The Role of QA in Determination of Effects of Shipping Procedures for PM2.5 Speciation Filters

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Before the
24th Annual National Conference on Managing Quality Systems
April 13, 2005

Overview

- The Evolution of the shipping study
- The Data Quality Objectives
- The Measurement Quality Objectives
- The Data Starts to Speak
- The Lessons Learned

Why is the Shipping Study Important?

- The current PM2.5 speciation trends and supplemental network annual shipping bill

$1,600,000

- EPA Budget-shrinking
- National Monitoring Strategy-evolving
- Speciation QA program-beefing up

Whoa!!!! Speciation? What are We Talking About?

- PM2.5 Chemical composition
- 24 - hr. integrated filter samples-3 media
- Multiple analyses
  - Gravimetric
  - Chromatographic
  - X-ray fluorescence and Thermo optical
- Results used for pollutant source attribution in SIP development

What Makes Speciation Shipping Expensive?

- ~250 sites collecting filter samples
  - 1 in 3 day or 1 in 6 day sampling -50/50
- Cold shipping requirement
  - Coolers with ice packs-35 lbs (16 kg)
  - Overnight delivery
  - Both Ways
  - Average $40 per cooler one way

Why ship cold?

Prevent losses of semi-volatiles?

How to Attack the Question

Devise a study where we can limit variables to just the procedure by which the sample filters are shipped

Seems simple enough……

Doesn't it ???

What are the Challenges

- Three different filter media-Teflon, Nylon, Quartz
- Which Sites do we pick
  - Lab vs reality?
  - Dominant Semi-volatiles: nitrates and organics
- Time!! – limited windows for optimum effect
- Money!! – adequate number of events $$$
- Quality!! – Instrument variability; operators' experience and expertise

The Study

Sites: dominant pollutants	Atlanta: sulfates, organic carbon Riverside, CA: nitrates Tacoma, WA: woodsmoke carbon
Instruments	2 Collocated Metone™ SASS
Channels per filter media	1-2, 2-1 Teflon alternating days 2-1, 1-2 Nylon alternating days 2- Quartz
Target no. sampling events	30 24-hr periods

Data Quality Objectives

First approximation – reliance on network data for collocated instruments

Species	Collocated Average (Abs Rel Diff)	Lab Average (Abs Rel Diff)
Mass	9.3%	4.6%
Organic C	14.2%	5.5%
Sulfate (IC)	8.2%	3.9%

Courtesy of James Flanagan, et.al., Ref 1.

Decision Points

Differences in measured pollutant concentrations would constitute a discernable and significant impact by ambient shipping if the values were at the 95% confidence limit:

- >10% for mass,
- >15% for nitrate and ammonium,
- >20% organic carbon, and
- >7% for sulfate.

