification of size selectors tested.

Separator	Type	Design Flow Rate (Lpm)	Notes
SCC 2.141	Cyclone	6.7	Serves as the inlet and final separator in the Met One SASS
SCC 1.829	Cyclone	5.0	Proposed to be used in the R&P Real-time Sulfate / Nitrate Monitors
AN 3.68	Cyclone	24.0	Serves as the final separator in the Andersen RAAS, internally coated Teflon
Spiral	Spiral	7.0	Previously served as the inlet and final separator in the Met One SASS
WINS	Impactor	16.7	Final separator in the FRM, refer to 40 CFR Part 50 Appendix L, previously tested

Table 2. Detailed dimensions of the AN 3.68 cyclone (all dimensions are presented in centimeters).

Dimension	SRI II	John and Reischl (1980)	AN 3.68
Cyclone diameter, Dc	3.66	3.658	3.68
Inlet diameter, Din	1.01	1.008	1.01
Exit diameter, De	1.05	1.052	1.09
Cone diameter, B	1.29	1.270	1.28
Height, H	6.62	5.923	7.07
Cylinder height, h	2.11	1.173	2.33
Cone height, z	4.71	4.750	4.74
Vortex finder depth, s	1.57	1.570	1.55
Cup height, Hcup	2.22		2.26
Cup diameter, Dcup	3.73		3.10

Table 3. Summary of modeled curve parameters, D_{84}, D_{16}, and GSD for the separators evaluated.

Separator	**SCC 2.141**		**SCC 1.829**	**AN 3.68**		**Spiral**		**FRM WINS**
Flow, Lpm	**6.7**	**7.0**	**5.0**	**24.0**	**28.1**	**7.0 ungreased**	**7.0 greased**	**16.7**
Modeled Curve Parameters								
a	1	1	1	1	1	1	1	1
b	-1	-1	-1	-1	-1	-1	-1	-1
c, D_{50}[1], µm	2.52	2.35	2.44	2.72	2.33	2.69	2.67	2.48
D	0.1823	0.1534	0.127	0.1926	0.1945	0.441	0.3568	0.3093
E	0.3005	0.2640	0.2160	0.6318	0.6688	1.3364	1.1837	3.3683
Summary of Curve								
D_{84}, µm	2.09	1.96	2.08	2.38	1.98	2.02	2.10	2.05
D_{16}, µm	3.22	3.04	3.16	3.17	2.76	3.39	3.22	2.85
GSD	1.24	1.24	1.23	1.15	1.18	1.30	1.24	1.18

[1] This value is the D_{50} in µm as well as the c parameter.

Table 4. Estimated measured mass concentration, deviation from FRM ideal, and percent bias from FRM ideal.

Separator	**SCC 2.141**		**SCC 1.829**	**AN 3.68**		**Spiral**		**FRM Ideal**
Flow, Lpm	**6.7**	**7.0**	**5.0**	**24.0**	**28.1**	**7.0 ungreased**	**7.0 greased**	**16.7**
Estimated Mass Concentration, µg/m^3								
Fine	79.6	78.6	79.4	80.8	78.2	78.6	79.3	78.5
Typical	35.1	34.6	34.8	35.2	34.1	34.8	34.9	34.3
Coarse	14.7	14.2	14.4	14.8	13.6	14.7	14.6	13.8
Difference in Mass Concentration from Ideal, µg/m^3								
Fine	1.1	0.1	0.9	2.2	-0.3	0.0	0.8	--
Typical	0.8	0.3	0.6	0.9	-0.2	0.5	0.6	--
Coarse	0.9	0.3	0.6	1.1	-0.2	0.9	0.8	--
Bias in Mass Concentration from Ideal								
Fine	1.4%	0.1%	1.1%	2.7%	-0.4%	0.0%	1.0%	--
Typical	2.3%	0.9%	1.7%	2.6%	-0.6%	1.4%	1.7%	--
Coarse	6.1%	2.1%	4.2%	7.4%	-1.5%	6.1%	5.5%	--

Table 5. Comparison of $PM_{2.5}$ mass, sulfate, and crustal material concentrations measured with reference method samplers and speciation samplers during the 4-City Study (Jan – Mar 1999).

RTP (Mean ± Std. Dev) µg/m^3			
Sampler	**Mass**	**Sulfates**	**Crustal**
FRM WINS	10.8 ± 5.1	3.1 ± 1.6	0.26 ± 0.20
Andersen AN 3.68	10.7 ± 5.2	3.1 ± 1.7	0.25 ± 0.18
Met One Spiral	11.8 ± 5.9	3.2 ± 1.8	0.36 ± 0.29

Philadelphia (Mean ± Std. Dev) µg/m^3			
Sampler	**Mass**	**Sulfates**	**Crustal**
FRM WINS	17.2 ± 8.8	3.9 ± 2.0	0.30 ± 0.19
Andersen AN 3.68	16.9 ± 8.8	3.6 ± 2.1	0.32 ± 0.2
Met One Spiral	17.7 ± 9.9	3.9 ± 2.1	0.54 ± 0.43

Phoenix (Mean ± Std. Dev) µg/m^3			
Sampler	**Mass**	**Sulfates**	**Crustal**
FRM WINS	15.9 ± 7.1	0.85 ± 0.42	1.1 ± 0.58
Andersen AN 3.68	15.7 ± 6.8	0.75 ± 0.38	1.3 ± 0.61
Met One Spiral	31.9 ± 18.4	0.97 ± 0.42	5.1 ± 2.8

Rubidoux (Mean ± Std. Dev) µg/m^3			
Sampler	**Mass**	**Sulfates**	**Crustal**
FRM WINS	26.0 ± 19.5	1.5 ± 1.5	0.89 ± 0.57
Andersen AN 3.68	25.6 ± 21.6	1.4 ± 1.6	0.95 ± 0.68
Met One Spiral	36.3 ± 25.5	1.5 ± 1.5	3.3 ± 3.0

Table 6. Comparison of $PM_{2.5}$ mass concentrations measured with a reference method sampler and the Met One speciation sampler operated with a SCC 2.141, a greased Spiral, and an ungreased Spiral. (Mar - Apr 1999).

Phoenix (28 Mar 1999 to 1 Apr 1999)

Sampler	**N**	**Mass Concentration Mean ± St. Dev $\mu g/m^3$**
FRM WINS	5	7.6 ± 3.0
Met One SCC 2.141	30	9.0 ± 4.0
Met One Greased Spiral	10	8.2 ± 3.8
Met One Ungreased Spiral	10	16.5 ± 7.6

RTP (4 Apr 1999 to 11 Apr 1999)

Sampler	**N**	**Mass Concentration Mean ± St. Dev $\mu g/m^3$**
FRM WINS	5	14.2 ± 2.7
Met One SCC 2.141	30	14.5 ± 3.6
Met One Greased Spiral	10	15.1 ± 3.2
Met One Ungreased Spiral	10	16.5 ± 3.9

