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MEXICO EMISSIONS INVENTORY PROGRAM MANUALS

VOLUME III - BASIC EMISSION ESTIMATING TECHNIQUES

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PREFACE

Air pollution can negatively impact public health when present in the atmosphere in sufficient quantities. Most rural areas rarely experience air quality problems, while elevated concentrations of air pollution are commonly found in many urban environments. Recently, urbanization and industrial activity throughout Mexico has increased, resulting in air quality concerns for several regions.

Air pollution results from a complex mix of, literally, thousands of sources, from industrial smoke stacks and motor vehicles, to the individual use of grooming products, household cleaners, and paints. Even plant and animal life can play an important role in the air pollution problem. Due to the complex nature of air pollution, detailed regional plans are needed to identify the emission sources and to develop methods for reducing the health impact from exposure to air pollution. Examples of air quality planning activities include:

- Application of air quality models;
- Examination of the sources emitting air pollution for emissions control analysis, where necessary;
- Development of emission projections to examine possible changes in future air quality;
- Analysis of emission trends; and
- Analysis of emissions transport from one region to another.

Development of fundamentally sound emissions inventories is a key aspect for each of these air quality planning functions.

Developing emission estimates to meet air quality planning needs requires continual development and refinement; "one time" inventory efforts are not conducive to the air quality planning process. For lasting benefit, an *inventory program* must be implemented so that accurate emission estimates can be developed for all important geographic regions, refined over time, and effectively applied in the air quality planning and monitoring process. Therefore, a set of inventory manuals is being developed that can be used throughout the country to help coordinate the development of consistent emission estimates. These manuals are intended for use by local, state, and federal staff, as well as by industry and private consultants. The purpose of these manuals is to assist in implementing the inventory program and in maintaining that program over time so that emissions inventories can be developed in periodic cycles and continually improved.

The manuals cover inventory program elements such as estimating emissions, program planning, database management, emissions validation, and other important topics. Figure 1 shows the complete series of manuals that will be developed to support a comprehensive inventory program. The main purpose of each manual is summarized below.

Volume I—Emissions Inventory Program Planning. This manual addresses the important planning issues that must be considered in an air emissions inventory program. Program planning is discussed not as an "up-front" activity, but rather as an ongoing process to ensure the long-term growth and success of an emissions inventory program. *Key Topics*: program purpose, inventory end uses, regulatory requirements, coordination at federal/state/local levels, staff and data management requirements, identifying and selecting special studies.

Volume II—Emissions Inventory Fundamentals. This manual presents the basic fundamentals of emissions inventory development and discusses inventory elements that apply to multiple source types (e.g., point and area) to avoid the need for repetition in multiple volumes. *Key Topics*: applicable regulations, rule effectiveness, rule penetration, pollutant definitions (e.g., how to properly exclude nonreactive volatile compounds), point/area source delineation, point/area source reconciliation.

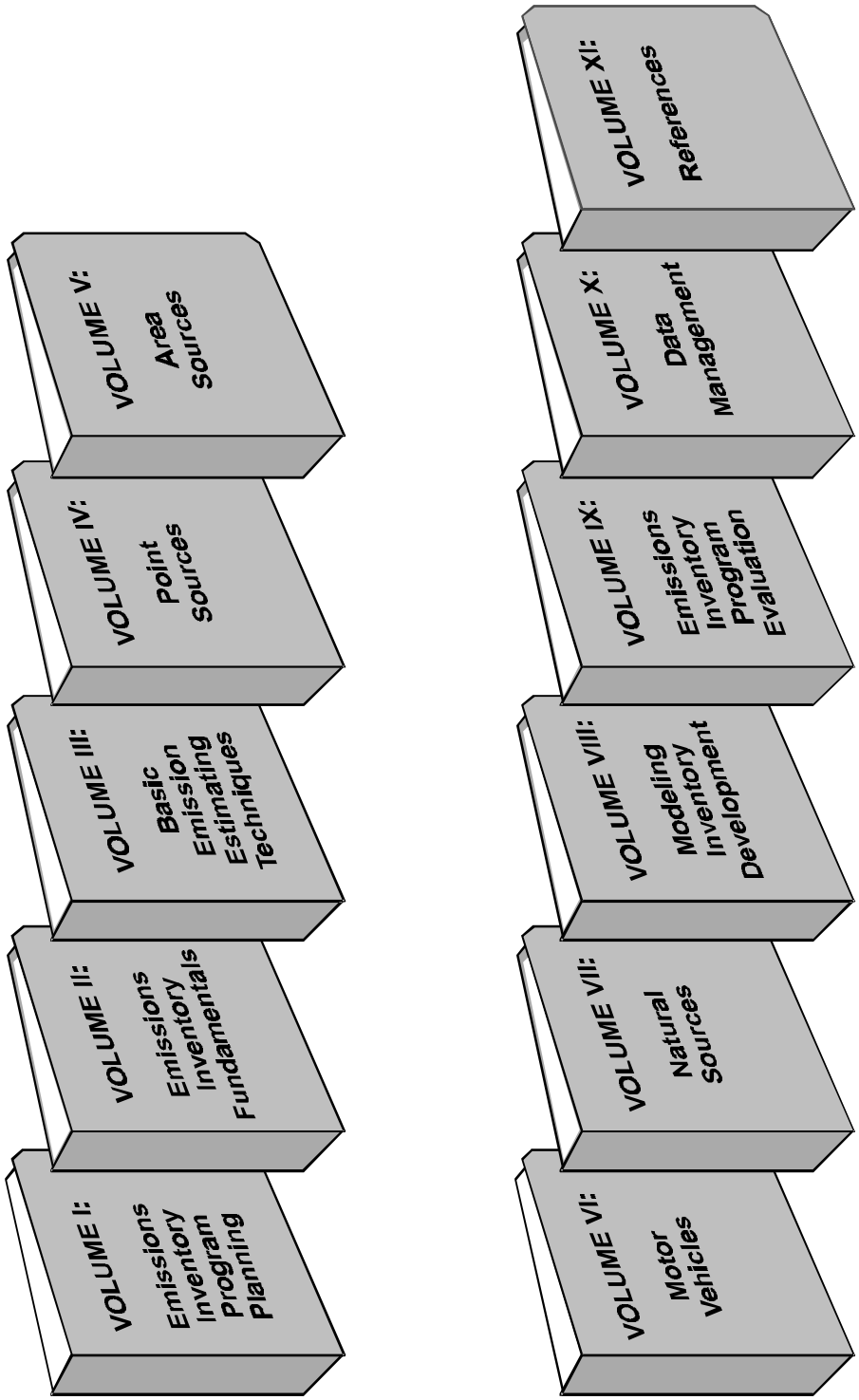

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Figure 1. Mexico Emissions Inventory Program Manuals

Volume III—Emissions Inventory Development: Basic Emission Estimating Techniques (EETs). This manual presents the basic EETs used to develop emission estimates, including examples and sample calculations. Inventory tools associated with each methodology are identified and included in Volume XI (References). *Key Topics*: source sampling, emissions models, surveying, emission factors, material balance, extrapolation.

Volume IV—Point Sources. This manual provides guidance for developing the point source emissions inventory. A cross-reference table is provided for each industry/device type combination (e.g., petroleum refining/combustion devices) with one or more of the basic EETs presented in Volume III. *Key Topics*: cross-reference table, stack parameters, control devices, design/process considerations, geographic differences and variability in Mexico, quality assurance/quality control (QA/QC), overlooked processes, data references, data collection forms.

Volume V—Area Sources (includes non-road mobile). This manual provides guidance for developing the area source emissions inventory. After the presentation of general area source information, a table is provided to cross-reference each area source category (e.g., asphalt application) with one or more of the basic EETs presented in Volume III. Then, source category-specific information is discussed for each source category defined in the table. *Key Topics*: area source categorization and definition, cross-reference table, control factors, geographic differences and variability in Mexico, QA/QC, data references, data collection forms (questionnaires).

Volume VI—Motor Vehicles. Because motor vehicles are inherently different from point and area sources, the available estimation methods and required data are also different. To estimate emissions from these complex sources, models are the preferred estimation tool. Many of these models utilize extensive test data applicable to a given country or region. This manual focuses primarily on the data development phase of estimating motor vehicle emissions. *Key Topics*: available estimation methods, primary/secondary/tertiary data and information, source categorization, emission factor sources, geographic variability within Mexico, QA/QC.

Volume VII—Natural Sources. This manual provides guidance for developing a natural source emissions inventory (i.e., biogenic volatile organic compounds [VOC] and soil oxides of nitrogen [NO_x]). In addition, this manual includes the theoretical aspects of emission calculations and discussion of specific models. *Key Topics*: source categorization and definition, emission mechanisms, basic emission algorithms, biomass determination, land use/land cover data development, temporal and meteorological adjustments, emission calculation approaches.

Volume VIII—Modeling Inventory Development. This manual provides guidance for developing inventory data for use in air quality models and addresses issues such as temporal allocation, spatial allocation, speciation, and projection of emission estimates. *Key Topics*: definition of modeling terms, seasonal adjustment, temporal allocation, spatial allocation, chemical speciation, projections (growth and control factors).

Volume IX—Emissions Inventory Program Evaluation. This manual consists of three parts: QA/QC, uncertainty analysis, and emissions verification. The QA/QC portion defines the overall QA/QC program and is written to complement source specific QA/QC procedures written into other manuals. The uncertainty analysis includes not only methods of assessing uncertainty in emission estimates, but also for assessing uncertainty in modeling values such as speciation profiles and emission projection factors. The emissions verification section describes various analyses that can be performed to examine the accuracy of the emission estimates. Examples include receptor modeling and trajectory analysis combined with specific data analysis techniques. *Key Topics*: description of concepts and definition of terms, inventory review protocol, completeness review, accuracy review, consistency review, recommended uncertainty EETs, applicable emission verification EETs.

Volume X—Data Management. This manual addresses the important needs associated with the data management element of the Mexico national emission inventory program. *Key Topics*: general-purpose data management systems and tools, specific-purpose software systems and tools, coding system, confidentiality, electronic submittal, frequency of updates, recordkeeping, Mexico-specific databases, reports.

Volume XI—References. This manual is a compendium of tools that can be used in emission inventory program development. Inventory tools referenced in the other manuals are included (i.e., hardcopy documents, electronic documents, and computer models).

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ACRONYMS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BIF	boiler and industrial furnace
Btu	British thermal unit
CAA	Clean Air Act
CANACINTRA	The Nacional Cámara de la Industria de la Transformación
CEM	continuous emission monitor
CFR	Code of Federal Regulations
CMAP	Mexican Classification of Activities and Products
CO	carbon monoxide
CO_2	carbon dioxide
DDF	Department of the Federal District
dscfm	dry standard cubic feet per minute
dscm	dry standard cubic meter
EET	emission estimating techniques
FIRE	Factor Information Retrieval System
ft^3	cubic feet
GHG	greenhouse gas
gr/dscf	grains per dry standard cubic feet
HAP	hazardous air pollutant
HCl	hydrogen chloride

hr	hour
ID	identification
INE	National Institute of Ecology
INEGI	Instituto Nacional de Estadística, Geografía e Informática
IPCC	Intergovernmental Panel on Climate Change
Kb	kilobyte
kg	kilogram
kJ	kilojoule
km	kilometer
L	liter
LAEEM	Landfill Air Emissions and Estimation Model
lb	pound
LPG	liquefied petroleum gas
m^3	cubic meter
Mg	megagram (i.e., 10^6g = 1 metric tonne)
mg	milligram
NH_3	ammonia
NO_x	oxides of nitrogen
O_2	oxygen
OAQPS	Office of Air Quality Planning and Standards
OH	hydroxyl radicals
PM	particulate matter

PM_{10}	particulate matter of 10 microns
ppbv	parts per billion by volume
ppmv	parts per million by volume
psig	pounds per square inch - gauge
QA	quality assurance
QC	quality control
RO_2	peroxy radicals
SO_2	sulfur dioxide
SO_x	oxides of sulfur
THC	total hydrocarbons
ton	English ton (i.e., 2,000 lbs)
tonne	metric ton (i.e., 1,000 kg)
tpy	tons per year
TSDF	treatment, storage, and disposal facilities
TSP	total suspended particulate
U.S.	United States
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic compounds
WHO	World Health Organization

1.0 INTRODUCTION

This manual presents the basic EETs used to develop point and area source (including non-road mobile) emission estimates. The basic EETs presented here were identified by examining inventory methods currently used in Mexico, Europe, Asia, and the United States (U.S.). Inventory techniques developed by the World Health Organization (WHO) and techniques used to develop global-scale greenhouse gas (GHG) emissions inventories were also reviewed. The six different basic EETs identified are:

- Source Sampling: direct measurements of the pollutant concentration in a known volume of gas and of the stack gas flow rate. Most commonly used for combustion emission sources.

- Emissions Models: equations developed when emissions are not directly related to a single parameter that may use computers if a large number of complex calculations are involved. For example, the U.S. Environmental Protection Agency (U.S. EPA) TANKS program is a computer emissions model used to estimate emissions from storage tanks.

- Surveying: questionnaires designed to collect emissions data. Often used to collect point source data developed at the facility level or area source data from a representative sampling of sources from a given source category.

- Emission Factors: ratios that relate the quantity of a pollutant emitted to a single unit of activity. The activity may be process-based data (e.g., throughput, hours of operation, surface area) or census-based data (e.g., population, employment).

- Material Balance: using measurements of all but the air component of a process to determine the air emissions. Most commonly used for solvent evaporation sources where data are not available to support the other approaches.

- Extrapolation: scaling emissions from a given source to another source based on a scaling parameter known for both sources (e.g., production quantity, land area, number of employees).

In this manual, each of the basic EETs is explained and discussed in detail. In addition, sample calculations are provided to illustrate the implementation of each basic EET.

The basic EETs manual is intended to be used in conjunction with the Point and Area Source Manuals (i.e., Volumes IV and V, respectively). The Point and Area Source Manuals each contain a table that cross-references each point or area source category with one or more of the basic EETs which may be used to develop emission estimates. For example, for Electric Utilities/Combustion Emissions, the Point Source Manual cross-reference table refers the user to source sampling, emission factors, or material balance as the basic EETs to use to develop emission estimates for this source category. These basic methods are described in this basic EETs manual.

The remainder of this manual is organized as follows:

- Section 2.0 presents the basic emission estimating equation and defines and provides general guidance on information sources for each equation variable;
- Section 3.0 addresses source sampling;
- Section 4.0 presents emissions models (mechanistic and multivariate);
- Section 5.0 discusses surveying;
- Section 6.0 covers emission factors (process-based and census-based);
- Section 7.0 describes material balance calculations;
- Section 8.0 explains extrapolation;
- Appendix III-A contains sample calculations for emissions models;
- Appendix III-B contains information on how to obtain U.S. EPA air emission estimating tools; and
- Appendix III-C contains an example surveying form for sample point source questionnaire (i.e., INE's Encuesta Industrial).