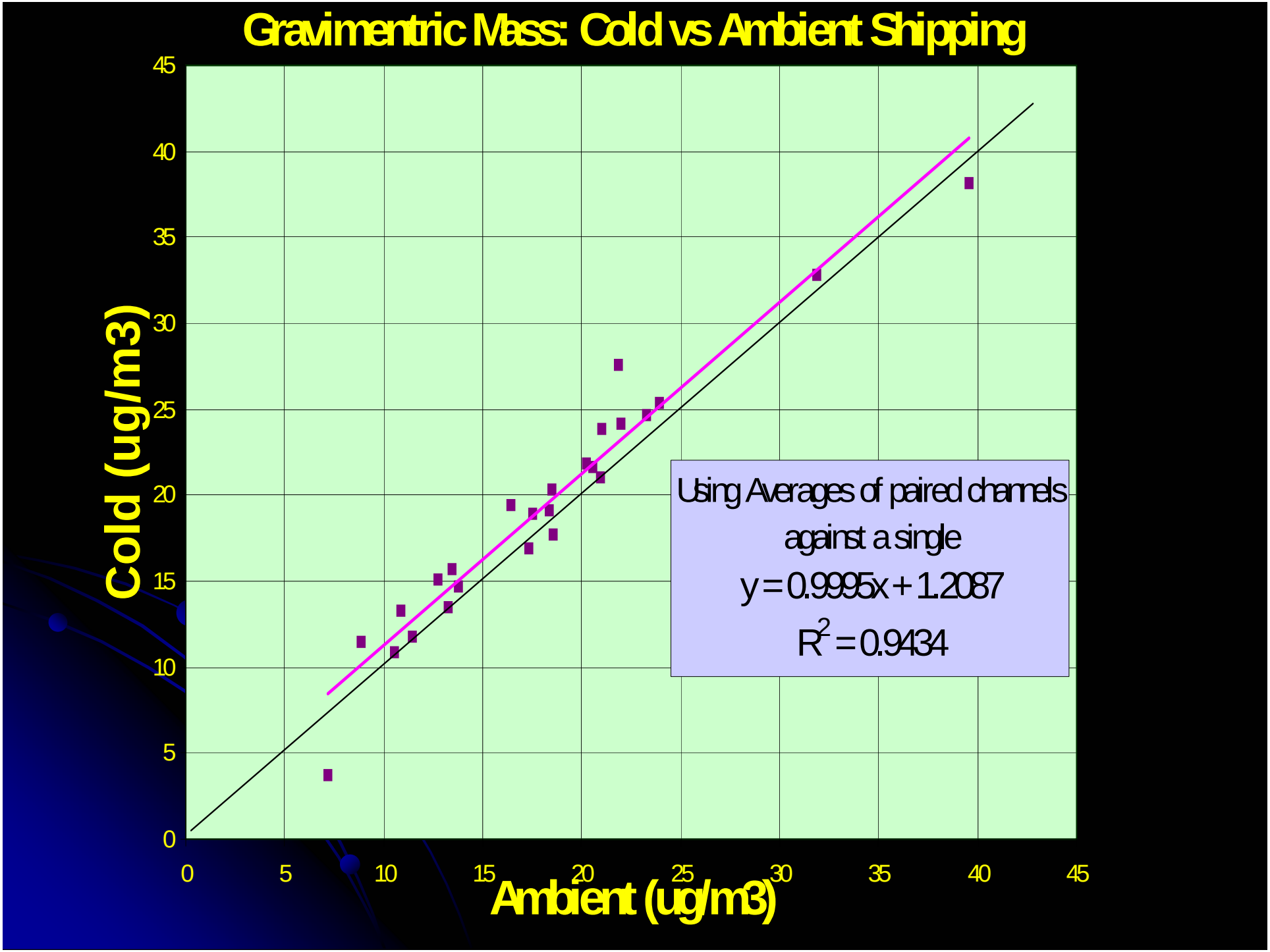
Ref [2],[3],[4]