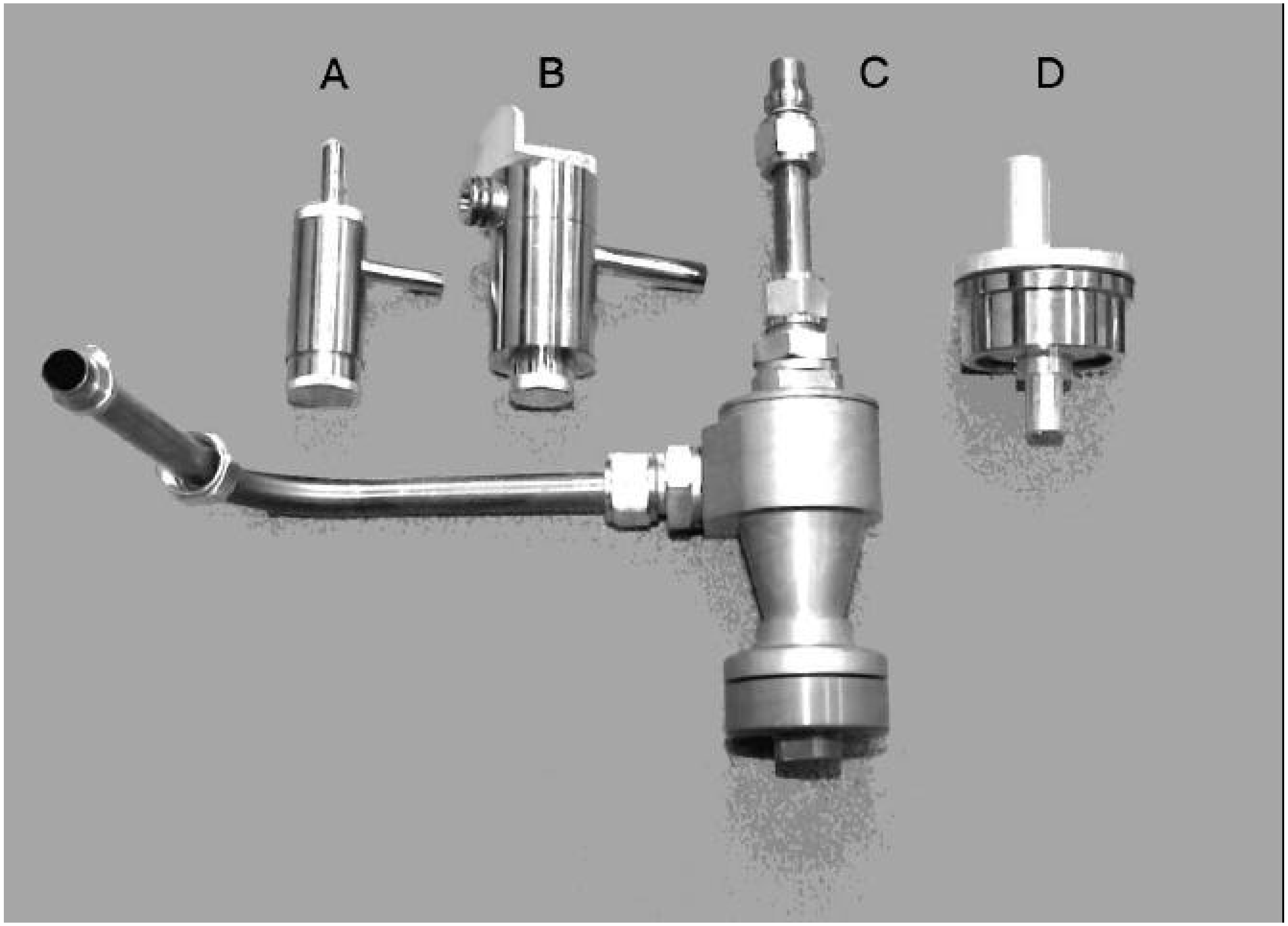

Figure 1. Photograph of particle separators evaluated: A) SCC 1.829, B) SCC 2.141, C) AN 3.68, D) Spiral.

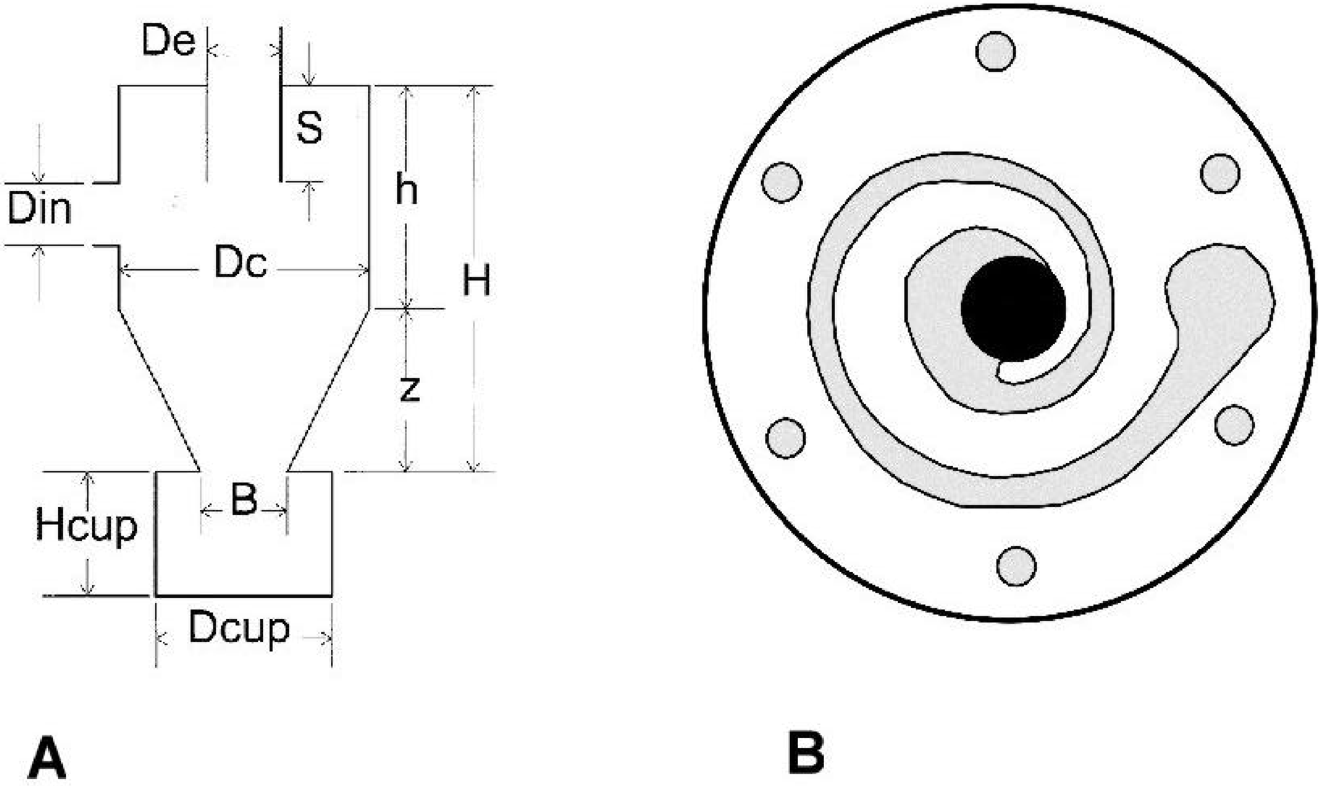

Figure 2. Schematic diagram of the particle separators tested illustrating the important component dimensions: A) Cyclone and B) Spiral.

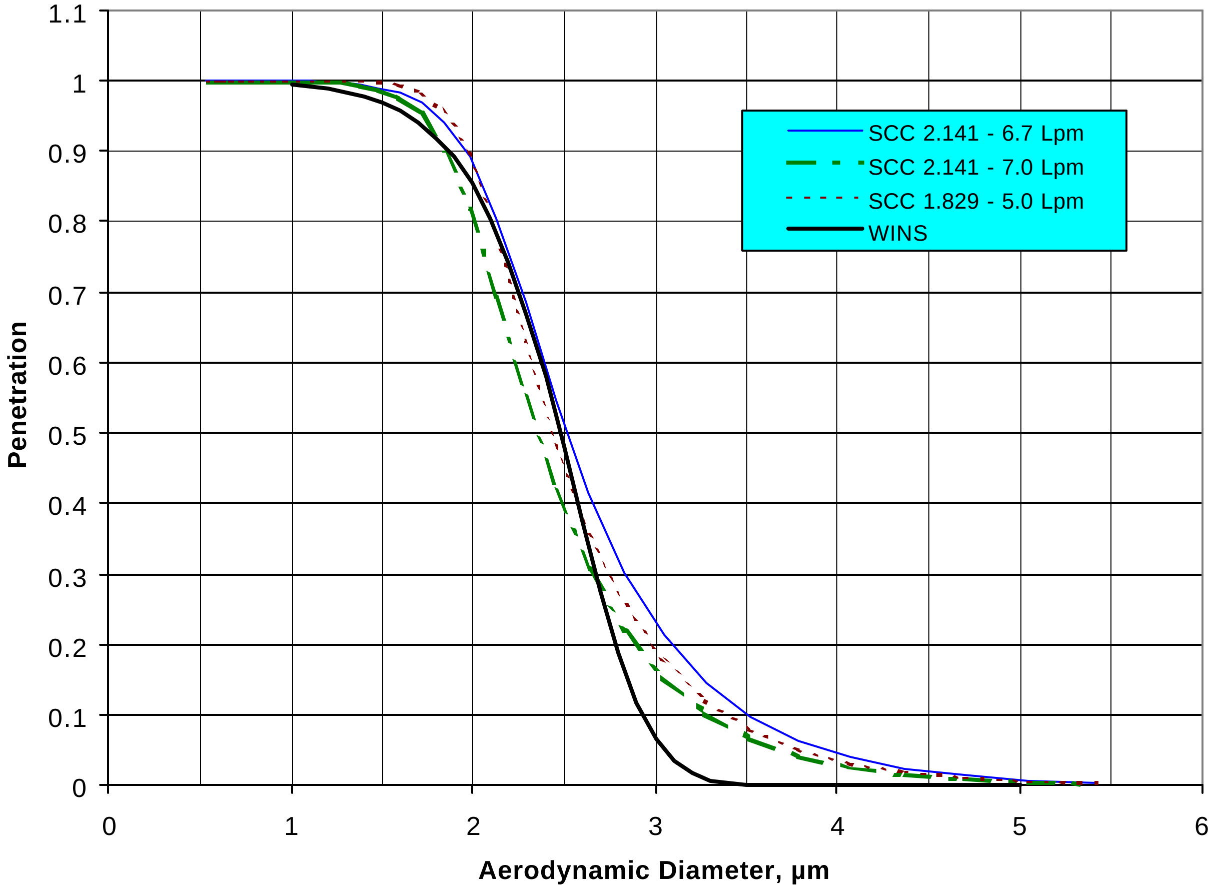

Figure 3. Size-selection curves for the SCC 2.141 and SCC 1.829.