2.0 FUNDAMENTAL EMISSION ESTIMATING EQUATION

Developing an emissions inventory program for Mexico will require a combination of approaches. No single emissions inventory method can be used to estimate emissions for all emission source categories. Figure 2-1 depicts various approaches for estimating emissions that should be considered when analyzing the costs versus the quality of the results. In regions with serious environmental impacts from air pollution, more sophisticated and costly emission determination methods may be warranted, such as source sampling. Conversely, in regions with minimal environmental problems, a less expensive estimation method such as the use of emission factors may be acceptable.

The fundamental emission estimating equation is:

$$\mathbf{E = A \times EF \times [1 - (CE/100 \times RE \times RP)] \times T \times M\%} \qquad (2\text{-}1)$$

where:

E	=	Emission Rate
A	=	Activity Rate (e.g., throughput, population, etc.)
EF	=	Emission Factor (lb/activity rate unit)
CE	=	Control Efficiency (%)
RE	=	Rule Effectiveness
RP	=	Rule Penetration
T	=	Temporal Adjustment
M%	=	Mass% of pollutant

The accuracy of the emission estimate is dependent upon the relative accuracy of each of these individual components. Errors introduced into any one of these components will affect the final emission estimate.

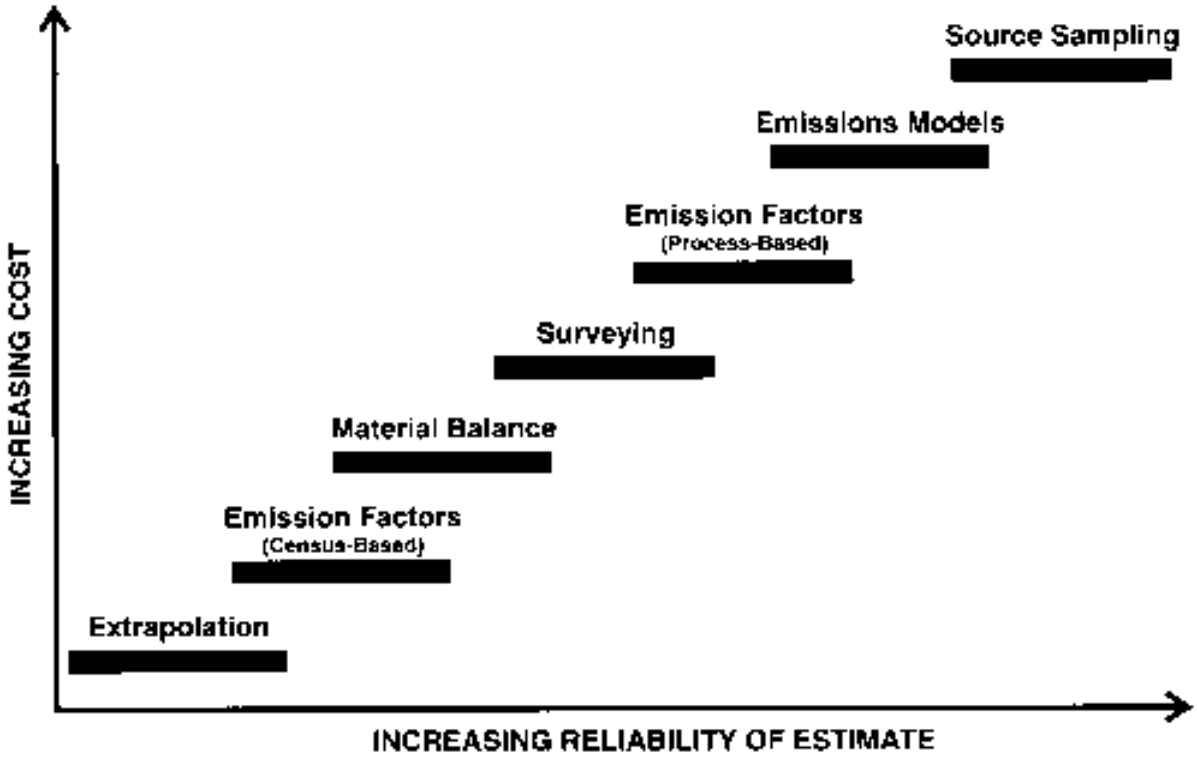


Figure 2-1. Emission Estimation Hierarchy

The information presented in this manual focuses on the first two components of the basic emission estimating equation: emission factor and activity rate. Control efficiencies are addressed more in the Point and Area Source Manuals (Volumes IV and V). Rule effectiveness and rule penetration are discussed further in the Emission Inventory Fundamentals Manual (Volume II). Temporal adjustment and pollutant mass percent (i.e., non-reactive compounds and speciation profiles) are explained in more detail in the Modeling Inventory Development Manual (Volume VIII). The rest of this section provides definitions for each component of the basic emission estimating equation and general guidance on where to find information for each one.

Activity Rate. Activity data are usually directly related to the emissive process. For industrial processes, activity data are generally reported as process weight rates (e.g., kg, ton, or L per month of material used or manufactured). Similarly, for fuel-burning equipment, activity data are reported as fuel consumption rates (e.g., tons, L, or m^3, or MJ per hour or per month). In many instances, conversion factors must be applied to convert reported consumption or production values to units that correspond to the emission factor throughput units (e.g., tons, barrels, etc.). In addition, if U.S. emission factors are used, conversions from standard to metric units may also be necessary. Point source activity data are usually process-based and will most likely be collected by facility personnel and reported in summary format to the agency (e.g., the industrial questionnaire). Area source activity data are often surrogates which are demonstrated or assumed to be correlated to the emissive process (e.g., number of employees). Area source activity data are usually collected by the agency from available census data (e.g., from the Instituto Nacional de Estadística, Geografía e Informática [INEGI]) or surveying of small facilities.

Emission Factor. An emission factor is a ratio that relates the quantity of a pollutant released to the atmosphere to a unit of activity. Emission factors are generally classified into two types: process-based and census-based. Process-based emission factors are commonly used to develop point source emission estimates, and are often combined with the activity data

collected from a surveying or material balance approach. Census-based emission factors, on the other hand, are widely used to develop area source emission estimates. The most comprehensive source for U.S.-specific emission factors for criteria pollutants is *AP-42 Compilation of Air Pollutant Emission Factors* (U.S. EPA, 1995a). Also, the U.S. EPA's Factor Information Retrieval System (FIRE) database is a consolidation of emission factors for both criteria and toxic air pollutants.

Control Efficiency. The overall control efficiency is the product of the capture device efficiency and the control device efficiency. The capture device efficiency indicates the percentage of the emission stream that is taken into the control system, and the control device efficiency indicates the percentage of the air pollutant that is removed from the emission stream before release to the atmosphere. Control device efficiency data may be determined for specific equipment from source tests measuring pollutant concentrations before and after application of the control device, from literature values (e.g., *Volume IV—Point Sources, Table 4-1*) or from the manufacturer's design specification or guaranteed performance specification. The overall control efficiency may also need to be adjusted to reflect control device downtime during maintenance operations or upset conditions.

Rule Effectiveness. Emissions inventory experience has shown regulatory programs to be less than 100 percent effective for most source categories. Rule effectiveness reflects the ability of a regulatory program to achieve the required emissions reductions. The intent of this factor is to account for the fact that most emission control equipment does not achieve emission reductions at the designed rates at all times and under all conditions. Process upsets, control equipment malfunctions, operator errors, equipment maintenance, and other nonroutine operations are typical examples of times when control device performance is expected to be less than optimal. A default fraction of 0.80 (equal to 80 percent effectiveness) was established by the U.S. EPA to estimate rule effectiveness required in some regions; however, the limited accuracy of using a single default value for all source categories has been questioned and

efforts continue to develop guidance for developing rule effectiveness factors for specific source types.

Rule Penetration. Rule penetration is the extent to which a regulation covers emissions from all sources within a source category. For example, a rule may be written such that only the larger surface coating facilities must comply with new control requirements. If area source emissions for all coating facilities are being estimated together as a single source category, then a rule penetration factor must be developed, since not all surface coating facilities will be subject to the rule, and therefore, not all surface coating emissions will be further controlled.

Temporal Adjustment. Most inventories traditionally estimate annual emissions. Hence, all procedures, emission factors, correction factors, and activity levels used in the inventory have been developed to represent annual average conditions. For certain air quality planning activities, temporal adjustments must be made to the annual emission estimates. For example, high photochemical ozone levels are generally associated with the warmer months of the year, while emissions from some sources vary seasonally. For air quality planning purposes, ozone precursor emissions should be determined during the months constituting the ozone season for ozone inventories. Peak ozone season for most areas of the U.S. is May through September. However, in Mexico City, the most critical ozone season is in the winter (i.e., from 15 November to 15 February). Regional air quality modeling efforts may require hourly emission rates. Default temporal profiles (i.e., hours/day, days/week, weeks/yr) are often used to develop hourly estimates from annual estimates.

Pollutant Mass Percent. In some instances, the pollutant or pollutant group defined by an emission factor is not the same as the pollutant or pollutant group defined for the emissions inventory. For example, several VOCs, are considered photochemically nonreactive by the U.S. EPA as defined in the Clean Air Act (CAA) and are not included in VOC emissions inventories in the U.S. (40 CFR 60, 1992). Many of the nonreactive compounds are halogenated VOCs, which find principal application as metal and fabric cleaners, refrigerants, and propellants

in aerosol products. A major industrial category employing these halogenated compounds is degreasing. As another example, the vast majority of landfill emissions are methane, which is not considered a VOC. To the extent that emissions from these various processes are known to be comprised of nonreactive VOC, they may be excluded from the total hydrocarbon (THC) emissions inventories (e.g., the national point source emissions inventory data, SNIFF) for certain emission inventory purposes such as ozone modeling. Similarly, particulate matter (PM) profiles showing particle size distribution data can be used to determine the mass percent of total suspended particulate (TSP) emissions that should be included in an inventory of particulate matter with an aerodynamic diameter less than 10 microns (PM_{10}).

The pollutant mass percent may also be used to estimate emissions of a given chemical species. For example, speciation profiles may be used to obtain data on the beryllium percent of the total PM emissions from mining operations or the benzene percent of the total VOC emissions from a storage tank.

3.0 SOURCE SAMPLING

This section describes the use of source sampling data for estimating emissions from point sources. Examples are provided to illustrate the calculation of emissions from data collected during the source tests. Specific source sampling methods and data reduction procedures can be found in published source sampling reference methods (40 CFR 60, 1992).

Due to the technical complexities of source sampling, substantial time and equipment is involved to obtain accurate and valid emissions data for numerous pollutants from a source. Consequently, conducting source sampling at a facility can be very expensive. However, if properly applied, source sampling can provide a better estimate of emissions from a source than emission factors or material balances. The use of source sampling data reduces the number of assumptions regarding the applicability of generalized emission factors, air pollution control device efficiencies, equipment variations, or fuel characteristics that are applied to similar types of emission sources in order to estimate emission rates of pollutants.

3.1 General Information

The purpose of any source sampling program is to determine the pollutant concentration in a gas stream or the pollutant emission rate from a stack or process exhaust vent. By measuring the pollutant concentration in a known volume of gas and determining the stack gas flow rate, the pollutant mass emission rate can be calculated.

Source tests are integrated, short-term measurements that are typically conducted over 1 to 4 hours. In order to collect a representative sample, three source tests should be conducted at a stack or vent for each pollutant of concern under a defined operating condition. Variations in the process operation during sampling can add a large degree of

variability to source sampling data. Therefore, key parameters of a process operation that can impact pollutant emissions from the source should be monitored during sample collection.

Collection of specific process data during the source tests is critical to correlating sampling results to process operation. For example, emissions will fluctuate as changes occur in the process (e.g., decreasing temperature of a combustion chamber may increase emissions of some pollutants). Collection of specific process data is also important to correlate emissions to process activity and to develop emission factors. For example, if 0.5 kg/hr NO_x is emitted during a 4 hour source test in which 400 liters of fuel were burned, then an emission factor of 0.005 kg of NO_x per liter of fuel can be determined. This source specific emission factor can then be used to estimate NO_x emissions from this source based on the amount of fuel burned.

Source sampling data should be used for emission estimation purposes only if the data were obtained under conditions that were representative of normal operating conditions at the process. Emission data determined from a source sampling event can be extrapolated to estimate annual emissions from a source if the process does not vary significantly in operation. If the process does vary significantly, then multiple source tests will need to be conducted to obtain representative emission results. If facility operation cannot be adequately characterized, then source sampling data should not be used to estimate emissions from the source.

The procedures for conducting source tests are described in various reference methods (e.g., U.S. EPA methods, boiler and industrial furnace (BIF) methods, etc.). Sampling methods that describe procedures for short-term sample collection are referred to as manual methods. These methods are usually specific for a source type (e.g., fossil fuel combustion sources, fuel gas streams at petroleum refineries, electric steam generators) and for a pollutant (e.g., particulate matter, hydrogen sulfide, lead) or class of compounds (e.g., dioxins, VOCs). The extractive sampling systems for these pollutants usually consist of an absorbing solution or media to capture the pollutant, a pump to pull the sample gas through the solution or media, and a dry gas meter to measure the sample gas volume. Since a different type of absorbing solution or

media is used for the collection of different pollutants, source sampling for a variety of pollutants (e.g., metals, particulate matter, dioxins) is complex, labor intensive, and expensive. A schematic of a manual sampling system used to determine particulate matter emissions from a stationary source (known as a Method 5 sampling train) is shown in Figure 3-1.

An alternative to manual source sampling is continuous monitoring, which takes into account process variability over time. Instruments or continuous emission monitors (CEMs) are typically used to measure stack gas concentrations of nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxide (CO), sulfur dioxide (SO_2), and total hydrocarbons (THC). There are also commercially available CEMs to measure opacity, hydrogen chloride (HCl) and ammonia (NH_3). CEMs can either be permanently installed at a source to generate data 24-hours a day or they can be used for emissions monitoring during a defined source testing period (e.g., for 1 to 4 hours). A CEM system consists of a pump to withdraw the sample gas from the source, a series of instruments or analyzers to analyze the gas for a specific pollutant, and a data acquisition system to record the data over time. A schematic of a CEM system is shown in Figure 3-2.

3.2 Example Calculations Using Source Sampling Data

Following the completion of a source test, the sampling data (including pollutant concentration and exhaust gas volumetric flow rate) are usually presented in a report. Most source sampling reports summarize emissions for each pollutant by expressing them in terms of either:

- A mass loading or emission rate (mass of pollutant emitted per unit of time); or
- An emission factor (mass of pollutant emitted per unit of process activity).