The Lynch-pin of the Study: Measurement Quality Objectives

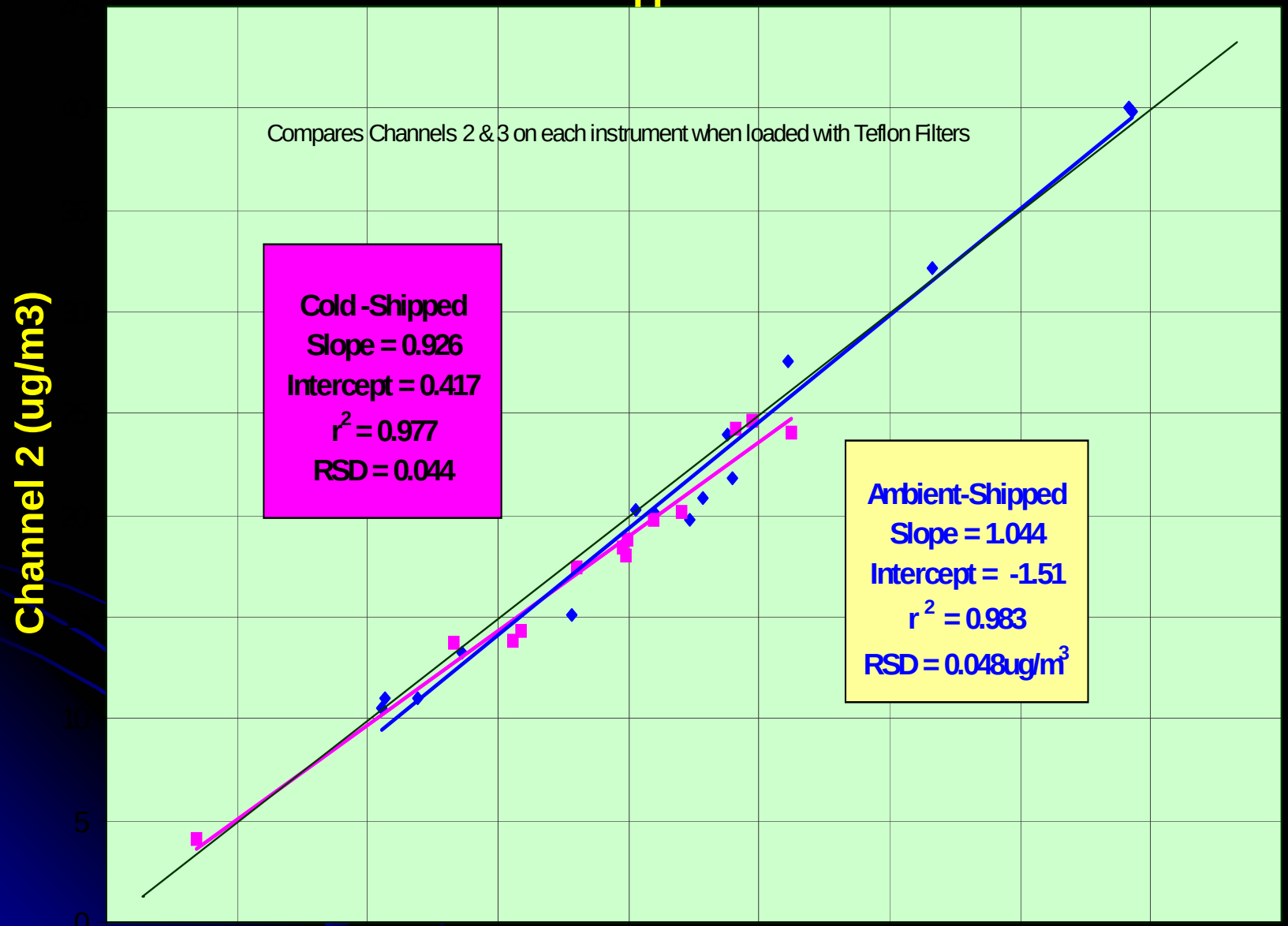
- Flowrates 6.7 l/min
- Paired Channel Concentrations within network collocated values