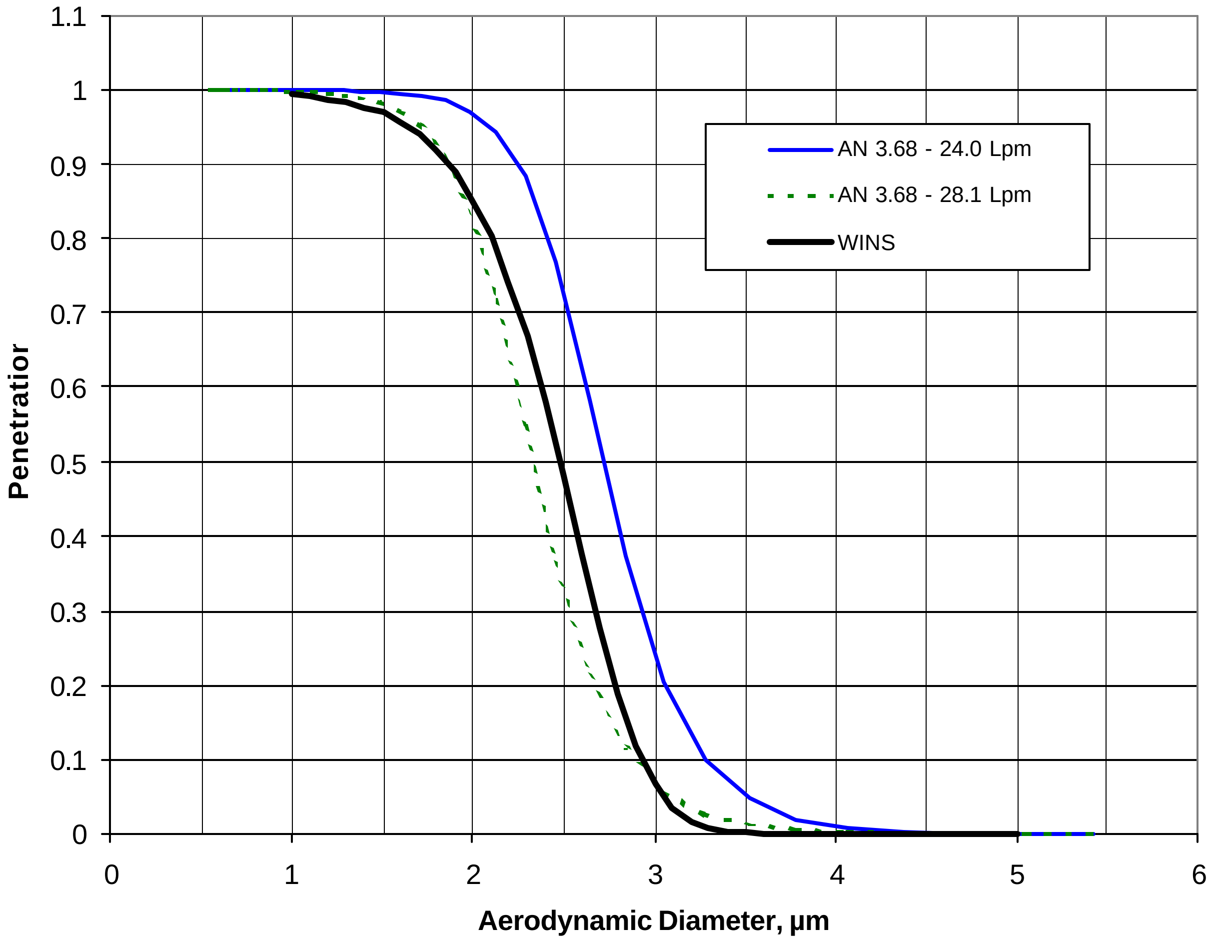

Figure 4. Size-selection curve for the AN 3.68 cyclone at two flow rates.

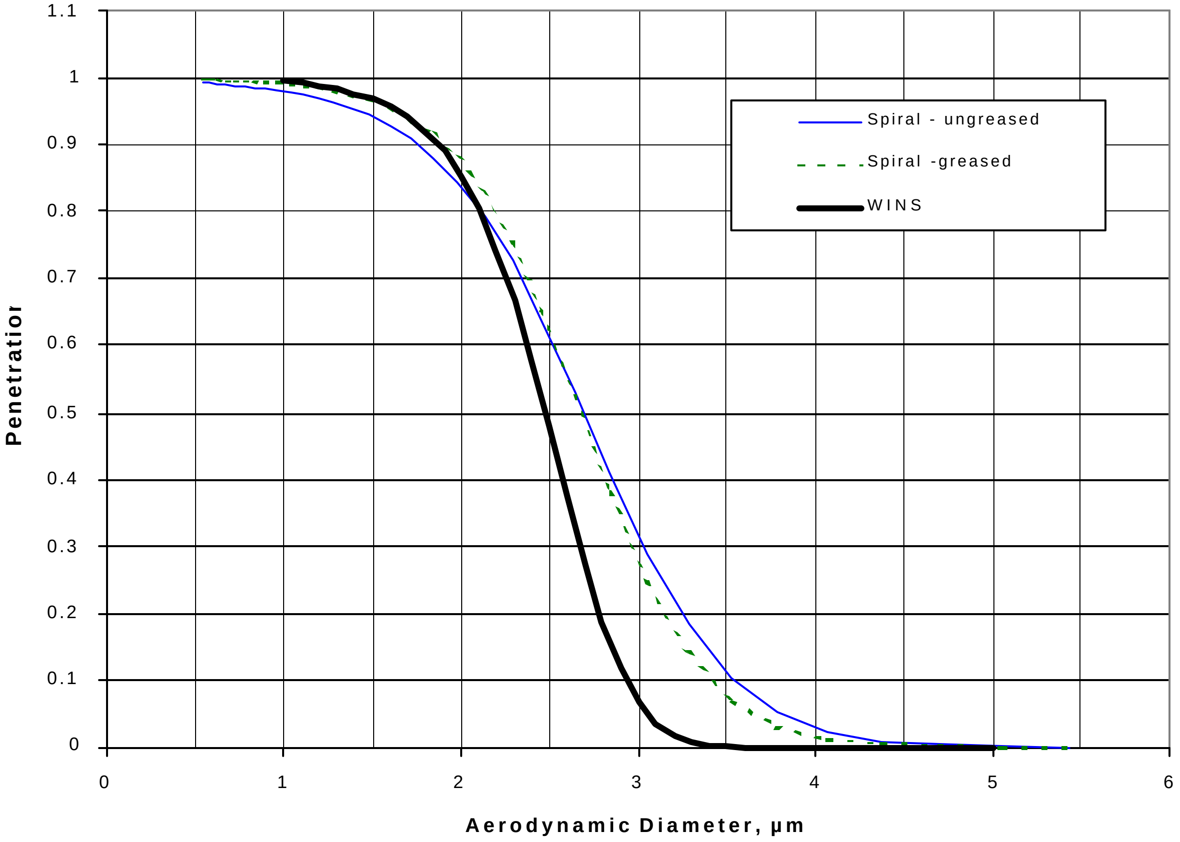

Figure 5. Size-selection curve for the Spiral with and without a greased coating.