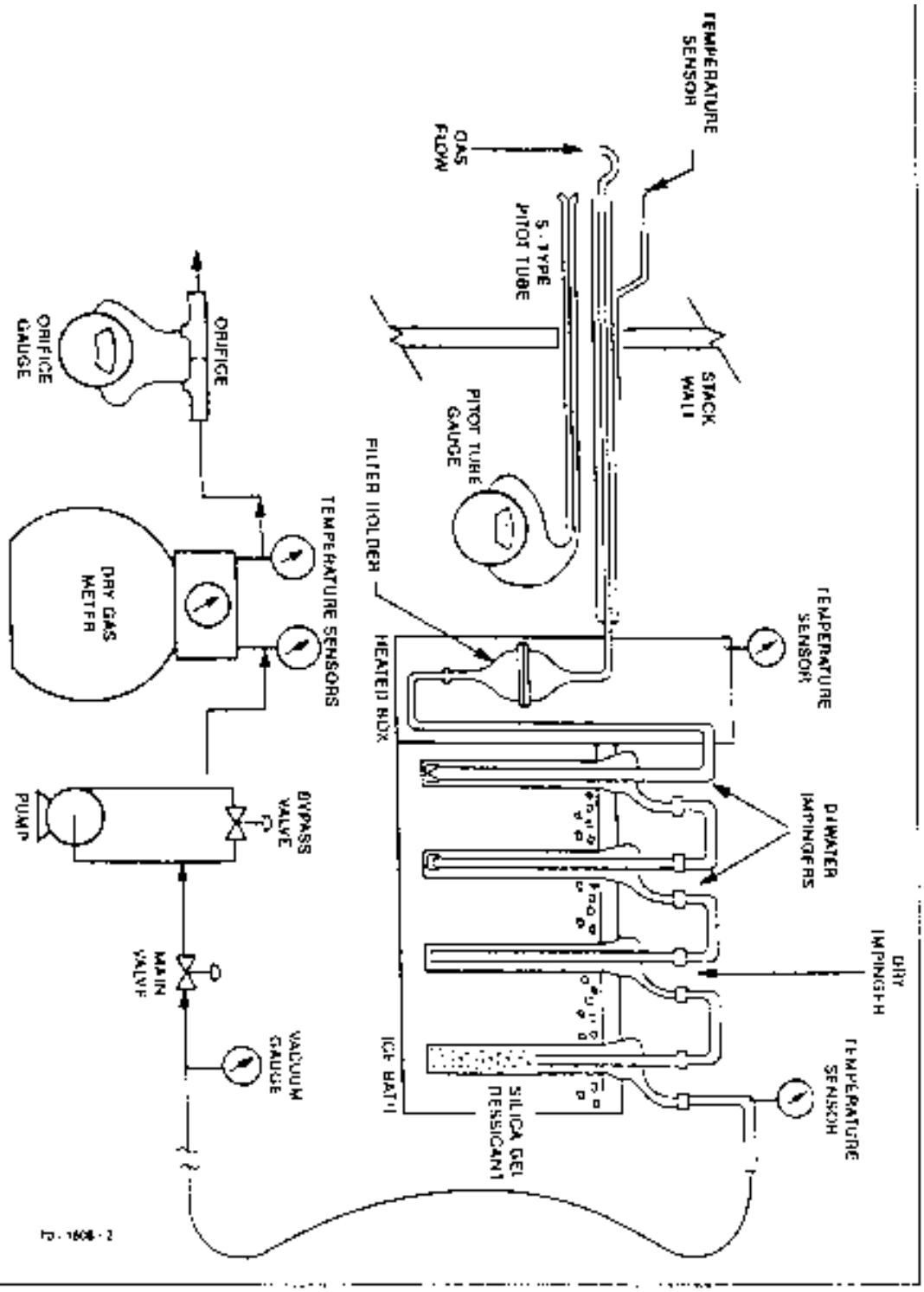


Figure 3-1. Sampling System for Particulate Matter (U.S. EPA Method 5 Sampling Train)

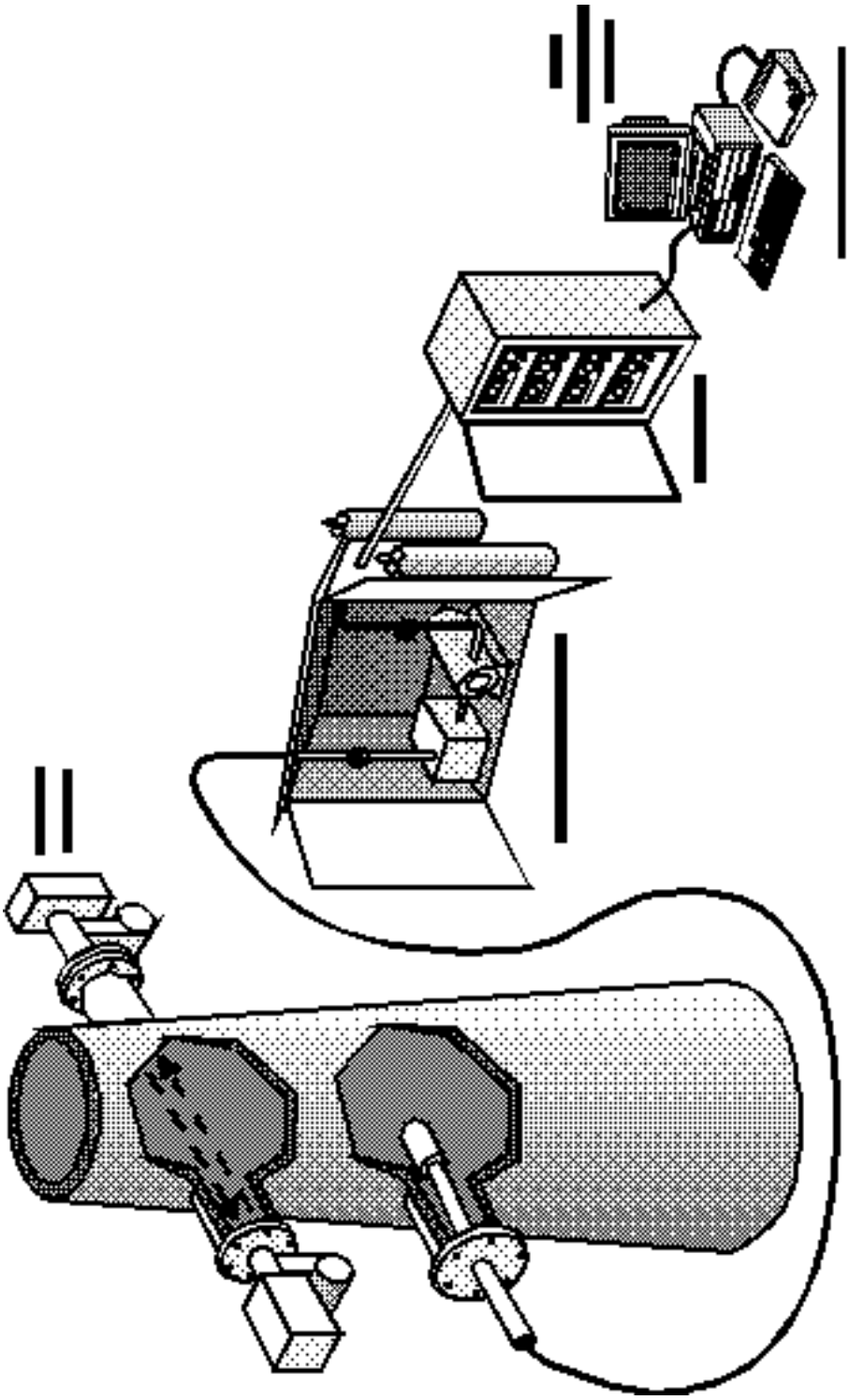


Figure 3-2. A continuous emission monitoring (CEM) system

The variables and symbols used for the calculations are listed in Table 3-1. The examples provided below show how to calculate mass emission rates or emission factors from source sampling data.

Given the following source specific data,

Example 3-1:

ΔV = 0.78 Normal cubic meters (Nm^3);

M_r = 5.5 milligrams (mg);

M_f = 9.5 mg;

Q = 34,170 Normal cubic meters per hour (Nm^3/hr);

T = 2,920 hours per year (hr/yr);

R = 118 million kilo Joules per hour (MMkJ/hr).

Calculate the exhaust gas particulate matter concentration, C_s, in units of milligrams per Normal cubic meter (mg/Nm^3):

Step 1

$$\mathbf{C_s = (M_r + M_f) / \Delta V} \qquad (3\text{-}1)$$

$$= (5.5 \text{ mg} + 9.5 \text{ mg}) / 0.78 \text{ Nm}^3$$
$$= 19.2 \text{ mg/Nm}^3$$

Calculate the mass emission rate, MER, in kilograms per hour (kg/hr):

Table 3-1

List of Variables and Symbols for Emission Calculations

Variable	Symbols	Units
Gas sample volume	ΔV[a]	Normal cubic meter [dry basis] (Nm^3)
Mass of particulate collected in the rinse sample	M_r	milligrams (mg)
Mass of particulate collected on the filter sample	M_f	mg
Exhaust gas volumetric flow rate at standard conditions	Q	Normal cubic meter per hour [dry basis] (Nm^3/hr)
Exhaust gas particulate matter concentration	C_s	milligrams per Normal cubic meter [dry basis] (mg/Nm^3)
Mass emission rate	MER	kilograms per hour (kg/hr)
Annual mass emission rate	MER_a	metric tons per year (metric ton/yr)
Annual hours of operation	T	hours per year (hr/yr)
Activity mass emission rate	MER_b	kilograms per million kilo Joule (kg/MMkJ)
Boiler heat input rate	R	MMkJ/hr
Pollutant concentration	C	parts per million by volume [dry basis] (ppmv).
Molecular weight of the pollutant	MW	gram per gram-mole (g/g-mole)
Molar volume	V	Volume occupied by one mole of ideal gas at standard temperature and pressure (0.024 m^3/g-mole at 20°C and 1 atmosphere)
Fuel factor from U.S. EPA Method 19	F_d[b]	dry standard cubic meters per Joule at 0% oxygen [dry basis] (dscm/J)
Measured oxygen concentration	O_2%	percent [dry basis]
Concentrations of hydrogen, carbon, sulfur, nitrogen, and oxygen	H, C, S, N, O	percent as determined by fuel analysis
Higher heating value of fuel	HHV	kilo Joule per kilogram (kJ/kg)

[a] Normal cubic meter is based on O°C and 760 mm Hg.

[b] standard cubic meter is based on 20°C and 760 mm Hg.

Step 2

$$\mathbf{MER = C_s \times Q/(10^6)} \qquad (3\text{-}2)$$

$$= 19.2\ mg/Nm^3 \times 34{,}170\ Nm^3/hr/(10^6\ mg/kg) = 0.66\ kg/hr$$

These data are expressed in typical units for particulate matter emissions. Results can also be expressed in other units such as milligrams per Normal cubic meter (dry basis) (mg/dscm) using standard conversion factors. Mass emission rates are often expressed on an annual basis (e.g., metric tons per year) as well. These estimates generally include an actual annual usage rate (i.e., hours per year), as most sources typically do not operate continuously throughout the entire year.

Assuming that the source discussed above operates 2,920 hr/yr, calculate the annual particulate matter mass emission rate (MER_a) in metric tons/yr:

Step 3

$$MER_a = MER \times T / 1{,}000 \qquad (3\text{-}3)$$

$$MER_a = 0.66\ kg/hr \times 2{,}920\ hr/yr / (1{,}000\ kg/metric\ ton)$$

$$MER_a = 1.93\ metric\ tons/yr$$

Some emissions data are also expressed on a per unit of activity basis as an emission factor. These emission factors are typically expressed as a weight of pollutant emitted per unit of process activity. As an example, calculate the activity mass emission rate (MER_b) of particulate matter from a boiler with a heat input rate of 118 MMkJ/hr:

Step 4

$$MER_b = MER / R \quad (3\text{-}4)$$

$$MER_b = 0.66 \text{ kg/hr} / (118 \text{ MMkJ/hr})$$

$$MER_b = 0.0056 \text{ kg/MMkJ}$$

Concentrations of pollutants that are present as a particulate or an aerosol (e.g., PM_{10}, lead, dioxins) are usually expressed in mass per units volume unit such as micrograms per Normal cubic meter. Concentrations of other pollutants that are present as a vapor (e.g., NO_x, SO_2, CO) are generally expressed in volume/volume units such as parts per million by volume (ppmv) or parts per billion (ppbv) units.

3.3 Example Calculations Using CEM Data

To determine SO_2, NO_x, THC, and/or CO emissions, a facility may install a CEM system which continuously measures pollutant concentrations (in ppmv). The CEM system is typically equipped with an oxygen (O_2) and/or CO_2 monitor; these gases are considered diluent gases (rather than pollutants) and they are monitored to serve as indicators of the exhaust gas flow rate and/or excess air flow. O_2 and CO_2 concentrations are typically reported in units of percent (by volume) since they are much higher than the levels of the other CEM gases noted (i.e., ppmv). Depending on the regulatory requirements and the type of source, these instruments may be either permanently installed to collect data continuously during unit operation or they may be used temporarily to collect data over a certain time period.

The CEM concentration data are generally transmitted from the instrument to a data logging system which is programmed to store the data and prepare reports in a site-specific

format. The concentration data are often averaged for specific time intervals (e.g., 10-minute, 1-hour, 24-hour).

In addition to the concentration units, the emissions data are often reported in other units, such as mass emission rates (e.g., kg/hr), or emission factors (kg/process unit). In order to convert the concentration units to these other data forms, additional data are required. To convert the concentration data to mass rate data, the exhaust gas volumetric flow rate (e.g., in units of Normal cubic meters per hour) must be either measured or estimated. The source may be equipped with an exhaust gas flow rate monitor which will provide continuous flow rate data to the system or the flow rate may be measured using a pitot tube. It is also possible to estimate the flow rate based on empirical measurements, fuel rate measurements, diluent gas concentrations, or air intake measurements (e.g., fan speed, damper positions). To convert the emission data to emission rate units (e.g., kg/MMkJ of heat input or kg/metric ton of coal fired), the process unit rate (e.g., MMkJ/hr, heat input or tons per hour of coal fired) must be either measured or estimated.

Empirical fuel factors, referred to as F-factors, may also be used to convert fuel usage rate data to heat input or gas flow rates. F-factors are usually specific to a fuel type (e.g., natural gas, #2 fuel oil). Examples of F-factors that have been adopted by the U.S. EPA are presented in Method 19 (40 CFR 60, 1992).

The variables and symbols used in the following calculations are listed in Table 3-1.

Table 3-2 presents an example output from a CEM system, consisting of SO_2, NO_x, CO, O_2, and flow rate monitors, installed on an oil-fired boiler exhaust stack. The data in the table represent a “snapshot” of emissions from the boiler over a 60 minute period.