Measurement Quality Control

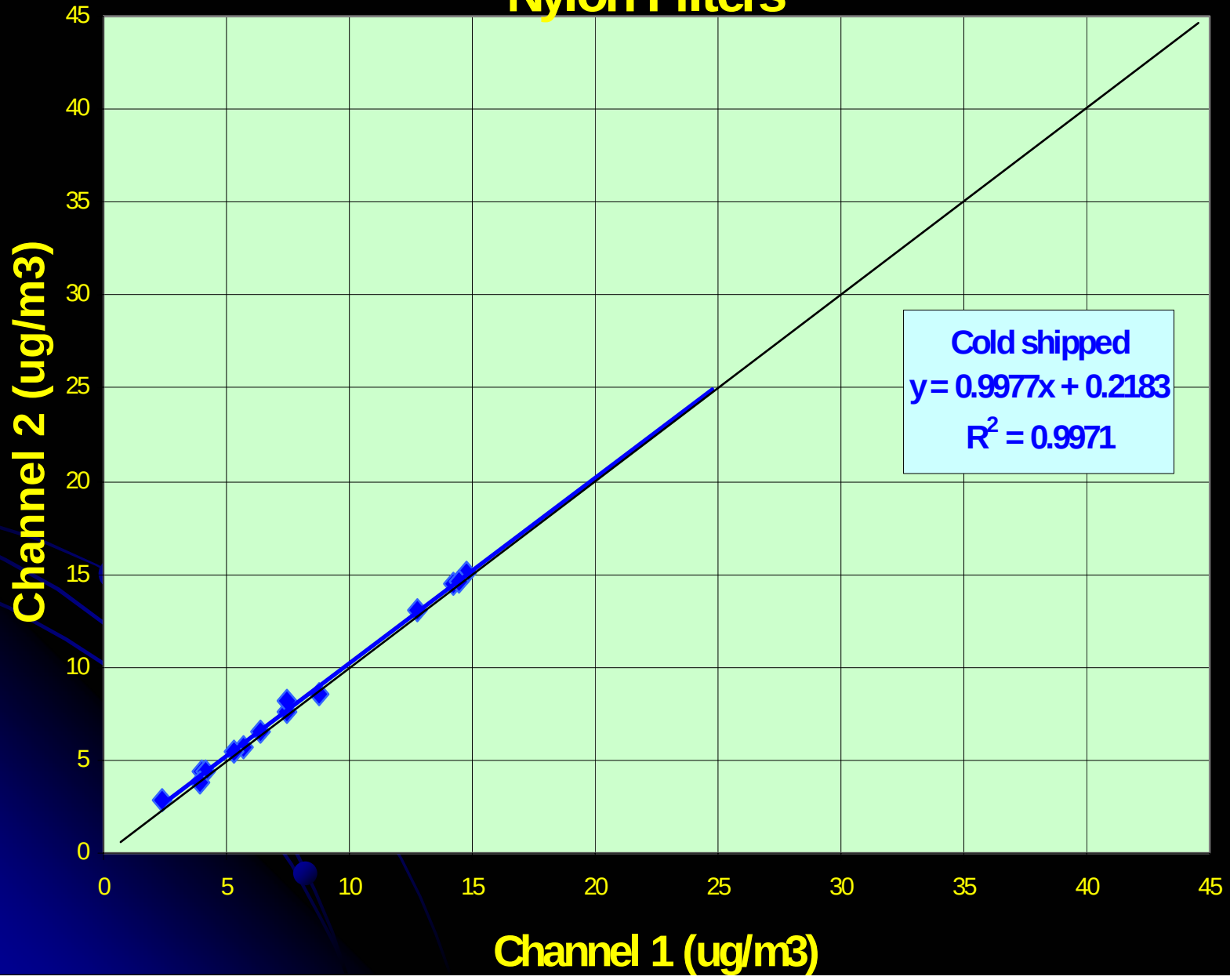
- Careful Instrument installation and calibration
- Operator Training
- Weekly Flowchecks and recalibration
- Trip and Field Blanks
- Skipped rainy days


Gravimentric Mass: Cold vs Ambient Shipping
Cold (ug/m3)
Ambient (ug/m3)
0
5
10
15
20
25
30
35
40
45
Using Averages of paired channels
against a single
y = 0.9995x + 1.2087
R2 = 0.9434