Appendix J

Comparison of Particulate Organic and Elemental Carbon Measurements Made with the IMPROVE and NIOSH Method 5040 Protocols

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Comparison of Particulate Organic and Elemental Carbon Measurements Made with the IMPROVE and NIOSH Method 5040 Protocols

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ABSTRACT

Two primary thermal optical methods are used to measure particulate carbon collected on quartz-fiber filters: thermal optical transmittance (TOT), and thermal optical reflectance (TOR). These two particulate carbon measurement methods were evaluated using two different protocols: National Institute of Occupational Safety and Health (NIOSH) Method 5040 that uses TOT; and Interagency Monitoring of Protected Visual Environments (IMPROVE) that uses TOR. The methods are based on the same measurement principle but differ in the method used to adjust for pyrolysis (transmittance or reflectance), temperatures for evolving carbon, and the amount of time at each temperature step. A combination of quality assurance, source, and ambient samples were used to evaluate the differences between the two protocols. Elemental carbon (EC) measured by the IMPROVE protocol is approximately twice that measured by the NIOSH protocol for urban particulate samples. The difference in the EC concentration measured by the two methods is primarily due the highest temperature used to evolve organic carbon (OC) in He, with the NIOSH and IMPROVE protocols using 550 and 850 /C, respectively. Adding the OC evolved in the NIOSH method from 550 to 850 /C to EC explained the difference between the protocols for urban samples. Total carbon concentrations measured using IMPROVE were approximately 10 percent higher than NIOSH. Measurement precision for the two protocols also was evaluated using triplicate analyses and the precision was similar for both methods.

INTRODUCTION

Carbonaceous material is a major component of particulate matter less than 2.5 m in aerodynamic diameter ($PM_{2.5}$) accounting for 25 to over 50 percent of the mass for samples collected in the United States (EPA, 1996; EPA, 1999). Thermal optical transmittance and thermal optical reflectance are the two primary thermal optical techniques used for the measuring particulate carbon. These two methods were evaluated using two different protocols: National Institute of Occupational Safety and Health (NIOSH) Method 5040 (Birch and Cary, 1996) that uses thermal optical transmittance; and Interagency Monitoring of Protected Visual Environments (IMPROVE) (Malm et al., 1994) that uses thermal optical reflectance. The NIOSH Method 5040 (Eller and Cassinelli, 1996) was evaluated using a thermal optical transmittance instrument (Sunset Laboratory , Forest Grove, OR) (Birch and Cary 1996, Birch 1998). Interagency Monitoring of Protected Visual Environments uses thermal optical reflectance developed by Chow et al. (1993) at Desert Research Institute (DRI) (Reno, NV). These two methods are based on a carbon analyzer designed by Huntzicker et al (1982). Both analyzers quantify carbon by heating filters to volatilize (or combust) the carbon, which is then oxidized in a granular bed of MnO_2, reduced to CH_4 in a Ni methanator, and quantified as CH_4 with a flame ionization detector. Organic carbon (OC) is evolved in an He atmosphere, while elemental carbon is evolved in an He/O_2 atmosphere. The methods use different techniques to correct for the formation of pyrolysis products and temperature programs for evolving organic and elemental carbon. In this analysis the two methods will be referred to as the NIOSH and IMPROVE protocols.

NIOSH and IMPROVE protocols have been used to analyze a large number of samples with 100,000 samples analyzed with the IMPROVE protocol (Chow et al., 1993) and at least 25,000 samples by the NIOSH protocol (Cary, Sunset Laboratory, personal communication). Currently DRI and other researchers have 6 thermal optical reflectance or thermal optical reflectance/transmittance instruments (5 at DRI, 1 at EPA (NERL)), and Sunset Labs and other researchers have 31 thermal optical transmittance instruments (2 at Sunset Laboratory, 2 at EPA (NERL/NRML), 7 international).

Carbonaceous particulate matter is classified into three main categories: organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) (Chow et al., 1993). These categories are defined operationally by application of the thermal/optical techniques. Organic carbon sources include combustion, biogenic, and photochemical process. Graphic-like EC sources are mainly combustion related. Carbonate carbon is typically associated with soil related sources (Appel et al., 1983) and usually constitutes less than 5 % of the TC (total carbon = EC + OC + CC) (Chow et al., 1993). The ratio of OC to EC has been determined for a large number of sources with the IMPROVE method, and the ratio depends on the source of the particulate matter: agricultural burning (3.2); unleaded gasoline vehicle exhaust (2.2), and diesel motor vehicle exhaust (1.2) (Watson et al.,1994). For these combustion sources, particulate carbon is a large fraction of the $PM_{2.5}$ mass: agricultural burning (TC = 45.4 %), unleaded vehicle exhaust (TC = 43.6 %); diesel motor vehicle exhaust (TC = 73 %).

A number of comparisons of particulate carbon methods have been conducted using various methods including thermal optical techniques. Cadle and Groblicki (1982) compared several measurement methods for elemental carbon, including organic extractions, nitric acid digestion, vacuum stripping, thermal methods, and the integrating plate method. Systematic but correlated differences were found between the methods. Hering and colleagues (Hering et al., 1990) conducted a comparison of seven variations of thermal carbon analysis methods. Similar results were found for OC and TC with an average ratio of method mean to sample mean ranging from 0.84 to 1.05, but the EC concentrations had a larger variation with ratios varying from 0.69 to 1.42. Cadle and Mulawa (1990) conducted a round-robin methods study with 11 laboratories and an automated thermal technique (Cadle et al., 1980). Elemental carbon concentrations had the largest range in the ratio between the thermal technique with a low of 0.90 and a high of 4.3. Total carbon and organic carbon showed better agreement with the thermal technique: TC range from 0.84 to 1.39 and OC range from 0.60to 1.16. Birch (1998) conducted a study that compared NIOSH, IMPROVE, and thermal techniques with coulometric detection of CO_2. Similar TC results (within 14 %) were observed, in the study, but the EC concentrations for the coulometric techniques biased high when compared to the thermal-optical techniques: 120 % for the urban sample, 69 % for the truck exhaust, and 80 percent for the fire station sample. Elemental carbon concentrations measured using the IMPROVE protocol were about twice the EC concentrations obtained from NIOSH for urban samples. The difference between the IMPROVE and NIOSH protocols was less for diesel with the IMPROVE reporting 31 percent more elemental carbon than the NIOSH method. Chow et al (2000) also have also found an average difference of 107 percent in the EC concentrations measured by NIOSH and IMPROVE that they attribute to tarry, apparently light absorbing, volatile compounds from that are evolved above 650 /C in the NIOSH protocol. Total carbon concentrations were 0.7 % different between the two protocols run on the same analyzer. Chow and colleagues have not compared their NIOSH protocol that was run on a GreenTek (Douglasville, GA) TOT/TOR analyzer to the NIOSH method run on a Sunset Laboratory TOT analyzer. The various carbon analysis methods showed more consistent agreement for TC, however, the measurement of EC is operationally defined. Since TC is the sum of OC and EC, a difference in the EC concentration between methods also effects the OC concentration, but by a smaller percentage since OC typically is 80 – 90 percent of the TC.

Differences in EC measured by the NIOSH and IMPROVE methods may be due to the different definitions of EC used by the IMPROVE and NIOSH methods: IMPROVE defines EC as graphitic carbon and light absorbing OC (Chow et al., 1993; Chow et al., 2000), and NIOSH defines EC only as graphitic-like or refractory carbon. These two definitions are used to justify the highest temperature step in the He atmosphere of 550 or 850 /C for IMPROVE or NIOSH, respectively. Higher temperatures provide a more selective measure of graphitic carbon by evolving higher molecular weight hydrocarbons during the OC step with particular relevance for quantifying diesel exhaust, which is mostly EC. The lower maximum temperature in IMPROVE results in an EC value that includes a mixture of graphitic carbon and light absorbing organic carbon, which is relevant to the IMPROVE Network objective of evaluating visibility (Chow et al., 2000; Malm et al., 1994).