Table 3-2

Example CEM Output for a Boiler Burning Fuel Oil

Period	O_2 (%V)	SO_2 (ppmv)	NO_x (ppmv)	CO (ppmv)	Stack Gas Flow Rate (Nm^3/hr)
11:00	2.1	1,004.0	216.2	31.5	33,964
11:15	2.0	1,100.0	200.6	25.5	34,361
11:30	2.1	1,050.0	216.7	25.1	32,891
11:45	1.9	1,070.0	220.5	20.8	34,890
12:00	1.9	1,070.0	213.8	19.4	34,749
Average:	2.0	1,058.8	213.6	24.5	34,171

[a] Based on a fuel heating value of 41,828 kJ/kg (18,000 Btu/lb).

3.3.1 Calculating Hourly Emissions from Concentration Measurements

Although CEMs can report real-time hourly emissions automatically, it may be necessary to manually estimate a source's annual emissions from hourly pollutant concentration data. This section describes how to calculate emissions from raw CEM concentration data.

Using the CEM data presented in Table 3-2, hourly SO_2 mass emissions for 11:00 can be calculated:

Example 3-2:

Step 1

$$MER = \frac{C \times MW \times Q}{(1{,}000 \times V \times 10^6)} \qquad (3\text{-}5)$$

$$= \frac{1{,}004 \text{ ppmv} \times 64 \text{ g/g-mole} \times 33{,}964 \text{ Nm}^3\text{/hr}}{(1{,}000 \text{ g/kg} \times 0.024 \text{ m}^3\text{/g-mole} \times 10^6)}$$

$$= 90.9 \text{ kg/hr}$$

To calculate the average SO_2 mass emission rate for the entire sampling period:

Step 2

$$MER_{ave} = \frac{C_{ave} \times MW \times Q_{ave}}{(1{,}000 \times V \times 10^6)} \qquad (3\text{-}6)$$

$$= \frac{1{,}058.8 \text{ ppmv} \times 64 \text{ g/g-mole} \times 34{,}171 \text{ Nm}^3\text{/hr}}{(1{,}000 \text{ g/kg} \times 0.024 \text{ m}^3\text{/g-mole} \times 10^6)}$$

$$= 96.5 \text{ kg/hr}$$

Annual SO_2 emission can be calculated using equation 3-3, assuming the boiler operates 2,920 hours per year:

Step 3

$$MER_a = 96.5 \text{ kg/hr} \times 2{,}920 \text{ hr/yr} \;/\; (1{,}000 \text{ kg/metric ton})$$

$$= 282 \text{ metric tons/yr}$$

Assuming the heat input of the boiler is 118 MMkJ/hr, the SO_2 activity emission rate can be calculated using equation 3-4:

Step 4

$$MER_b = 96.5 \text{ kg/hr} / (118 \text{ MMkJ/hr})$$

$$= 0.82 \text{ kg/MMkJ}$$

3.3.2 Calculating Stack Gas Flow Rate

When direct measurements of stack gas flow rates are not available, Q can be calculated using fuel factors (F-factors). The F-factor is the ratio of gas volume of the products of combustion to the heat content of the fuel and includes all components of combustion less water. This factor can be calculated from fuel ultimate analysis results using the following equation.

$$\mathbf{F_d = \frac{10^6 [3.64(\%H) + 1.53(\%C) + 0.57(\%S) + 0.14(\%N) - 0.46(\%O)]}{HHV}} \qquad (3\text{-}7)$$

Fuel heating values are available in publications such as *Steam, Its Generation and Use* (Stultz and Kitto, 1992). The average F-factors are provided in U.S. EPA Reference Method 19 for different fuels and are shown in Table 3-3.

Using the CEM data in Table 3-2 and the F-factor for oil shown in Table 3-3, the stack gas flow rate of the boiler can be calculated.

Example 3-3:

$$Q = F_d \times \left(\frac{20.9\%}{20.9\% - O_2\%} \right) \times R \times 10^9 \qquad (3\text{-}8)$$

$$= 2.47 \times 10^{-7} \text{ dscm/J} \left(\frac{20.9\%}{20.9\% - 2\%} \right) \times 118 \text{ MMkJ/hr} \times 10^9 \text{ J/MMkJ}$$

$$= 32{,}230 \text{ dscm/hr}$$

Table 3-3

F_d Factors for Various Fuels[a]

Fuel Type	F_d	
	dscm/J[b]	dscf/MMBtu
Coal		
Anthracite[c]	2.71×10^{-7}	10,100
Bituminous[c]	2.62×10^{-7}	9,780
Lignite	2.65×10^{-7}	9,860
Oil[d]	2.47×10^{-7}	9,190
Gas		
Natural	2.34×10^{-7}	8,710
Propane	2.34×10^{-7}	8,710
Butane	2.34×10^{-7}	8,710
Wood	2.48×10^{-7}	9,240
Wood Bark	2.58×10^{-7}	9,600

[a] Determined at standard conditions: 20°C (68°F) and 760 mm Hg (29.92 in. Hg).
[b] dscm/J = dry standard cubic meters per Joule
[c] As classified according to ASTM Method D 388-77.
[d] Crude, residual, or distillate.

4.0 EMISSIONS MODELS

Many emission estimates are developed using an emission factor which assumes a linear relationship (i.e., an “emission factor”) between the emission rate and a unit of activity (e.g., quantity of fuel consumed, production rate, population, employment, etc). For certain source categories, the functional relationship between emissions and multiple process and environmental variables are studied sufficiently to support the development of complex models. If these emissions models require complex calculations or large amounts of input data, they are likely to be computer-based.

While emissions models are designed to yield more accurate emission estimates than an emission factor approach, the accuracy of the emission estimate will always be dependent on the quality of the input data and the assumptions underlying the model. Therefore, before deciding to use a modeling approach for a given source type, it is important to compare the data needs of an emissions model with the data available. The data requirements for such models vary. To estimate emissions, one or many physical parameters may be needed from the source for which the model will be used.

Some emissions models developed in other countries may be used in Mexico. In these cases, it is especially important to consult the user’s manuals for these models to identify any default values that are assumed in the absence of user-defined values, and to try and evaluate whether these default values are appropriate for use in Mexico. Also, it is important to check that the metric units of the available data are correctly converted to the standard/English units required, if U.S. models are used.

Emissions models may be classified into three types: adaptive, mechanistic, and multivariate. Adaptive models are based on software that integrates neural network, fuzzy logic, and chaotic systems into one software package (Collins and Terhune, 1994). During the setup stage, the software is trained with historic operating and emissions data. Operating parameters

are then monitored and used by the software system (or "soft CEM") to predict emissions at a cost less than the application of a true CEM device. However, the purchase cost of adaptive software can still be quite expensive, approaching US$100,000. Therefore, adaptive models are not recommended for near-term inventory efforts in Mexico due to the high cost associated with implementation, and are not discussed any further in the Basic EETs Manual at this time. The rest of this section provides further description and examples of mechanistic and multivariate models.

4.1 Mechanistic Models

Mechanistic models are based on equations that have been developed using the fundamentals of chemistry, physics, and biology to describe the emission rate for a particular source type. Important VOC emitters for which a number of variables are needed to calculate emissions are petroleum product storage and handling operations (e.g., aboveground and underground storage tanks, tank car/tank truck loading, barge/ship loading, and gasoline dispensing at service stations).

The remainder of this section presents information on U.S. EPA models developed to estimate emissions from the following source categories:

- Storage Tanks;
- Petroleum Product Loading Operations;
- Landfills;
- Water and Wastewater Air Emissions Models; and
- Fugitive Dust.

For each source category, a brief summary of the emission model equations is presented, followed by a summary of the required data parameters and the recommended U.S. default values. Sample calculations for each model may be found in Appendix III-A. In cases where a computer model is available from the U.S. EPA, a brief description has been included.

For more information about U.S. EPA models and other air emission estimating tools:

- CHIEF Bulletin Board System (BBS):
  95-919-541-5742 (dial in by modem)

- Info CHIEF Help Desk
  95-919-541-5285 (phone)
  95-919-541-5680 (fax)

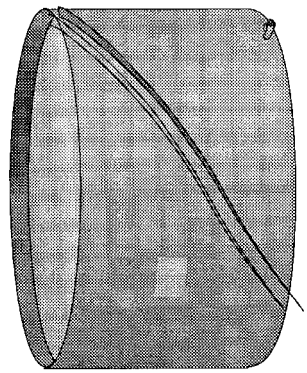
Copies of many of the brochures distributed by the Info CHIEF Help Desk may be found in Appendix III-B.

4.1.1 Storage Tanks

The current U.S. EPA emission model equations for storage tanks are the best examples of mechanistic models. For example, the fixed roof storage tank model applies heat transfer and other principles to model breathing losses as shown in Figure 4-1.

The disadvantage of using the TANKS program or *AP-42* equations is that more resources are required to gather the input data and use the equations or program than using other approximations. If there is only a small amount of emissions, the extra effort may not be warranted. A compromise is to develop region-specific default emission factors using the *AP-42* equations or TANKS program that reflect average temperature, tank conditions, and chemical contents for the inventory region.

Organic Storage Tank Breathing Losses



VOC emitted from vapor expansion and contraction due to changes in temperature and pressure.

Emissions = $f(V_V, W_V, \Delta P_V, P_{VA}, P_A, \Delta T_V, T_{LA})$

Where:

- V_V = vapor space volume of tank
- W_V = vapor density of stored liquid
- ΔP_V = daily vapor range of stored liquid
- P_{VA} = vapor pressure at daily average liquid surface temperature
- P_A = atmospheric pressure
- ΔT_V = daily vapor temperature range of stored liquid
- T_{LA} = daily average liquid surface temperature

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Figure 4-1. Example of Mechanistic Modeling

Fixed Roof Tanks

Emission Model Equations—The two significant types of emissions from fixed roof storage tanks are standing storage and working losses. Standing storage loss is the expulsion of vapor from a tank through vapor expansion and contraction, which are the results of changes in temperature and barometric pressure. This loss occurs without any liquid level change in the tank.

The combined loss from filling and emptying is called working loss. Evaporation during filling operations is a result of an increase in the liquid level in the tank. As the liquid level increase, the pressure inside the tank exceeds the relief pressure and vapors are expelled from the tank. Evaporative loss during emptying occurs when air drawn into the tank during liquid removal becomes saturated with organic vapor and expands, thus exceeding the capacity of the vapor space.

Fixed roof tank emissions vary as a function of vessel capacity, vapor pressure of the stored liquid, utilization rate of the tank, and atmospheric conditions at the tank location. The emission model equations are summarized below. The detailed equations may be found in *AP-42, Section 7.1* (U.S. EPA, 1995a). Required data parameters and U.S. default values are listed in Table 4-1.

Total emission losses from fixed roof tanks are defined as:

$$\mathbf{L_T = L_S + L_W} \quad (4\text{-}1)$$

where: L_T = total losses, lb/yr;
L_S = standing storage losses, lb/yr; and
L_W = working losses, lb/yr.

Standing (breathing) loss:

$$\mathbf{L_S = 365\ V_V W_V K_E K_S} \quad (4\text{-}2)$$

where: V_V = vapor space volume, ft^3;
W_V = vapor density, lb/ft^3;
K_E = vapor space expansion factor, dimensionless; and
K_S = vented vapor saturation factor, dimensionless.

Working loss:

$$\mathbf{L_W = 0.0010\ M_V P_{VA} Q K_N K_P} \quad (4\text{-}3)$$

where: M_V = vapor molecular weight, lb/lb-mole;
P_{VA} = vapor pressure at daily average liquid temperature, psia;
Q = annual net throughput, bbl/yr;
K_N = turnover factor, dimensionless; and
K_P = working loss product factor, dimensionless.
(0.75 for crude oils, 1.0 for all other organic liquids)

Floating Roof Tanks

Emission Model Equations—Total emissions from floating roof tanks are the sum of withdrawal losses and standing storage losses. Withdrawal losses occur as the liquid level, and thus the floating roof, is lowered. Some liquid remains attached to the tank surface and is exposed to the atmosphere. Evaporative losses will occur until the tank is filled and the exposed surface, with the liquid, is covered again. In internal floating roof tanks with column-supported fixed roofs, some liquid also clings to the columns.

Table 4-1

Fixed Roof Tanks
Required Data Parameters and U.S. Default Values

Parameter Description	Variable	U.S. Default Value
Tank Diameter	D	
Tank Shell Height	H_S	
Tank Liquid Height	H_L	
Tank Cone Roof Slope	S_R	0.0625
Tank Dome Roof Radius	R_R	Tank Diameter (D)
Tank Capacity	V_{LX}	
Tank Paint Color	Used to determine	
Tank Paint Condition	Used to determine	
Tank Paint Solar Absorption		0.17 (i.e., white paint in good condition)
Tank breather vent pressure setting	P_{BP}	0.03 psig
Tank breather vent vacuum setting	P_{BV}	-0.03 psig
Material Throughput	Q	
Material Vapor Molecular Weight	M_V	Molecular weight values provided for selected petrochemicals.
Material Vapor Pressure at Average, Maximum, and Minimum Liquid Surface Temperatures	P_{VA}, P_{VX}, and P_{VN} at T_{LA}, T_{LX}, and T_{LN}	Vapor pressure values provided for selected petrochemicals. Vapor pressure correlations based on RVP and S available for crude oils and refined petroleum stocks.
Material Reid Vapor Pressure	RVP	Values provided for selected refined petroleum stocks.
Material Distillation Slope	S	Values provided for selected refined petroleum stocks.
Location Daily Maximum and Minimum Ambient Temperatures	T_{AX} and T_{AN}	Values provided for various U.S. locations.
Location Total Solar Insolation Factor	I	Values provided for various U.S. locations.

Standing storage losses from floating roof tanks include rim seal and roof fitting losses. Rim seal and roof fitting losses can occur through many complex mechanisms such as wind-induced loss, breathing loss from temperature and pressure changes, loss from permeation of the seal material or loss from a wicking effect of the liquid. For internal floating roof tanks, standing losses also may include deck seam losses to the extent that the seams may not be completely vapor tight.

The emission model equations are summarized below. The detailed equations and supporting data tables and figures may be found in *AP-42, Section 7.1* (U.S. EPA, February 1996). Required data parameter and U.S. default values are listed in Table 4-2.

Total emission losses from floating roof tanks are defined as:

$$L_T = L_R + L_{WD} + L_F + L_D \quad (4\text{-}4)$$

where:

L_T	=	total losses, lb/yr;
L_R	=	rim seal losses, lb/yr;
L_{WD}	=	withdrawal losses, lb/yr;
L_F	=	deck fitting losses, lb/yr; and
L_D	=	deck seam losses, lb/yr.

Rim seal loss (L_R):

$$(K_{Ra} + K_{Rb} \times v^n) \times \frac{P_{VA}/14.7}{[1 + (1 - P_{VA}/14.7)^{0.5}]^2} \times D \times M_v \quad (4\text{-}5)$$

(Note: the v^n term is only used for external floating roof tanks.)