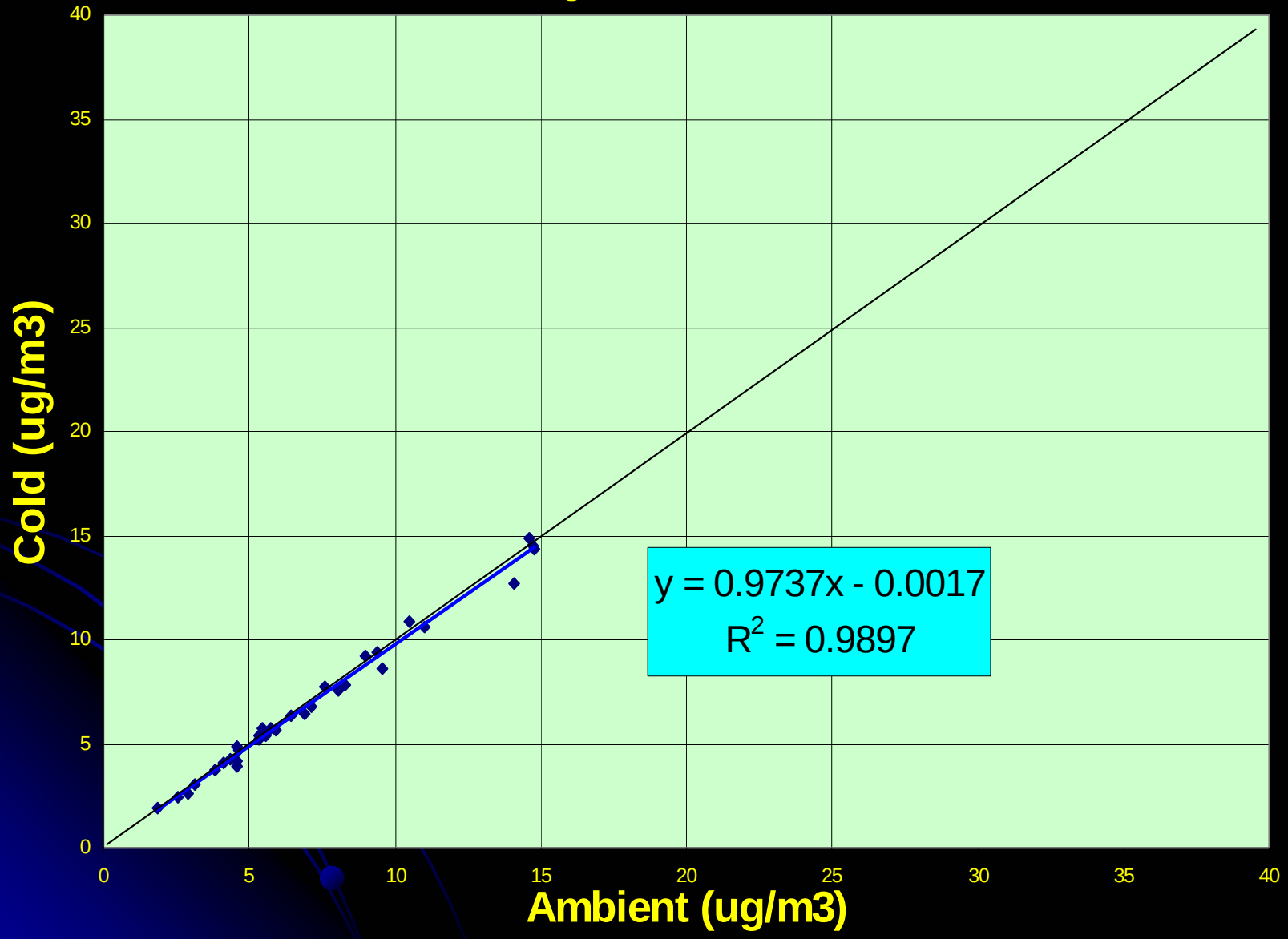
Comparison of Channels 2 & 3 Collecting Total Mass Shipped Cold and Ambient



Comparison of Sulfates on Channels 1 & 2
Nylon Filters



Sulfate from Cold- vs Ambient-Shipped Nylon Filters



Lessons Learned

- The DQO process helps design the study
- Setting and diligently pursuing MQO's is crucial to getting believable results
  - Make sure the instrumentation is completely serviced
  - The Data Quality Assessment can reveal things about the network
  - Weather can be a huge determinant factor
- Scope of this kind of study is a challenge logistically
  - Labor, materials and hardware (boxes), scheduling

Conclusions

- Appears Instruments sampled consistently on Nylon and Teflon Channels (#1-3)
- Some loss of mass does seem noticeable, but the difference appears to be within network variability DQOs.
- Sulfates do not appear to affect loss of mass
- More analysis of the Nitrate and carbon losses and variability should be conducted

References

- [1] James B. Flanagan, Edward E. Rickman, Max R. Peterson, Eva D. Hardison, Lisa Greene, Andrea McWilliams, William F. Gutknecht, and R.K.M. Jayanty, Speciation Trends Network: Evaluation Of Whole-System Uncertainties Using Collocated Data. 2005 AAAR PM Supersites Program and Related Studies International Specialty Conference, Atlanta, GA, February 7-11, 2005.
- [2] Evaluation of PM2.5 Chemical Speciation Samplers for Use in the EPA National PM2.5 Chemical Speciation Network, Paul A. Solomon ,William Mitchell, Michael Tolocka, Gary Norris, David Gemmill Russell Wiener, EPA-454/R-01-005, May 2001.
- [3] Final Report: Evaluation of PM2.5 Speciation Sampler Performance and Related Sample Collection and Stability Issues
- [4] Recommendations Of The Expert Panel On The EPA Speciation Network Final Summary-8/3/99, By Petros Koutrakis, Chair, Speciation Expert Panel. http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/lvpanel.pdf.