EXPERIMENTAL DESIGN

The IMPROVE and NIOSH particulate carbon analysis techniques were compared using ambient $PM_{2.5}$ samples from 3 cities with different sources of carbon, and with quality assurance standards of sucrose, wood smoke, diesel, diesel spiked with carbonate, and blank filters. A summary of the samples used in this comparison is shown in Table 1. The laboratories did not know the composition of the samples or the spiking solutions

Sunset Laboratory evaluated the samples with NIOSH Method 5040 and DRI evaluated the samples with the IMPROVE Method. Temperature programs for each laboratory are shown in Table 2. The NIOSH and IMPROVE methods use a 1.45 and 0.516 cm^2 punch from a quartz-fiber filter for analysis, respectively. The IMPROVE method does not use a constant time for each ramp, but instead allows the FID to return to baseline before moving to the next step and quantifies the carbon evolved in each step (OC1, OC2, OC3, OC4, EC1, EC2, and EC3). The split between organic and elemental carbon is based on when the reflectance or transmittance in the oxidizing atmosphere returns to the value at the start of the analysis in the He atmosphere. An example of the two protocols from the analysis of a Phoenix urban PM2.5 sample is shown in Figure 1. The top plot shows the temperature programs, the middle shows the FID response, and the bottom plot shows the laser signal and indicates the point where the reflectance or transmittance returns to the initial value. As can be seen from the transmittance and reflectance plot, with the addition of the He/O_2 mixture the EC continues to evolve until it the laser signal reaches the level for a blank or clean filter. Calibration procedures for the NIOSH and IMPROVE techniques are not the same. The NIOSH protocol uses sucrose dissolved in water as the primary standard while IMPROVE uses a combination of sucrose dissolved in water, potassium hydrogen phthalate dissolved in water, and National Institute of Standards and Technology (NIST) traceable carbon dioxide/balance He, and methane/balance He gases.

A NIOSH laboratory (Cincinnati, OH) provided quality assurance samples. Sunset Laboratory and DRI were each sent a quality assurance sample set: sucrose solution and a 47-mm quartz fiber filter, carbonate solution, quartz-fiber filter with diesel particulate, and a quartz-fiber filter with wood smoke particulate matter. To determine the potential interference of carbonate when present in a carbonaceous particulate sample (in this case diesel), the sample portion was analyzed with and without a carbonate spike. However, EC results should be the same in both cases if carbonate does not interfere. All of the standards were provided in triplicate to allow for calculation of the measurement precision of the calibration and source samples. In the NIOSH method, CC is routinely determined above 620 C in He, however, in IMPROVE CC is not normally quantified, but is included in the EC2 peak. Quantification of CC by IMPROVE is performed by acidifying a second filter punch before analysis and obtaining the CC by difference.

Ambient samples were selected from the Philadelphia and Phoenix $PM_{2.5}$ Chemical Speciation Sampler Evaluation sites (Solomon et al., 2000; Tolocka et al., 2000), and the Spokane Particulate Matter and Health Study (Haller et al.,1999). Philadelphia particulate carbon is a mix of automobile and industrial sources (Dzubay et al., 1988), while Phoenix is a mix of automobile and photochemical organic aerosols (Chow et al., 1991; Norris et al., 2000). The Philadelphia and Phoenix samples were evaluated with and without XAD denuders upstream of the quartz-fiber filter to remove organic gases (Gundel et al., 1995). Spokane filters were collected in November and December when the particulate carbon is predominately from wood smoke (Haller et al.,1999). Two additional wood stove emissions source samples (dry oak cordwood) from the EPA's, National Risk Management Laboratory

(Research Triangle Park, NC) also were evaluated. Samples from the 3 cities and the source samples represent a wide range of OC concentrations and EC/OC ratios. Differences between the methods are highlighted by using the combination of samples from cities with different sources of carbon, and source samples.

RESULTS

Samples were provided first to DRI and then shipped to Sunset Laboratory. This comparison used a combination of spiked samples, source samples, and PM$_{2.5}$ samples from Phoenix and Philadelphia. Measurement precision was evaluated using source samples provided by NIOSH. Results from the analyses are divided into calibration, wood smoke, diesel and spiked diesel exhaust, and ambient samples from Phoenix and Philadelphia.

Sample blanks

The level of detection for the NIOSH method is 0.2 g/cm^2 carbon. Additional detail is provided on the LOD for the IMPROVE method: 0.5 – 1.0 g/cm^2 for OC, 0.0 – 0.2 g/cm^2 for EC, and 0.0 – 0.4 g/cm^2 for carbonate. The pre-cleaned blank sample used for evaluating the calibration had TC concentrations of 0.39 and 0.30 g/cm^2 for the NIOSH and IMPROVE methods, respectively. Three field blanks were evaluated from the PM$_{2.5}$ Chemical Speciation Sampler Evaluation Study: NIOSH TC average = 0.93, range = 0.75 – 1.23 g/cm^2; IMPROVE TC average = 1.11, range = 0.87 – 1.55 g/cm^2.

Calibration

Calibration of the NIOSH and IMPROVE methods was evaluated using a sucrose standard (Chow et al., 1993; Birch, 1998). Each lab was provided with a pre-cleaned quartz fiber-filter and the labs spiked a punch of the filter with 10 L of a supplied sucrose solution with 30.1 g C per 10 L. Both techniques reported TC and OC concentrations within 4 percent of the spiked carbon concentration. Total carbon concentrations were 4 percent higher for the IMPROVE compared to NIOSH. Since sucrose does not contain EC, any EC generated in the analysis is due to pyrolysis that is adjusted for using optical techniques. Each method yielded similar EC concentrations with the labs reporting 0.26 and 0.27 g/cm^2 for NIOSH and IMPROVE, respectively. The measured EC/TC results are less than 1%, suggesting the pyrolysis adjustment is highly accurate.

Wood smoke

Wood smoke source and wood smoke dominated ambient samples were evaluated in this comparison. The IMPROVE and NIOSH OC and TC were on average, within 5 % of each other. OC and EC precision by both method were within 5 %. However, these methods reported large variations in the EC concentrations. The IMPROVE EC was on average 175 percent greater than NIOSH EC for a triplicate analysis of the smoldering wood smoke sample shown in Table 3a. Both techniques had relatively low measurement precision with a coefficient of variation of 21 and 23 percent for NIOSH and IMPROVE, respectively. This low precision is expected since the average EC concentration of was near the EC LOD of 0.2 g/ cm^2 for NIOSH and IMPROVE (Chow et al., 1993; Birch and Cary, 1996). Highly loaded wood smoke source samples from a wood stove burning dry oak cordwood had average percent differences of 5, 6, and 5 for OC, EC, and TC, respectively. These results shown in

Table 3b suggest both methods give similar results for the heavily loaded wood smoke source sample in this comparison. Spokane wood smoke samples shown in Table 3c, showed a smaller difference in the EC concentrations relative to the smoldering wood, but not the highly loaded wood smoke samples with an average difference of 21 percent. Differences in the EC concentrations for the Spokane samples were dependent on the loading, with the greatest difference of 71 percent with samples SP3 that had the highest OC loading of 26 g/cm^2 (based on NIOSH).

Diesel Exhaust

A diesel truck source sample provided by NIOSH was evaluated in triplicate. Average OC, EC, and the coefficient of variation for the samples are shown in Table 4a. The IMPROVE EC was 30 percent higher than the NIOSH EC. Total carbon measured by IMPROVE was also 7 percent higher than the NIOSH TC. The precision for the NIOSH EC (1 percent) was slightly lower than the IMPROVE EC precision (4 percent). These results are similar to those presented by Birch (1998) for truck exhaust: IMPROVE 2 percent, NIOSH 2 to 11 percent (4 labs reported precision for the NIOSH method).

The diesel truck exhaust was spiked with Trona solution, a sodium carbonate ore containing both carbonate and bicarbonate. A 10 L carbonate spike of 1.60 g/ L C was added to the diesel sample. Results for the diesel and diesel spiked with carbonate expressed in g C are shown in Table 4b. Neither analysis showed a significant change in EC. Based on TC, the spike recovery was 105 and 98 percent for the NIOSH and IMPROVE protocols, respectively. The NIOSH protocol quantifies CC as part of the routine analysis since CC evolves at 620 /C. In IMPROVE CC evolves as part of EC2 but is not usually quantified. A CC of 14.9 g C was reported by Sunset, which is close to the 16.0 g C that was added to the diesel sample. Sunset Laboratory noted in their results that the carbonate might form “glasses” that would cause the laser transmittance to increase, causing an over-reporting of the EC. For the IMPROVE protocol, CC evolved in OC3 (450 /C). This finding is different than previous reported by Chow and colleagues (1993) who reported CC would show up in EC2. This may indicate the composition of the sample may have changed with the addition of the Trona solution.

Phoenix and Philadelphia

Samples were selected from the Phoenix and Philadelphia that represented a range of loadings. For both cities, a set of 6 days of collocated samples was selected from those collected with a Versatile Air Pollutant Sampler (VAPS, Pinto et al., 1998) with an XAD denuder, an IMPROVE sampler, and a Anderson Reference Ambient Air Sampler (RAAS) (Solomon et al., 2000). The VAPS, IMPROVE, and RAAS collected 21.6, 32.8, and 10.5 cubic meters of sample on a 47 mm quartz filter, respectively. Use of the different samplers provided range of loadings for each day. One additional sample from a Met-One SASS from Phoenix was included in this comparison since DRI indicated the sample had a non-white punch after the analysis, which may indicate the presence of minerals. An analysis by Tolocka et al. (2000), discusses the comparison between the XAD denuded and non-denuded samples.