Withdrawal loss (L_{WD}):

$$L_{WD} = \frac{0.943 \times Q \times C \times W_L}{D} \times \left(1 + \frac{N_c \times F_c}{D}\right) \quad (4\text{-}6)$$

Deck fitting loss (L_F):

$$L_F = F_F \times \frac{P_{VA}/14.7}{[1 + (1 - P_{VA}/14.7)^{0.5}]^2} \times M_v \times K_c \quad (4\text{-}7)$$

Deck seam loss (L_D):

$$_D = K_D \times S_D \times D^2 \times \frac{P_{VA}/14.7}{[1 + (1 - P_{VA}/14.7)^{0.5}]^2} \times M_v \times K \qquad (4\text{-}8)$$

where:

K_{Ra}	=	zero windspeed rim seal loss factor, lb-mole/ft·yr
K_{Ra}	=	wind speed dependent rim seal loss factor, lb-mole/(mph)^n ft·yr
v	=	average wind speed at tank site, mph;
n	=	seal-related wind speed exponent;
P_{VA}	=	true vapor pressure at daily average surface temperature, psia;
D	=	tank diameter, ft;
M_v	=	vapor molecular weight of liquid, lb/lb-mol;
K_c	=	product factor (0.4 for crude oils, 1.0 for all other organic liquids);
Q	=	throughput, bbl/yr;
C	=	clingage factor, bbl/1000 ft^2;
W_L	=	density of liquid, lb/gal;
N_c	=	number of columns;
F_c	=	effective column diameter, ft; and
F_F	=	roof/deck fitting loss factor, lb-mol/yr;
K_D	=	deck seam loss per unit seam length factor, lb-mol/ft yr (0.34 for bolted, 0.0 for welded); and
S_D	=	deck seam length factor, ft/ft^2.

Table 4-2

Floating Roof Tanks
Required Data Parameters and U.S. Default Values

Parameter Description	Variable	U.S. Default Value
Tank Diameter	D	
Tank Number of Columns	N_C	Look-up table based on Tank Diameter (D).
Tank Effective Column Diameter	F_C	1.0 feet
Tank Shell Condition	Used to determine C (light rust, dense rust, gunite lining).	
Tank Clingage Factor	C	
Tank Location Wind Speed	v (also used to determine F_F)	Values provided for various U.S. locations.
Tank Construction (Welded or Riveted)	Used to determine K_{Ra}, K_{Rb}, and n	
Tank Deck Construction	Used to determine K_D (bolted or welded) and S_D (size of sheets or panels).	
Tank Deck Fitting Loss Factor	F_F	Can be calculated from tank-specific counts of number of deck fittings.
Tank Seal System (types of primary, secondary seals)	Used to determine K_{Ra}, K_{Rb}, and n	
Tank Seal Factors (and seal-related wind speed exponent)	K_{Ra}, K_{Rb}, n	For externals, use values for welded, average fit, mechanical shoe primary seal. For internals, use values for average fit, vapor-mounted primary seal only.
Tank Deck Seam Length Factor	S_D	Sd = 0.2 for bolted decks, 0.0 for welded decks.
Material Throughput	Q	
Material Vapor Molecular Weight	M_V	Molecular weight values provided for selected petrochemicals.
Material Vapor Pressure at Average Liquid Surface Temperature	P_{VA} at T_{LA}	Vapor pressure values provided for selected petrochemicals. Vapor pressure correlations based on RVP and S available for crude oils and refined petroleum stocks.

U.S. EPA Computer Model

The TANKS program is designed to estimate emissions of VOCs from storage tanks. The user provides specific information concerning the storage tank and its contents; the TANKS program then estimates the annual or seasonal emissions and produces a report. The emissions can be separated into breathing and working losses (U.S. EPA, 1996).

The TANKS program has a chemical database of over 100 organic liquids and meteorology (met.) data from over 250 cities in the U. S. The user may add new chemicals and cities (with met. data) to their version of the database. The tank styles addressed in the program include vertical and horizontal fixed roof tanks, and internal and external floating roof tanks. The tank contents can consist of single or multiple liquid components.

TANKS Version 3.0 is currently available. The emission estimating equations that form the basis of the TANKS 3.0 software program were developed by the American Petroleum Institute (API). The API retains the copyright to these equations but has granted permission for the nonexclusive, noncommercial distribution of this material to governmental and regulatory agencies. The API, however, reserves the rights regarding all commercial duplication and distribution of its material. Therefore, the TANKS program is available for public use, but the program cannot be sold without written permission from the API.

The TANKS 3.0 program is written in FoxPro2.5,™ a dBase-compatible language, and is distributed by the U.S. EPA through the CHIEF BBS or through the mail on diskette. TANKS 3.0 may require revisions and modifications to ensure consistency with U.S. EPA emission calculations methodology. The U.S. EPA welcomes feedback on the program from users to identify limitations and to suggest changes to be incorporated in future versions of TANKS.

4.1.2 Petroleum Product Loading Operations

Loading losses are the primary source of evaporative emissions of petroleum products from rail tank car, tank truck, and marine vessels. Loading losses occur as organic vapors in "empty" cargo tanks are displaced to the atmosphere by the liquid being loaded into the tanks.

Emission Model Equations—The emission model equation is presented below. More detailed information may be found in *AP-42, Section 4.4* (U.S. EPA, 1995a). Required data parameters and U.S. default values are listed in Table 4-3.

$$\mathbf{E = Q \times EF} \qquad (4\text{-}9)$$

where:
- E = average annual mass emission rate, lb/yr;
- Q = volume loaded, Mgal/yr; and
- EF = emission factor, lb/Mgal.

$$= \mathbf{12.46 \times \frac{S \times P \times M_v}{T}} \qquad (4\text{-}10)$$

where:
- S = a saturation factor (based on fill method and service);
- P = true vapor pressure of liquid loaded, psia;
- M_V = molecular weight of vapors, lb/lb-mol; and
- T = temperature of bulk liquid loaded, °R.

U.S. EPA Computer Model

Due to the simplicity of this model equation, no computer model is currently available.

Table 4-3

Loading Operations
Required Data Parameters and U.S. Default Values

Parameter Description	Variable	U.S. Default Value
Loading Fill Method	Used to determine S (splash or submerged).	
Loading Service	Used to determine S (clean, dedicated normal, or dedicated vapor balance).	
Material Throughput	Q	
Material Saturation Factor	S	Look-up table based on fill method and service.
Material Vapor Molecular Weight	M_V	Molecular weight values provided for selected petrochemicals in *AP-42, Section 7.1*.
Material Vapor Pressure at Average Liquid Surface Temperature	P	Vapor pressure values provided for selected petrochemicals in *AP-42, Section 7.1*. Vapor pressure correlations based on RVP and S available for crude oils and refined petroleum stocks.
Material Bulk Loading Temperature	T	

4.1.3 Landfills

Methane and carbon dioxide (CO_2) are the primary constituents of landfill gas, and are produced by microorganisms within the landfill under anaerobic conditions. Though toxic pollutant concentrations are typically very small, because landfill gas emission volumes can be very large, landfills are often included in air toxics emission inventories. The rate of emissions from a landfill is governed by gas production and transport mechanisms. Production mechanisms involve the production of the emission constituent in its vapor phase through vaporization, biological decomposition, or chemical reaction. Transport mechanisms involve the transportation of a volatile constituent in its vapor phase to the surface on the landfill, through the air boundary layer above the landfill, and into the atmosphere.

Emission Model Equations

Uncontrolled methane emissions may be estimated for individual landfill by using the theoretical first-order kinetic model of methane production developed by the U.S. EPA. The emission model equation is presented below. More detailed information may be found in *AP-42, Section 2.7* (U.S. EPA, 1995a). Required data parameters and U.S. default values are listed in Table 4-4.

$$\mathbf{Q_{CH4} = L_o \times R \times (e^{-kc} - e^{-kt})} \qquad (4\text{-}11)$$

where:

Q_{CH4}	=	methane generation rate at time t, m^3/yr;
L_o	=	methane generation potential, m^3CH_4/Mg refuse;
R	=	average annual refuse acceptance rate during active life, Mg/yr;
e	=	base log, unitless;
k	=	methane generation rate constant, yr^{-1};
c	=	time since landfill closure, yrs (c = 0 for active landfills); and
t	=	time since the initial refuse placement, yrs.

Table 4-4

Landfills
Required Data Parameters and U.S. Default Values

Parameter Description	Variable	U.S. Default Value
Methane generation potential	L_o	8120 m^3CH_4/Mg refuse. Based on 80th percentile of the literature value range (i.e., 200-9540 m^3CH_4/Mg refuse).
Average annual refuse acceptance rate during active life	R	
Methane generation rate constant	k	0.02 yr^{-1}. Based on the New Source Performance Standard (NSPS) default value.
Time since landfill closure	c	
Time since the initial refuse placement	t	

U.S. EPA Computer Model

The Landfill Air Emissions and Estimation Model (LAEEM) is a computer program specifically designed to monitor the emissions from landfills. The system allows the user to enter specific information regarding the characteristics and capacity of an individual landfill and to project the emissions of methane, CO, nonmethane organic compounds, and individual hazardous air pollutants (HAPs) over time using the Scholl Canyon decay model for landfill gas production estimation. The Scholl Canyon Model is a first-order decay equation that uses site-specific characteristics for estimating the gas generation rate. In the absence of site-specific data, the program provides conservative default values as presented in Table 4-4. The user also may tailor decay rate characteristics on an individual basis. An integrated decay rate constant calculator is provided for landfills that may be operating a gas recovery system to allow more accurate assessments of decay attributes. Outputs may be reviewed in either tabular or graphical

forms. A help system is also provided with information on the model operation as well as details on assumptions and defaults used by the system.

The model is IBM™-PC compatible, requires at least 512 kilobytes (Kb) of memory, and can be used with a monochrome or color graphics adaptor. Reading the user's guide before using the model is recommended.

4.1.4 Waste and Wastewater Air Emissions Models

The U.S. EPA's Office of Air Quality Planning and Standards (OAQPS) has developed air emission models for hazardous waste treatment, storage, and disposal facilities (TSDF).

VOCs in surface impoundments, land treatment facilities, landfills, wastepiles, or wastewater collection and treatment systems can escape to the environment from waste and wastewater through a variety of pathways. To allow reasonable estimates of organic compounds disappearance, one must know which pathways predominate for a given chemical, type of waste site, and set of meteorological conditions. Table 4-5 summarizes the relative importance of the nine pathways for the emissions models developed for the various hazardous waste emission sources (U.S. EPA, 1994).

Emission Model Equations

A pathway is considered to be any process that removes VOCs from a site. The removal may be physical (as in volatilization of a solvent from a surface impoundment) or chemical (as in oxidation of an alcohol in a wastewater treatment plant). Pathways may be considered as rate processes, with rate often strongly dependent on concentration of the disappearing species and temperature of the system.

Each pathway is briefly defined below. However, the emission model equations developed to describe these pathways are very complex. Detailed discussion of the emission

Table 4-5

Pathways for Hazardous Waste Area Emission Sources[a]

Pathway	Surface Impoundments	Wastewater Treatment Plants		Land Treatment	Landfill
		Aerated	Non-aerated		
Volatilization	I	I	I	I	I
Biodegradation	I	I	I	I	S
Photodecomposition	S	N	N	N	N
Hydrolysis	S	S	S	N	N
Oxidation/reduction	N	N	N	N	N
Adsorption	N	S	S	N	N
Hydroxyl radical reaction	N	N	N	N	N
Migration[b]	N	N	N	N	N
Runoff[b]	N	N	N	N	N

I = Important
S = Secondary
N = Negligible or not applicable

[a] Individual chemicals in a given site type may have dominant pathways different from the ones shown here.
[b] Water migration and runoff are considered to have negligible effects on ground and surface water in a properly sited, operated, and maintained RCRA permitted hazardous waste treatment, storage, and disposal facility.

Sources: U.S. EPA, 1994.

model equations and sample calculations for each pathway may be found in the document *Air Emissions Models For Waste and Wastewater (EPA-453/R-94-080A)* (U.S. EPA, 1994), available from the CHIEF bulletin board.

- **Volatilization** occurs when molecules of a dissolved substance escape to an adjacent gas phase.

- **Adsorption** takes place when molecules of a dissolved chemical (in a liquid-solid system) become physically attached to elements of the solid phase. Chemical bonding may also occur (chemisorption).

- **Migration** occurs when chemicals applied to soils are transported through the soils to groundwater.

- **Runoff** occurs when chemicals at or near the soil may be washed away by rain.

- **Biological decomposition** takes place when microbes break down organic compounds for metabolic processes.

- **Photochemical decomposition** may occur when a chemical absorbs light and react (direct photolysis) or the chemical reacts because of light absorption by surrounding elements (indirect photolysis).

- **Hydrolysis** occurs when a chemical reacts with water.

- **Oxidation/reduction** is another pathway. Organic compounds in aquatic systems may be oxidized by oxygen (particularly as single oxygen, $^1O_2$) or other oxidants such as hydroxyl radicals (OH) and peroxy radicals (RO_2). In anaerobic environments, reduction reactions may take place.

- **Hydroxyl radical reactions** may occur through addition of a hydroxyl radical, abstraction of a hydrogen atom, or both.

Required Data Parameters

Different data parameters required for each waste and wastewater emissions model. Table 4-6 provide some examples of the data parameters needed to support these emission models.

Table 4-6

Waste and Wastewater Models
Example Required Data Parameters

Parameter	Units
Ratio of the area of waste to area of air flow in drain	dimensionless
Fraction of entering organic lost to atmosphere	dimensionless
Partition coefficient	mol fraction gas per mol fraction liquid
Length of collection conduit	m
Length of drain	m
Underflow rate	m^3/s
Diameter of drain	m
Radius of underflow conduit	m
Depth of liquid in underflow	m
Wind velocity	m/s
Relative humidity	percent
Collection system temperature	deg.C
Cross-sectional area of vent holes	cm^2
Height of manhole cover above surface	m

U.S. EPA Computer Model

CHEMDAT8—CHEMDAT8 is a Lotus 123® spreadsheet prepared by the U.S. EPA's Emissions Standard Division that includes analytical models for estimating VOCs from TSDF processes. The original models include disposal impoundments, closed landfills, land treatment facilities, and aeration and nonaeration impoundment processes. Predicted emissions can be viewed on the screen or printed. A graphical presentation of the relationships between emission prediction and vapor pressure and between emission prediction and the partition

coefficient is also available. The resulting scatter diagrams can be printed via PrintGraph®, another Lotus® program.

The models in CHEMDAT8 can be applied to other types of TSDF processes besides those contained in the original design. The nonaerated impoundment model in CHEMDAT8 can estimate emissions from storage surface impoundments and open-top wastewater treatment tanks. The CHEMDAT8 model for predicting emissions from surface treatment impoundments and aerated wastewater treatment tanks is the aerated impoundment model. The land treatment model in CHEMDAT8 can estimate emissions from land treatment soil, open landfills, and wastepiles. Emissions from an oil film surface in a land treatment facility or an oil film on surface impoundments can be predicted via the oil film model in CHEMDAT8. When a CHEMDAT8 model is not available to predict emissions, the equations shown in the reports that provide the background to the model can be used to perform hand calculations of emissions.