A summary of the average sample EC and OC loadings for Phoenix and Philadelphia are given in Tables 5a and 5b, respectively. No significant quantities of carbonate were measured on the samples by the NIOSH method. Phoenix EC concentrations were significantly different with averages of 3.75 and 6.73 g/cm^2 for NIOSH and IMPROVE, respectively. Philadelphia EC concentrations also showed a similar discrepancy with averages of 3.10 and 6.13 g/cm^2 for NIOSH and IMPROVE, respectively. Organic carbon concentrations were on average 9 percent higher for the NIOSH vs. the IMPROVE method. Total carbon was on average 9 percent lower for the NIOSH vs. the IMPROVE method. Carbonate at a concentration greater than the detection limit of 0.5 g/cm^2 (Bob Cary, Sunset Laboratory, personal communication) determined by the NIOSH method was not observed on one Phoenix sample that had a non-white punch after the IMPROVE analysis. The IMPROVE analysis comments for non-white samples suggest that carbonate may be present in the sample. The EC, OC, and TC concentrations were significantly different ($p < 0.001$) when the methods were compared using a paired t-test and the Wilcoxon Signed Rank Test. Tables 5a and 5b summarize the statistics from the paired data. Linear regression was used to evaluate the linear relationship between IMPROVE and NIOSH protocols in Phoenix and Philadelphia. Slopes for EC, OC, and TC were not significantly different for each city, and the intercepts were not significantly different from zero. Overall regression results are summarized in Figure 1. Measurements of the EC with NIOSH and IMPROVE were significantly different: IMPROVE EC = NIOSH EC * (1.95) - (0.25), $r^2= 0.92$. Total carbon measurements were also significantly different, which may be due to difference calibration techniques.

The difference in EC between the NIOSH and IMPROVE protocols was investigated further by integrating the carbon evolved from 550 /C to the addition of oxygen in the NIOSH method using software developed by Sunset Laboratory (Calc800). This fraction (labeled as OC5) was added to the EC and subtracted from the OC, generating adjusted NIOSH parameters OC$^-$ and EC$^+$. The OC5 fraction was calculated using thermogram data provided by Sunset Laboratory for 33 of the 37 samples. On average, this fraction accounts for 20 % of the OC measured by the NIOSH protocol. The adjusted NIOSH EC is in excellent agreement with IMPROVE EC as shown in Figure 2. The linear relationship for EC is IMPROVE EC = NIOSH EC * 1.03 – 0.61, $r^2= 0.90$, and the relationships for OC and TC are shown in Table 6. A similar adjustment was also tried by Chow et al. (2000), however they added the OC evolved from 650 to 850 /C and found NIOSH EC was 18 percent higher than the IMPROVE. This difference is most likely due to the carbon that evolves between 550 and 650 /C. We consider our adjustment to be the preferable approach to relate NIOSH and IMPROVE EC measurements because the method proposed by Chow et al (2000) does not include the carbon evolved from 550 and 650 /C.

RESULTS AND CONCLUSIONS

Particulate carbon typically represents a large fraction of $PM_{2.5}$, therefore the measurement of OC and EC is critical. The methods are based on the same measurement principle but differ in the method used to adjust for pyrolysis (transmittance or reflectance), temperatures for evolving carbon, and the amount of time at each temperature step. These result in the reporting of different concentrations of EC and, OC by each method. Two conclusions can be made based on this methods comparison: IMPROVE EC > NIOSH EC, and IMPROVE TC > NIOSH TC. The difference in EC concentrations appear to depend on the source of the sample, with the percent differences ranging from 175 percent for a smoldering wood smoke sample to 5 percent for a wood smoke impacted sample with low a loading. Consistent differences were found with urban $PM_{2.5}$ samples, with IMPROVE EC being a factor of two higher than the NIOSH EC. Measurement precision for the two protocols was similar, with the poorest precision for the smoldering wood smoke sample with a low EC loading. Additional samples from non-urban locations need to be evaluated to determine if the association is the same for urban motor vehicle dominated and non-urban biogenic/secondary aerosol samples. More research is needed to understand the composition of carbon evolved at temperatures greater than 550 /C (Chow et al., 2000) since the OC evolved at greater than 550 /C may explain differences in the EC concentrations for urban samples in this study. This high temperature organic carbon may be pyrolysis products from heating the sample from ambient to 550 /C, real components formed in the atmosphere, or a combination of both.

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Table 1. Samples analyzed with the NIOSH and IMPROVE protocols

Sample	Number	Description
W/O XAD Denuder		
Philadelphia	12	Carbon from motor vehicles and industrial processes
Phoenix	13	Carbon from motor vehicles and secondary aerosols
Spokane	4	Carbon from motor vehicles and wood smoke
Wood smoke source samples	2	2 wood smoke source samples from the EPA, Research Triangle Park, NC
With XAD Denuder		
Philadelphia	6	
Phoenix	6	
Quality Assurance		
Sucrose	3	Triplicate evaluation of the calibration
Wood Smoke	3	Triplicate evaluation of a wood smoke sample
Diesel	3	Triplicate evaluation of a diesel sample
Diesel spike with carbonate	3	Triplicate evaluation of spiked sample

Table 2. Temperature programs used for the NIOSH and IMPROVE protocols.

Carrier gas	NIOSH	IMPROVE
He	250 /C, 30 sec	OC1: 120 /C
He	500 /C, 30 sec	OC2: 250 /C
He	650 /C, 60 sec	OC3: 450 /C
He	850 /C, 90 sec	OC4: 550 /C
	Cool to 650 /C	
2 % O_2 balance He	650 /C, 60 sec	EC1: 550 /C
2 % O_2 balance He	750 /C, 60 sec	EC2: 700 /C
2 % O_2 balance He	850 /C, 60 sec	EC3: 800 /C
2 % O_2 balance He	940 /C, 120 sec	

Table 3a. Smoldering wood smoke sample (g/cm^2)

	N_OC*	I_OC**	N_EC	I_EC	N_TC	I_TC	EC/TC
Mean	51.7	53.4	0.1	1.3	51.8	54.7	0.01
Standard Deviation	0.5	1.1	0.0	0.3	0.5	1.3	---
N	3	3	3	3	3	3	---
CV %	0.9	2.1	20.8	22.9	0.9	2.3	---
Difference % ***	-3		-175		-5		---
Ratio****	1.0		0.1		0.9		---

* N = NIOSH, ** I = IMPROVE, *** 100 * (NIOSH minus IMPROVE, divided by their average), **** NIOSH/IMPROVE

Table 3b. Wood smoke source sample (g/cm^2)

	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC	EC/TC
EPAEL1	386.7	345.5	8.0	7.9	394.7	353.7	0.0
EPAEL2	260.5	265.7	10.7	9.5	271.2	275.2	0.0
EPAEL3 (blank)	0.3	0.2	0.1	0.0	0.4	0.2	0.1
EPAEL1 Difference %	11.2		0.4		11.0		---
EPAEL2 Difference %	-2.0		11.8		11.0		---
EPAEL3 Difference %	---		---		---		---
EPAEL1 Ratio	1.1		1.0		1.1		---
EPAEL2 Ratio	1.0		1.1		1.0		---
EPAEL3 Ratio	---		---		---		---

Table 3c. Spokane, Washington ambient air samples (g/cm^2)

	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC	EC/TC
SP1	4.0	4.1	0.6	0.6	4.5	4.7	0.1
SP3	26.6	25.8	3.4	7.2	30.0	32.9	0.2
SP4	3.3	3.3	0.4	0.4	3.8	3.9	0.1
SP1 Difference %	- 2.7		-5.3		-3.1		---
SP3 Difference %	3.0		-71.0		- 9.5		---
SP4 Difference %	1.2		14.4		-2.4		---

SP1 Ratio	1.0	0.9	1.0	---
SP2 Ratio	1.0	0.5	0.9	---
SP3 Ratio	1.o	1.2	1.0	—

Table 4a. Diesel Truck (g/cm^2)

	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC	EC/TC
Mean	16.4	16.3	4.5	6.1	20.9	22.4	0.2
Standard Deviation	0.1	0.7	0.0	0.3	0.2	1.0	---
N	3	3	3	3	3	3	---
CV %	0.9	4.1	0.5	4.9	0.7	4.3	---
Difference %	0.9		-29.6		- 6.6		---
Ratio	1.0		0.7		0.9		---