This eighth version of the CHEMDAT spreadsheet contains several major operational modifications. In CHEMDAT8, the user can select a subset of target compounds for investigation. The user can also specify which TSDF processes are to be considered during a session. These two selections improve the efficiency of CHEMDAT8 relative to some of the earlier versions by minimizing storage requirements as well as actual loading and execution time.

Default input parameters in the CHEMDAT8 diskette demonstrate sample calculations. However, the input parameters can be changed to reflect different TSDF characteristics and then recalculate emissions under these modified conditions. Furthermore, the list of 60 compounds currently in CHEMDAT8 can be augmented by an additional 700 chemicals. Procedures for introducing data for additional compounds into CHEMDAT8 are described in the supporting documentation report.

WATER8

WATER8 is a menu-driven computer program that is intended for estimating emissions from wastewater treatment systems only. WATER8 uses some of the same models found in CHEMDAT8, but has data for a total of 800 compounds. The WATER8 program also has graphic enhancements to aid the user in visualizing the system being modeled.

4.1.5 Fugitive Dust

Significant atmospheric dust arises from the mechanical disturbance of granular material exposed to the air. Dust generated from these open sources is termed “fugitive”, because it is not discharged to the atmosphere in a confined flow stream. Common sources of fugitive dust include paved and unpaved roads, agricultural tilling operations, aggregate storage piles, and heavy construction operations. The dust-generation process is caused by pulverization and abrasion of surface materials by application of mechanical force through implements (i.e., wheels, blades, etc.) and by entrainment of dust particles by the action of turbulent air currents, such as wind erosion of an exposed surface by wind speeds greater than 19 km/hr (12 miles/hr).

Various emission model equations have been developed by U.S. EPA to estimate emissions from these fugitive dust sources. More detailed information may be found in *AP-42, Section 13.2* (U.S. EPA, 1995a).

Emission Model Equations—Example emission model equations are presented below. More detailed information may be found in *AP-42, Section 13.2.1* (U.S. EPA, 1995a). Required data parameters and U.S. default values are listed in Table 4-7.

Unpaved Roads

$$\mathbf{E = VKT \times EF} \tag{4-12}$$

where:
- E = average annual mass emission rate, kg/yr;
- VKT = vehicle kilometers traveled, VKT/yr;
- EF = emission factor, kg/VKT.

$$= k(1.7)\left(\frac{s}{12}\right)\left(\frac{S}{48}\right)\left(\frac{W}{2.7}\right)^{0.7}\left(\frac{w}{4}\right)^{0.5}\left(\frac{365-p}{365}\right) \text{ (kg/VI} \tag{4-13}$$

where:
- k = particle size multiplier, dimensionless;
- s = silt content of road surface material, %;
- S = mean vehicle speed, km/hr;
- W = mean vehicle weight, Mg;
- w = mean number of wheels;
- p = number of days with a least 0.254 mm (0.01 in.) of precipitation per year.

Paved Roads

$$\mathbf{E = VKT \times EF} \tag{4-14}$$

where:
- E = average annual mass emission rate, g/yr;
- VKT = vehicle kilometers traveled, VKT/yr;
- EF = emissions factor, g/VKT.

$$EF = k\left(\frac{sL}{2}\right)^{0.65}\left(\frac{W}{3}\right)^{1.5} \tag{4-15}$$

where:
- k = base emission factor for particle size range (g/VKT)
- sL = road surface silt loading (g/m^2)
- W = average weight (tons) of the vehicles traveling the road

Heavy Construction Operations

$$E = A \times T \times EF \tag{4-16}$$

where:
- E = average annual mass emission rate, Mg/yr
- A = construction area, hectares
- T = construction time, months
- EF = emission factor
- = 2.69 Mg/hectare/month

Aggregate Handling and Storage Piles

$$E = Q \times EF \tag{4-17}$$

where:
- E = average annual mass emission rate, kg/yr
- Q = quantity of material transferred, Mg/yr
- EF = emission factor, kg/Mg

$$EF = k(0.0016)\frac{\left(\frac{U}{2.2}\right)^{1.3}}{\left(\frac{M}{2}\right)^{1.4}} \tag{4-18}$$

where:
- k = particle size multiplier, dimensionless
- U = mean wind speed, m/s
- M = material moisture content, %

Industrial Wind Erosion

$$E = A \times EF \tag{4-19}$$

where:
- E = average annual mass emission rate, g/yr
- A = area of surface material subject to disturbance, m^2
- EF = emission factor, $g/m^2/yr$

$$EF = k \sum_{i=1}^{N} P_i \tag{4-20}$$

where:
- k = particle size multiplier, dimensionless
- N = number of disturbances per year
- P_i = erosion potential corresponding to the fastest mile of wind for the ith period between disturbances g/m^2

Table 4-7

Fugitive Dust
Required Data Parameters and U.S. Default Values

Parameter Description	Variable	U.S. Default Value
Particle size for which emissions are to be estimated	Used to determine k	
Particle size multiplier	k	
Silt content of road surface material	s	Table of default values presented by industry and road use/surface material.
Mean vehicle speed	S	Range of test condition values was 21-64 km/hr.
Mean vehicle weight	W	Range of test condition values was 2.7-142 Mg.
Mean number of wheels	w	Range of test condition values was 4-13 wheels.
Number of days with at least 0.254 mm (0.01 in.) of rain per year	p	Regional data provided for the U.S.
Road surface silt loading	sL	Table of values presented by U.S. State and City.
Surface material area	A	
Construction time	T	
Quantity of material transferred	Q	
Mean wind speed	U	
Material moisture content	M	Table of values presented by industry and surface material.
Number of disturbances per year	N	
Erosion potential function	P_i	

U.S. EPA Computer Model

In 1990, the U.S. EPA developed two programs to help estimate fugitive dust emissions from mechanical disturbances (i.e., unpaved roads, paved roads, materials handling, agricultural tilling, and construction/demolition) and wind erosion. These computer programs are based on the material presented in the document, *Control of Open Fugitive Dust Sources* (U.S. EPA, 1988). The Help feature provides definitions for terms with which the user might not be familiar. In addition, for certain variables, typical or suggested default values are given. For example, the number of days with significant rainfall is given for over 175 U.S. cities and the mean annual wind speed is provided for over 120 U.S. cities.

The fugitive dust programs are distributed by the U.S. EPA through the CHIEF BBS or through the mail on diskette. For further information, the reader is referred to *The User's Manual for the PM_{10} Open Fugitive Dust Source Computer Model Package* (U.S. EPA, 1990).

Because these programs have not been updated since 1990, they are not as user-friendly as more recently developed software. In many cases, it would probably be more efficient for users to develop their own spreadsheets with the emission model equations.

As another option, the PART5 mobile model may be used to estimate fugitive dust emissions from paved and unpaved roads.

4.2 Multivariate Emissions Models

A multivariate emissions model is a hybrid methodology that combines various traditional inventory approaches and site-specific information within an extrapolation framework. As its name suggests, a multivariate emissions model expresses emission estimates in terms of a set of variables that help characterize the system being modeled. This approach is particularly well-suited for regions that have limited records and statistics to apply traditional inventory techniques. The fundamental concept is to develop emission estimates based on land use/land cover characteristics. For example, agricultural, residential, commercial, and industrial

geographic sites all have different emission characteristics. These emissions differences can be characterized using different variables that describe emissions activity of land use/land cover type.

Although the use of multivariate models will likely have higher initial costs than other inventory methods due to the model development step, the ease of application and possible reduction in future inventory maintenance costs make this a very attractive approach. Another significant advantage of multivariate models is that they are based on local data. This allows the effects of local conditions to be included in the emissions estimates. Some possible source types in Mexico that could be estimated with a multivariate emissions model include construction activities, agricultural activities, and solvent use. The general approach for developing a multivariate emissions model is outlined in section 4.2.1 and a conceptual example is provided in section 4.2.2.

4.2.1 Developing a Multivariate Emissions Model

The first step in developing a multivariate emissions model is the identification of the variables that characterize the overall system that the model is intended to cover. These variables will differ from system to system. Using agricultural activities as an example, these variables could be a type of crop (orchards, row vegetables, etc.), acreage, or harvested quantity. For construction activities, these variables could be a type of construction (building, road, railway, etc.), construction size, or construction cost. Each one of these variables can be used to describe the magnitude of emissions from these sources. For example, construction of two kilometers of road would generate more particulate emissions than construction of one kilometer of road.

The second step of multivariate model development is the determination of which emission source types should be included in the model. For agricultural activities, this would likely be defined as agricultural tilling, harvesting, and equipment exhaust emissions. For construction activities, this could be much more complex and could include earth moving, materials handling, equipment exhaust, and other emission source types. The total number of emission source types covered in the model is ultimately determined by the emission activities of the system that is being characterized.

After defining the source types to include in the multivariate model, the next step is the development of the emissions data to be used in the model. Emissions from each source type at a single site (construction, agricultural, etc.) are estimated using methods from the literature (i.e. empirical equations) and site-specific data. In order to create a statistically robust multivariate model, it is necessary to repeat this estimation for a number of other sites.

Total estimated emissions from each geographical site would then be plotted versus each of the variables identified as characterizing the entire system. Sites that differ considerably from representative sites may produce significantly higher or lower emissions estimates that could adversely affect the statistical analysis. These data points may be considered "outliers" and excluded from further analysis. From these plotted data, a "best-fit" emission rate for each site variable can be statistically determined (i.e., kg of PM_{10}/acre of tomatoes, kg of PM_{10}/US$ of building construction, etc.). Statistical analysis is then used to assess the imprecision of each best-fit emission factor and to quantify the uncertainty of the emissions estimates. From this analysis, the most statistically accurate relationship is selected. It is likely that this relationship will be a simple linear relationship, but it is possible that it might be exponential, logarithmic, or piecewise (i.e., construction costs less than US $10 million might have one best-fit relationship, while those with a cost greater than US $10 million might have a different one).

After the determination of the most appropriate best-fit relationship, regional emissions can be estimated by inserting regional data into the model.

4.2.2 Example Multivariate Model - Construction Activities

Construction activities are a widely distributed area source and can be a significant source of particulate matter (PM_{10}). Because construction activities are so widespread, it is usually not feasible to estimate emissions from each individual construction site. This makes construction activities an ideal candidate for multivariate models. The following example conceptually illustrates the development of a multivariate emissions model. Actual multivariate models must be derived using the steps outlined below.

Identification of System Variables. There are several variables related to construction activities that characterize the overall system (PM_{10} emissions). Some of the more basic system variables include:

- Construction type (buildings, roads, railway, etc.);
- Construction size (building area, excavation volume, amount of concrete poured, etc.);
- Project value; and
- Number of construction workers.

Other variables might be applicable for certain special types of construction activities.

Determination of Emission Source Types. Construction activities generate PM_{10} emissions from a number emission sources such as:

- Demolition and debris removal;
- Excavation and other earth moving;
- Vehicle and equipment exhaust;
- Materials handling; and
- Reentrained dust.

Development of Emissions Data. Emissions for a single construction site are estimated by aggregating calculated emissions from each of the source types as shown in the following equation:

$$\mathbf{E_{tot} = (x_{d,c,e,m,r})(y_{d,c,e,m,r})} \quad (4\text{-}21)$$

where: E_{tot} = total site emissions;
x = activity rate;
y = emission factor;
d = demolition and debris removal;
c = excavation and other earth moving;
e = vehicle and equipment exhaust;
m = materials handling; and
r = reentrained dust.

Table 4-8 lists the site-specific activity rates (x_i) and empirical emission factors (y_i) needed to estimate construction emissions. The site-specific parameters contained within the empirical emission factors are also included.

Plotting Emissions Data. After obtaining site-wide PM_{10} emissions totals (E_{tot}) for several different building construction sites, these totals would then be plotted against construction site area, construction project value, number of construction workers, and any other relevant system variables. Hypothetical data for six sites (labeled E_1 through E_6) are plotted in Figure 4-2.

Statistical Analysis of Plotted Data. The next step is to statistically determine the "best-fit" relationship among the different data plots. For the hypothetical data plotted in Figure 4-2, it is assumed that the "best-fit" relationship is a simple linear regression that intercepts the y-intercept at the origin (i.e., no construction activity will result in no PM_{10} emissions).

In this hypothetical example, comparison of the resultant R^2 values indicates that the strongest statistical relationship exists between PM_{10} emissions and construction area. In

Table 4-8

Activity Rates and Emission Factor Parameters Needed to Estimate Construction Emissions

Emission Source Type	Activity Rate (x_i)	Emission Factor (y_i)	Required Site-Specific Parameters
Demolition/ debris removal (d)	Amount of demolition material (Mg)	kg PM_{10}/Mg demolition material[a]	Wind speed (m/s) Demolition material moisture content (%)
Excavation/ earth moving (c)	Vehicle VKT	kg PM_{10}/VKT[a]	Equipment type
Vehicle/ equipment exhaust (e)	Hours of operation	g PM_{10}/hour of operation[b]	Equipment type Fuel type Rated horsepower Operating load
Materials handling (m)	Amount of handled material (Mg)	kg PM_{10}/Mg handled material[a]	Wind speed (m/s) Storage pile moisture content (%)
Reentrained dust (r)	Vehicle VKT	kg PM_{10}/VKT[a]	Silt content (%) Vehicle speed (km/hr) Vehicle weight (Mg) Mean number of vehicle wheels (-) Precipitation (Number of days with $\geq$ 0.254 mm precipitation per year)

[a] Empirical equations for demolition/debris removal, excavation/earth moving, materials handling, and reentrained dust can be found in *Fugitive Dust Background Document and Technical Information Document for Best Available Control Measures* (U.S. EPA, 1992)

[b] Emission factors (g/hp-hr) for different equipment types can be found in *Nonroad Engine and Vehicle Emission Study Report* (U.S. EPA, 1991a). Mexico-specific emission factors might need to be developed.

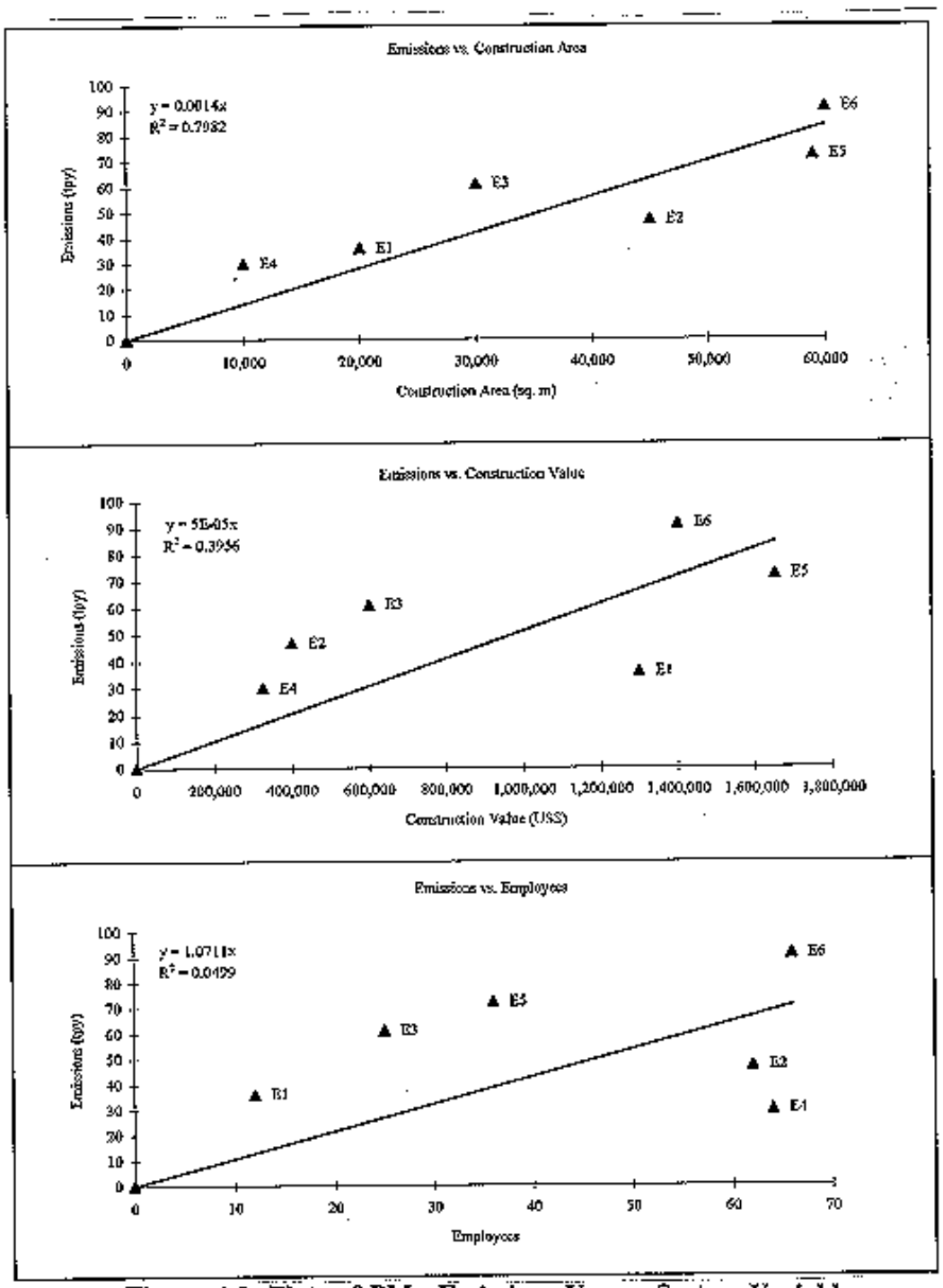

Figure 4-2. Plots of PM_{10} Emissions Versus System Variables

actual situations, emissions likely will not be dependent on one system variable; rather, they will probably be dependent on several system variables.

Calculation of Regional Emissions. Now that the "best-fit" relationship between PM_{10} emissions and construction area has been established as being statistically valid, the application of this relationship to calculate region-wide emissions is quite straightforward. As can be seen in the Figure 4-2 plot of emissions versus construction area, the equation that determines the linear regression is:

$$\text{Total } PM_{10} \text{ Emissions (tpy)} = 0.0014 \times \text{Construction Area } (m^2)$$

If the total hypothetical regional construction area is 2,600,000 m^2, then the regional PM_{10} construction emissions are:

$$0.0014 \times (2{,}600{,}000\ m^2) = 3{,}640 \text{ tpy } PM_{10}$$

5.0 SURVEYING

A survey questionnaire is the technique commonly used to gather point source emissions inventory data (Figure 5-1). The questionnaire should be sent to each facility and request information about the characteristics of each emitting device at the facility. Using a questionnaire to gather point source emissions data in Mexico is not new; the National Institute of Ecology (INE) has been gathering point source data with this technique for several years. A copy of the national point source questionnaire is shown in Appendix III-B.

A survey approach can also be used to gather information needed to calculate area source estimates or used to develop region-specific emission factors for the development of certain area source emission estimates. Figure 5-2 illustrates the process for area sources.

Conducting a survey consists of several steps. For either a survey of point or area sources, the first step is to determine an appropriate sample size and to identify the facilities/subcategories and process differences within the surveyed source category. Next, mailing lists must be prepared; questionnaires must be designed, assembled, and mailed or delivered; data-handling procedures must be prepared and organized; and response-receiving systems must be established. Considerable thought and planning must be dedicated to the design of a new questionnaire or the modification of an existing one. The success rate of a surveying effort is largely dependent on whether the survey is backed by a regulatory agency and also the conciseness, ease of use, and generality of the questionnaire. In addition the questionnaire responses must be subjected to thorough QA/QC reviews to eliminate invalid data (e.g., supersonic stack exit gas velocities). The cost of a surveying effort is a function of the completeness and specificity of the questionnaire, the extent of the target audience, and the thoroughness of the QA/QC follow-on activities.

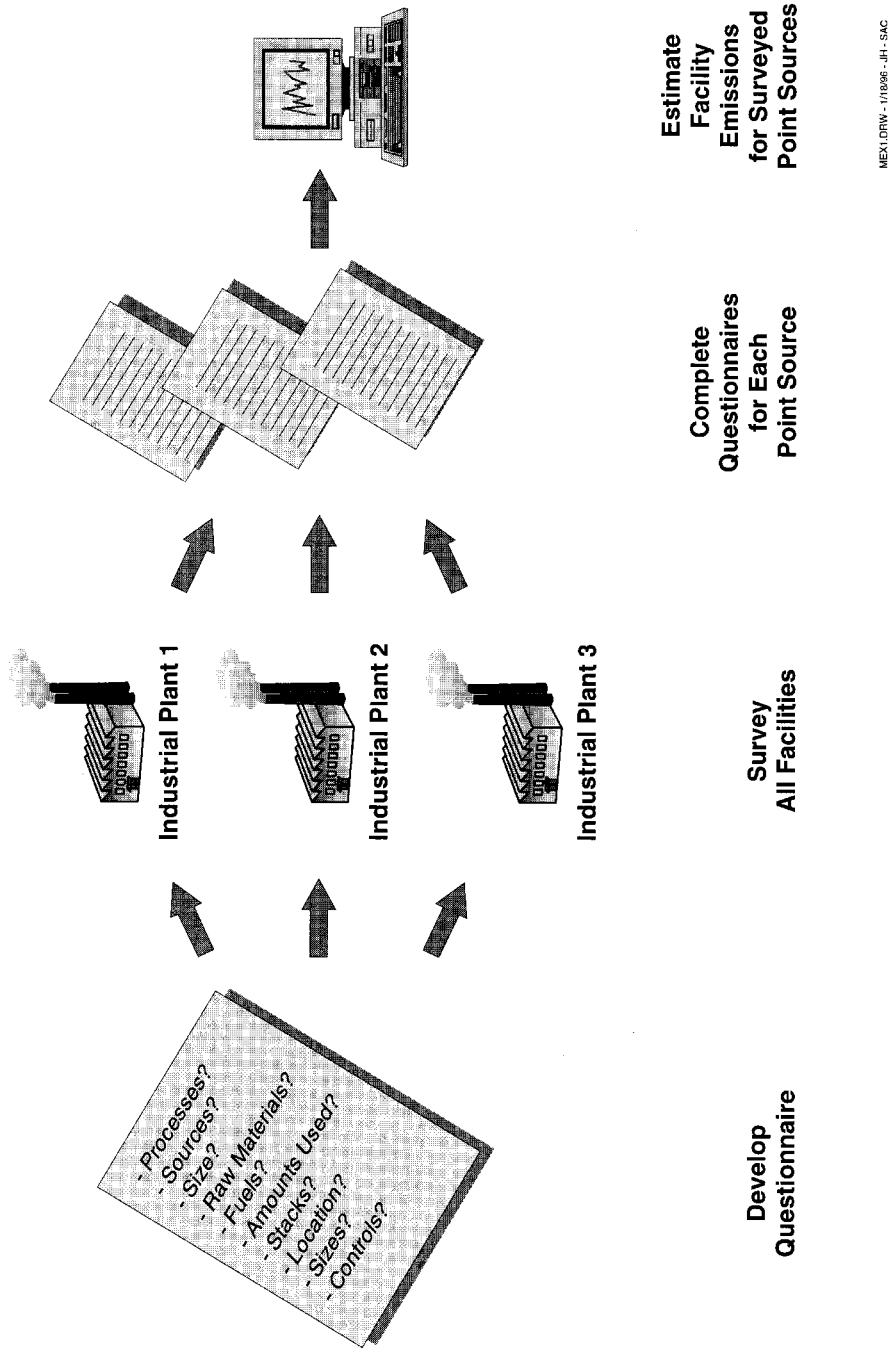

Figure 5-1. Example of Point Source Surveying

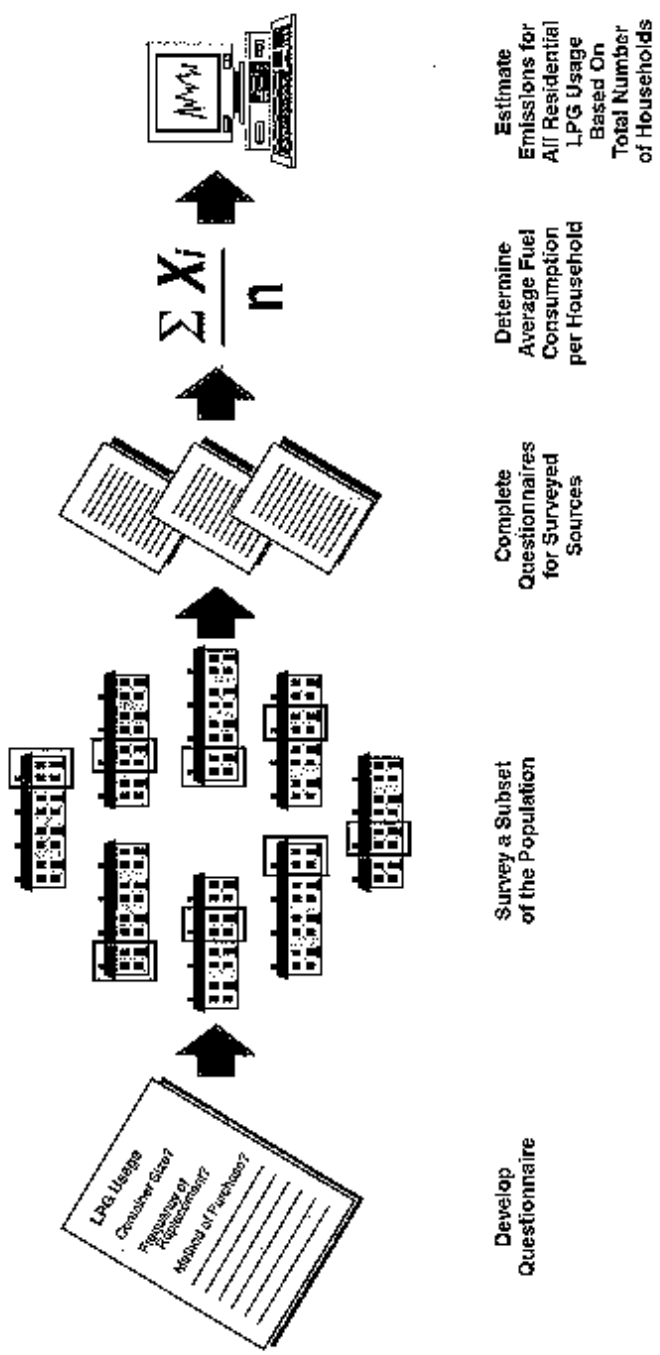

Figure 5-2. Example of Area Source Surveying

The material presented in the remainder of this section is intended to introduce the reader to the concept of surveying and provide background information on the techniques used to conduct a successful survey. These techniques are applicable to both point and area sources. For more information about the use of specific questionnaires, see the document entitled *Development of Questionnaires for Various Emission Inventory Uses* (Holman and Collins, 1979).

5.1 Initial Planning

Although not complicated, there are several important considerations to keep in mind while planning and conducting a survey effort. This section summarizes the most important considerations, which are applicable to both point and area sources alike. The key to a good survey effort is adequate planning. Important points to consider during the initial planning phase for both point and area source surveys are:

- Historically, paper copies of questionnaires have been sent to individual facilities. Another approach is to use computer media (floppy disks or electronic transmission) instead of paper to return or update questionnaire responses to the agency. This technique can also include the use of standardized computer forms or software so that data submitted to the agency is in a format easily handled by agency personnel. This technique has not been used in Mexico, but other regions have found several benefits from this approach. If properly designed the electronic questionnaire can be easier to complete and minimizes data entry and QA reviews.

- Compile distribution lists from a number of different sources, using several sources and cross checking those sources.

- Secure any administrative clearances needed under federal or state rules to conduct a survey of the private sector.

- Explain the reasons for the survey during the initial contact phase, whether it is by phone or mail.

- Consider who should contact the survey recipient. Response rates for industry surveys may be higher if the state or federal agency, not a contractor, contacts the survey recipient.

- The survey process takes several steps including identifying the correct recipient. To identify the correct recipient at a facility, arrange convenient

times for an interview and actually talk to the recipient and answer the survey questions. For example the steps might be:

- Contact the facility by letter or by phone to inform them about the survey, and set up a convenient time for answering questions. Be certain that the person contacted is able to answer the survey questions.

- Send the survey questions to the recipient.

- Place a second call to interview the recipient about the survey questions.

Once the facilities have been identified and the questionnaire(s) developed, surveying point sources is straightforward. Several important items for planning an area source survey are summarized below.

- Investigate and subdivide the source category if necessary. Many area source categories, such as degreasing and surface coating consist of different processes used by many different industries. Uses of particular processes can vary widely from one industry to the next. Stratify the population of sources if necessary (see Section 5.3).

- Design the survey for a reasonable point in the product distribution process. In the case of many solvent use categories, a survey could be sent to either manufacturers, distributors, retailers, or users, but the most practical choice might be just manufacturers or just distributors.

- Consider future needs in survey form planning; plan ahead if possible. For example, the survey may collect data/information for emission calculations. As part of the air quality planning process, emission projections are also anticipated. Therefore, consider collecting emissions projection information at the same time the basic data are collected.

- For area sources, plan how the information gathered through the survey will be scaled up for the entire inventory region, since the survey design will probably cover only a sample of all sources and it is unlikely that the survey will have a 100 percent response rate. Identify a reasonable surrogate activity, if necessary, and plan on collecting that information in the survey (see Section 5.4).