Table 4b. Diesel filters spiked with 10 L of Trona solution (g C) *, **

	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC	N_CC
Diesel	23.8	8.4	6.5	3.1	30.3	11.5	0.0
Diesel + CC	23.8	25.8	7.6	2.6	31.5	28.4	19.9***
Spike	0.0	17.4	0.9	-0.5	0.8	16.8	14.9****
N	3	3	3	3	3	3	3
CV %	---	3.3	37.2	- 28.6	2.5	4.3	0.0

N*1.45 cm^2 or I*0.516 cm^2 (punch area) ** 10 L Trona solution contains 16 g C, respectively,
*** value high since one spike was 20 L instead of 10, **** Adjusted for spike volume

Table 5a. Philadelphia samples (g/cm^2)

C	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC
Mean	11.7	10.0	3.1	6.1	14.8	16.1
Standard Deviation	6.5	5.4	1.6	3.5	8.0	8.6
N	18	18	18	18	18	18
Percent Diff	15.8		-65.7		-8.5	
N/I	1.2		0.5		0.9	
Paired t-test*	< 0.001		< 0.001		< 0.001	
Wilcoxon **	< 0.001		< 0.001		< 0.001	

* p-value, ** Wilcoxon signed rank test

Table 5b. Phoenix samples (g/cm^2)

C	N_OC	I_OC	N_EC	I_EC	N_TC	I_TC
Mean	16.3	15.4	3.8	6.8	20.1	22.2
Standard Deviation	8.6	8.1	2.0	3.8	10.4	11.7
N	19	19	19	19	19	19
Percent Diff	5.5		-57.3		-10.3	
N/I	1.1		0.6		0.9	
Paired t-test*	0.001		< 0.001		< 0.001	
Wilcoxon **	0.001		< 0.001		< 0.001	

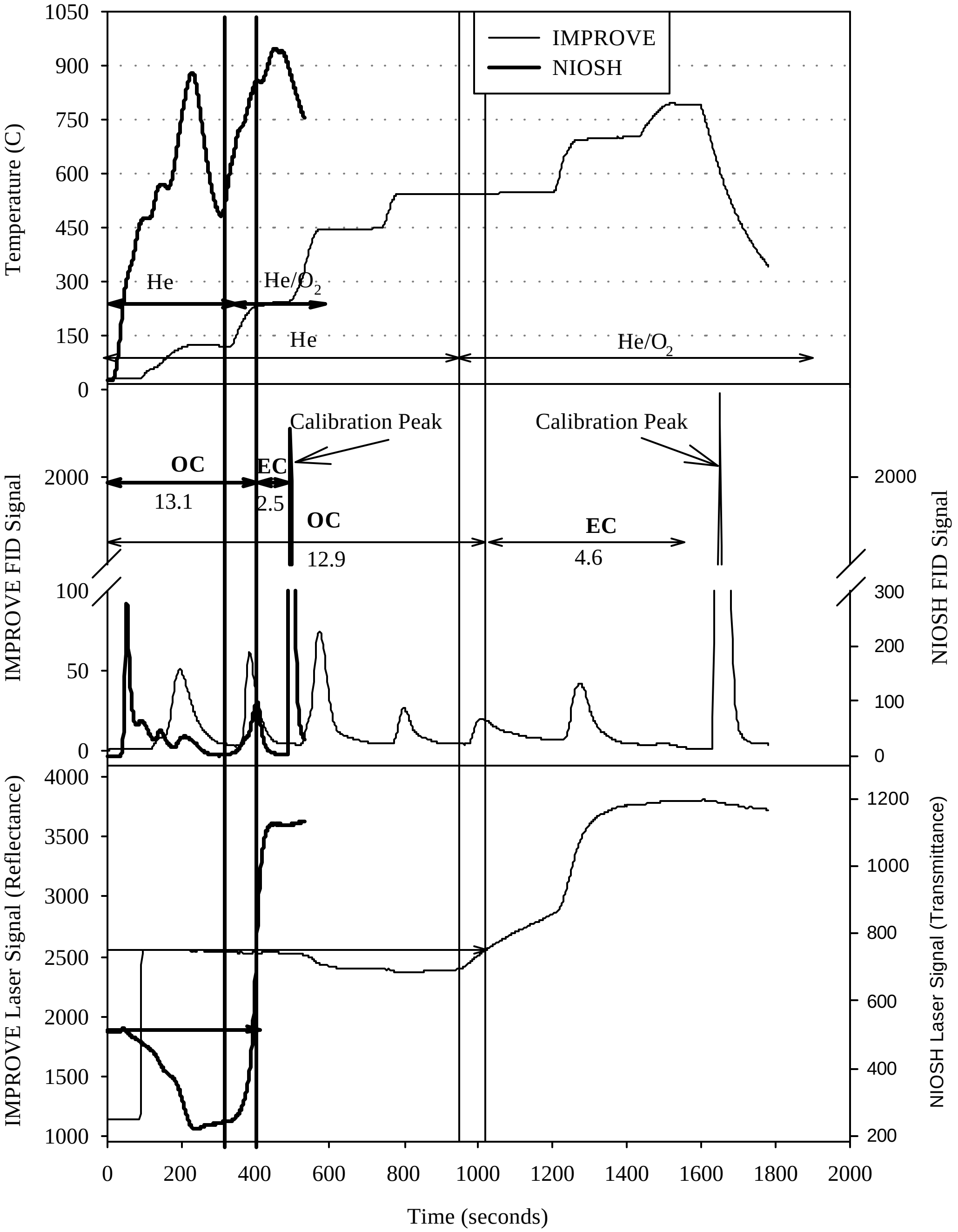
* p-value, ** Wilcoxon signed rank test

Figure Captions

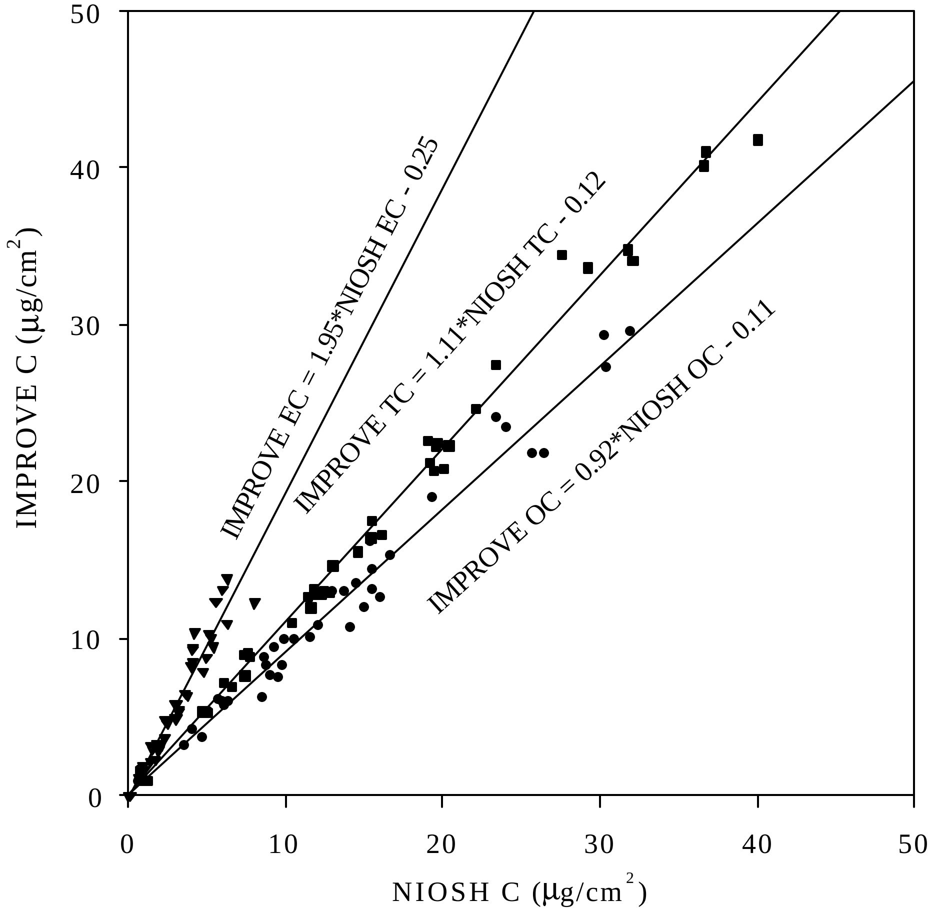
Figure 1. Comparison of the NIOSH and IMPROVE protocols with an urban sample from Phoenix.

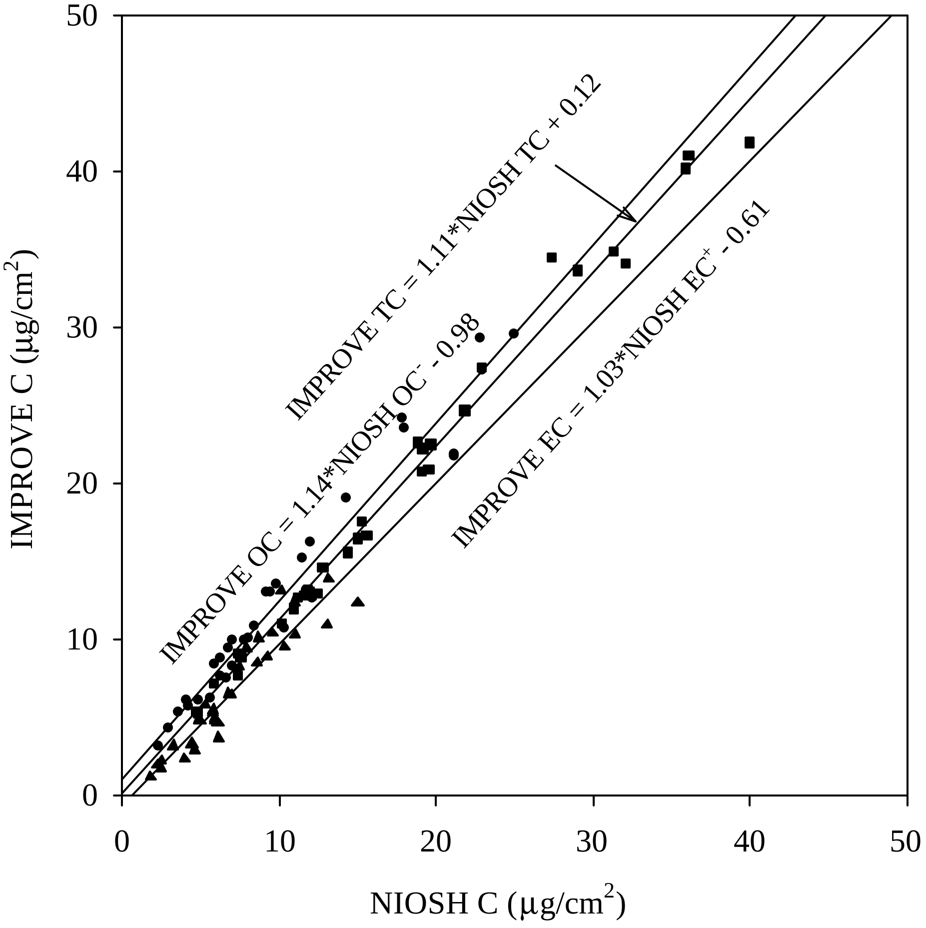
Figure 2. Comparison of urban $PM_{2.5}$ EC, OC, and TC measured with the IMPROVE and NIOSH protocols.

Figure 3. Comparison of urban $PM_{2.5}$ EC, OC, and TC measured with the IMPROVE and adjusted NIOSH protocols.



IMPROVE
NIOSH
Temperature (C)
1050
900
750
600
450
300
150
0
He
He/O2
He
He/O2
Calibration Peak
Calibration Peak
OC
EC
13.1
2.5
OC
12.9
EC
4.6
IMPROVE FID Signal
2000
100
50
0
NIOSH FID Signal
2000
300
200
100
0
IMPROVE Laser Signal (Reflectance)
4000
3500
3000
2500
2000
1500
1000
NIOSH Laser Signal (Transmittance)
1200
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time (seconds)


IMPROVE EC = 1.95*NIOSH EC - 0.25
IMPROVE TC = 1.11*NIOSH TC - 0.12
IMPROVE OC = 0.92*NIOSH OC - 0.11
IMPROVE C (μg/cm^2)
NIOSH C (μg/cm^2)
0
10
20
30
40
50
0
10
20
30
40
50


50
40
30
20
10
0
0
10
20
30
40
50
IMPROVE C (µg/cm^2)
NIOSH C (µg/cm^2)
IMPROVE TC = 1.11*NIOSH TC + 0.12
IMPROVE OC = 1.14*NIOSH OC$^-$ - 0.98
IMPROVE EC = 1.03*NIOSH EC$^+$ - 0.61

TECHNICAL REPORT DATA

(Please read Instructions on reverse before completing)

1. REPORT NO. EPA-454/R-01/005	2.	3. RECIPIENT'S ACCESSION NO.
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16. ABSTRACT To develop improved source-receptor relationships and for better understanding the causes of high PM2.5 concentrations in the atmosphere, it is necessary to not only determine concentrations of PM2.5 mass, the NAAQS indicator, but also the chemical components of PM2.5. A sampling program of this type, which will consist of up to 300 sites nationwide has been initiated by EPA (Speciation Guidance Document, 1999 at http://www.epa.gov/ttn/amtic/ pmspec.html). Since the PM2.5 Federal Reference Method (FRM) using only Teflon filters is not suitable for determining the chemical composition of the collected aerosol, since carbon can not be directly measured (Speciation Guidance Document, 1999), EPA solicited innovative designs for speciation samplers, based on performance specifications. This led to the development of three slightly different candidate samplers manufactured by Andersen Samplers, MetOne, and University Research Glassware (URG). These samplers are designed to allow for a nearly complete mass balance of the collected aerosol, while minimizing sampling artifacts for nitrate and allowing flexibility for minimizing organic carbon artifacts in the future. Due to the need to have consistency across this national network, the Speciation Expert Panel (Recommendations of the 1998 Expert Panel, 1998 at http://www.epa.gov/ttn/amtic/ pmspec. html) recommended a methods comparison field study among the new speciation samplers, historically used samplers, and the PM2.5 FRM. The program plan for EPA's Chemical Speciation Sampler Evaluation Study (1999, http://www.epa. gov/ttn/amtic/casacinf.html) details the approach and implementation of the study. This report presents the approach and results from the 4-City intercomparison study; Phase 1, of the full evaluation of these samplers.

Because of potential sampling artifacts when using filters and potential differences in inlet cutpoints and sample fractionators, the chemical speciation samplers must be able to properly determine the chemical components of PM2.5 under a variety of atmospheric and environmental conditions. Four locations, with different atmospheric chemical and meteorological conditions were chosen and included: Rubidoux, CA (high nitrate and carbon and low sulfate), Phoenix, AZ (high crustal material and moderate carbon and nitrate), Philadelphia, PA (high sulfate, moderate carbon, and low nitrate), and Research Triangle Park (RTP), NC (low PM2.5 concentrations). The latter site also allowed for a more thorough evaluation of the samplers' in-field operational performance as it was located near EPA offices in RTP. In addition to the three candidate samplers, a Versatile Air Pollution Sampler (VAPS), an IMPROVE sampler, and an FRM were collocated at each site. Replicate samplers were located at Rubidoux. Samples were collected for up to 20 days during January and February, 1999 using state personnel (Rubidoux and Phoenix) or EPA contractors (Philadelphia and RTP). All sampling periods were 24-hrs in duration. Mass and trace elements were determined on Teflon filters; sulfate, nitrate, and ammonium were determined on either Teflon, pre-fired quartz-fiber, or nylon filters depending on the sampler; and OC/EC were determined on pre-fired quartz-fiber filters. To minimize variability, all filter preparation, filter changing, and chemical analyses for a particular species were preformed by one contractor. Quality assurance/quality control followed EPA guidelines (QAPP for the Four-City PM2.5 Chemical Speciation Sampler Evaluation Study, January, 1999 Research Triangle Institute, Project Number 07263-030).

In general, the performance of the candidate samplers is reasonable for their first use in the field. All samplers had operational problems that increased their variability, most of which have been addressed by the manufactures. Tradeoffs exist among the samplers for ease of use, flexibility for sampling, and cost. Performance of the samplers was excellent for sulfate and reasonable for other stable species. However, real differences among the samplers exist for nitrate and organic carbon and possibly ammonium as collected in the IMPROVE sampler. These differences are significant and can possibly affect design of compliance strategies for controlling PM2.5 mass concentrations in air, as total differences as high as 3-5 :g/m3 are observed among the samplers for these two species.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
PM Chemical Speciation, nitrate, sulfate, organic carbon, elemental carbon, trace elements, Rubidoux, Phoenix, Philadelphia, PM2.5 mass and composition	Air Pollution control	

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