- When data collection is based on sites identified by their Mexican Classification of Activities and Products (CMAP) Code, and the source

category process may or may not take place at every site with that CMAP Code, refine the distribution list by identifying the sites that do use the process;

- For instance, industrial surface coating is typically associated with a number of CMAP Codes, but not all of the facilities under a particular CMAP Code may have surface coating operations.

- Calling a facility before sending the survey can make the distribution more efficient. It will also identify the proportion of facilities in an CMAP Code that do or do not use a process, which is useful for scaling up area source survey data.

5.2 Facility Identification

A necessary step in the survey is the preparation of a contact list that tabulates the name, address, and general process category (e.g., wood products manufacture) of each facility that could be surveyed. The purpose of the contact list is to identify the individual facilities that will be surveyed. The size of the resulting contact list gives an agency an indication of the numbers and types of sources that can effectively be considered in the survey within resource limitations. In this regard, the contact list can be used to help an agency determine whether the resources allocated for the compilation effort will be sufficient, and provide the basic information needed to develop a sampling subset. The correct number of samples (returned and correctly completed questionnaires) must be determined based on statistically sound sampling techniques, the priority given to the category, and the resources available.

The contact list should be compiled from a variety of information sources, including:

- Listings of air emission sources included in existing emissions inventory is a good starting point.

- Listings of water pollution sources and hazardous waste generators may be used to identify potential sources in various CMAPs.

- Air pollution control agency files may provide valuable information on the location and types of sources in the region of concern. These files can also be used later to cross-check certain information supplied on questionnaires.

- Other government agency files maintained by labor departments and tax departments frequently aid in the preparation of the mailing list. Such files will include various state industrial directories in which companies are listed alphabetically by CMAP Code and municipality.

- Local industrial directories may provide a current list of the sources that operate in the inventory region. These are often organized by CMAP code and may provide employment data. For example, facility listings along the border can be obtained from the Maquiladora Association.

- National publications can be used when available. However, the information in them may be older and less accurate than local primary references.

The mailing list should be organized to facilitate the necessary mailing and follow-up activities. A logical order in which to list companies is by state or municipality, then by CMAP Code, and finally, alphabetically. Ordering the list in this manner will increase the efficiency of all subsequent data-handling tasks and will allow a quicker QC check of the list.

5.3 Sample Selection

For area sources, developing the surveying plan will entail decisions regarding the selection (or sampling) of facilities to include in the survey effort. Depending on the objectives of the survey effort, different sampling techniques can be used. Table 5-1 lists several different sample selection techniques that can be used. For the development of area source emission estimates, typically either random sampling or random stratified sample selection techniques will be typically used. If the population of sources is small enough, the entire population can be selected. If the population is large and it’s not possible to survey every facility, then a subset of the population must be selected. Careful consideration must be given to sample selection so that the survey results remain unbiased. A thorough discussion of the statistical procedures for selecting samples is beyond the scope of this section. The reader is referred to more detailed

Table 5-1

Types of Survey Sampling Methods

Method	Description	Conditions When the Sampling Design is Useful[a]
Haphazard sampling	"Any sampling location will do" Take samples at convenient locations or times. Can lead to biased estimates.	A very homogeneous population over time and space is essential if unbiased estimates of population parameters are needed. This method of selection is *not* recommended due to difficulty in verifying this assumption.
Judgement sampling	Subjective selection by an individual. Select samples that appear to be "representative" of average conditions. Can lead to biased estimates. Accuracy is difficult to measure.	The target population should be clearly defined, homogeneous, and completely assessable so that sample selection bias is not a problem. Conversely, specific samples are selected for their unique value and interest rather than for making inferences to a wider population.
Simple random sampling	Each population unit has an equal chance of being selected for measurement. Selection of one unit does not influence selection of other units.	The simplest random sampling design. Other designs below will frequently give more accurate estimates of means if the population contains trends or patterns of emission rates.
Stratified random sampling	Divide target population into nonoverlapping parts. Sampling locations are selected from each stratum by simple random sampling.	Useful when a heterogeneous population can be broken down into parts that are internally homogeneous. For example, solvent usage might be stratified according to the end product produced.
Multi-stage sampling	Divide target population into primary units. Select a set of primary units using simple random sampling. Randomly subsample each of the selected primary units. Example: collect soil samples (primary units) at random, then select one or more aliquots at random from each subsample.	Needed when measurements are made on subsamples of the field sample. This technique has limited applicability to emissions inventory development.
Cluster sampling	Clusters of individual units chosen at random. All units in chosen clusters are measured.	Useful when population units cluster together (schools of fish, clumps of plants, etc.) and every unit in each randomly selected cluster can be measured. This techniques has limited applicability to emissions inventory development.

Table 5-1

Types of Survey Sampling Methods

Method	Description	Conditions When the Sampling Design is Useful[a]
Systematic sampling	Take measurements at locations and/or times according to a spatial or temporal pattern. For example: at equidistant intervals along a line or on a grid pattern.	Usually the method of choice when estimating trends or patterns of emissions over space. Also useful for estimating the mean when trends and patterns are not present or they are known a priori or when strictly random methods are impractical.
Double sampling	If data using one measurement technique has a strong linear relationship to data obtained with less expense or effort using another measurement technique, more samples can be taken using the less expensive method. The linear relationship between the two techniques is then applied to estimate the mean for the more expensive method.	Useful when there is a strong linear relationship between the variable of interest and a less expensive or more easily measured variable.
Search sampling	Used to geographically locate pollution sources or to find "hot spots" of elevated contamination.	Useful when historical information, site knowledge, or prior samples indicate where the object of the search may be found. This technique has limited applicability to emissions inventory development. This approach, however, could be used to develop information that would describe the spatial characteristics of emissions in relationship to a specific parameter (for example, lawn and garden equipment use versus household income).

[a] Gilbert, 1987.

discussions on this subject such as the text books *Sampling Techniques* (Cochran, 1977) and *Statistical Methods for Environmental Pollution Monitoring* (Gilbert, 1987).

The concept of a stratified random sampling approach can be very useful for developing area source emissions estimates, as well as developing data for use in multivariate emissions models. In this technique, the population of N units is divided into subpopulations N_1, N_2,...,N_L units. These subpopulations, or strata, are nonoverlapping, and together they comprise the entire population. When the strata have been determined, a sample is drawn from each, with drawings made independently in different strata. The sample sizes are denoted by n_1, n_2,...n_L, respectively. From an emissions inventory perspective, the primary reason for conducting this type of sampling approach is to divide a heterogeneous population into subsets, each of which is more likely to be internally homogeneous. A conceptual example is provided below.

Example 5-1

Most urban areas with a diversified economy contain numerous, small manufacturing facilities which may be using solvents, primarily through coating, degreasing, or wipe cleaning operations. Many of these facilities will not be included in the point source inventory and will be comprised of numerous, diverse manufacturing operations (e.g., wood products manufacture and coating; plastics coating; miscellaneous metal parts manufacture and coating; etc). Due to the large number of operations and their differences in raw material and production characteristics, it is necessary to develop a survey approach that will accurately collect information that can be statistically extrapolated to the entire population of non-point source facilities. A stratified random survey can be used to solve this problem.

The first stratum might divide the facilities into groups based on two digit CMAP code so that like facilities are grouped together (i.e., facilities manufacturing like materials are likely to have similar emission characteristics). A second stratum might be considered necessary to distinguish between large and smaller facilities to prevent biases resulting from the different rates of material usage that could occur because of facility operating efficiency. Once the survey is completed and emissions have been calculated, the emissions data can be correlated with the strata used to define the subpopulations, in this case two digit CMAP and number of employees.

5.4 Determination of Sample Size

The number of surveys that are mailed out will be dependent upon available resources and initial goals established for the accuracy of the results. This subsection provides a brief overview of the statistical procedures for selecting an appropriate sample size given a specified accuracy goal. For a more through explanation of the following material, please consult a standard text book on statistics.

For many area source surveys, the goal is to establish an average value for a particular set of parameters that can be used to estimate emissions for the entire population of sources. For example, the average amount of coating material may be determined, or the average amount of liquefied petroleum gas (LPG) used per household. In general, the "error" or uncertainty in the average value developed from the survey results can be minimized by sampling more and more sources. The uncertainty in the mean value (x) can be stated as follows:

$$\mathbf{x = \pm \quad A} \qquad (5\text{-}1)$$

where: = The sample standard deviation
A = t statistic divided by the number of samples ($t/\sqrt{n}$).

The t statistic varies with sample size and desired level of confidence. As more samples are taken, the level of uncertainty in the average value decreases. However, a point of diminishing returns is quickly reached as the number of samples approaches 20. Figure 5-3 illustrates this concept by plotting A (i.e., $t/\sqrt{n}$) versus number of samples taken. This particular plot is for a 90% confidence level.

If desired, a more rigorous approach to determining the appropriate sample size can be determined by specifying the amount of acceptable error. Establishing the sample size based on acceptable error requires an iterative approach that begins with an initial survey. Assuming a 50% response rate, limit the initial survey to approximately 40 questionnaires so that

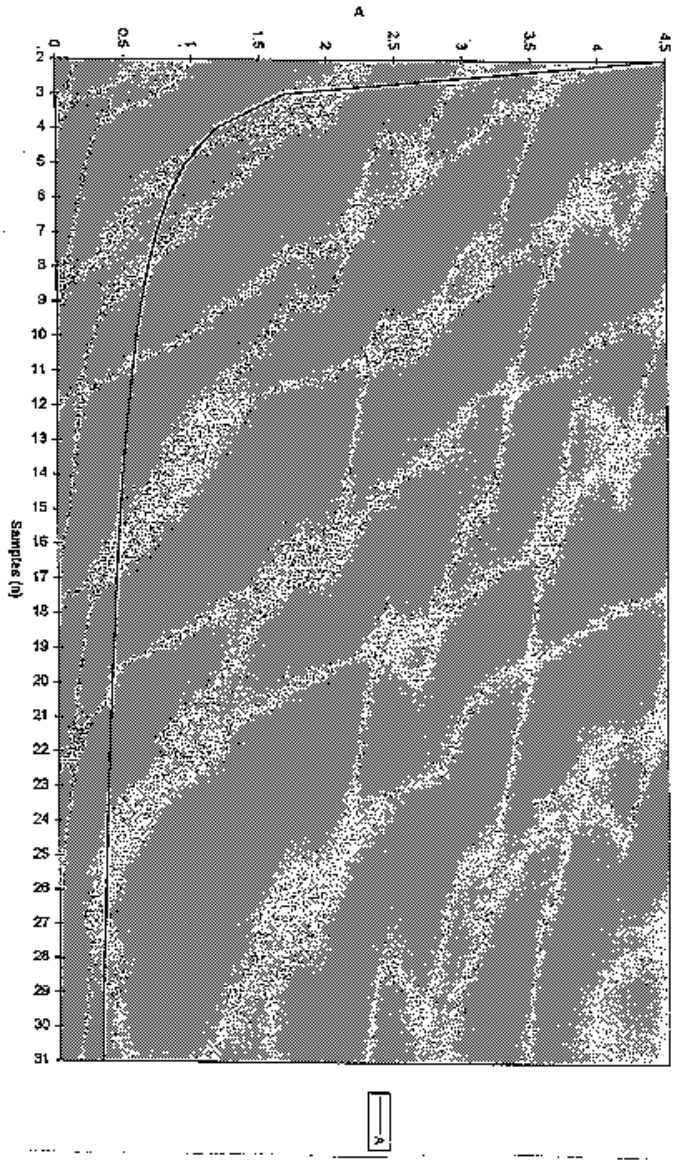

Figure 5-3. Influence of Sample Size on Uncertainty

about 20 responses are received. From the results of the initial survey, a specific sample size can be estimated based the survey error goals:

$$n = \left(\frac{Z_{/2}}{e} \right)^2 \qquad (5\text{-}2)$$

Where:

n	=	sample size
	=	standard deviation of the population
e	=	limit of error (usually in the range of 5 to 10 percent of the value of the mean)
	=	confidence level
$Z_{/2}$	=	index derived from the normal curve which corresponds to the desired confidence level:

percent	$Z_{/2}$
95	1.96
99	2.58
99.7	3.00
90	1.65

A simple example illustrating this concept is presented below for a hypothetical survey applied to residential LPG usage.

Example 5-2

Assume that no more than a 10% error at the 90% confidence level is desired for a survey of residential LPG usage. From the hypothetical survey, the average LPG usage determined from the initial questionnaires is 1,000 liters with a standard deviation of 400 liters. Using these data in equation 5-2, the number of needed samples is:

$$n = \left(\frac{1.65 \ x \ 400}{0.10 \ x \ 1{,}000} \right)^2$$

$$= 44 \text{ samples}$$

5.5 Limiting the Size of the Mail Survey

If more sources are identified on the mailing list than can be realistically handled with available resources, an agency should screen the mailing list in some manner to reduce the number of facilities to be sent questionnaires. This can be done in a number of ways.

In many instances, the number of employees in a company will be known, and an estimate of the emissions potential can be made by applying emissions per employee factors where available. This will provide a rough estimate of the emissions potential of those facilities, which can then be used to select a sample of facilities that represent a range of emissions to receive the questionnaire. Another way to reduce the mailing list is to contact the intended recipients of the survey by telephone before mailing the survey. These brief contacts with plant managers or other appropriate employees will indicate whether the pollutant emitting process takes place at the facility. If the process is not used at the facility, this response can be recorded and no further contact with the facility is necessary thus reducing the number of surveys that are sent out.

5.6 Designing the Questionnaires

A questionnaire should be prepared for each source category that is surveyed. These questionnaires can use industry-specific terminology that is familiar to those working in a particular industry, which will enhance communication, reduce confusion, and increase inventory accuracy. It may also be productive to first work with a small focus group of sources in the industry to refine and “test market” the questionnaire. Input from knowledgeable industrial personnel will help to eliminate ambiguity in responses and misunderstandings about the goals of the survey. Although a survey questionnaire that is tailored to a particular industry or process has many advantages, there are also several disadvantages. One disadvantage is that designing many industry-specific questionnaires can require significant resources. Second, the returned questionnaires will have different data storage requirements because of the variations in format for different industries.

Developing a questionnaire involves identifying and writing the appropriate questions, establishing a suitable format, and developing a cover letter and instructions for filling out the questionnaire. The basic rule is to design the questionnaire for the person who will be asked to complete it. An agency should consider that the person who will complete the questionnaire may not have the benefit of a technical background in air pollution, engineering, or physical sciences. Hence, questionnaires and instructions should not be designed to require specialized technical training to be understood. Each question should be self-explanatory or accompanied by clear directions. All necessary information should be solicited on the questionnaire, thus avoiding later requests for additional data. Any additional data needed for subsequent application of a dispersion or photochemical model should also be collected at this time.

The format of the questionnaire should be as simple and functional as possible. When data handling is to be done by computer, time will be saved if the questionnaire format is designed such that the data entry personnel can readily enter the information directly from each questionnaire. If computerized data reporting is encouraged, agency time may be saved on data entry. The questionnaire should be well-spaced for easy readability and should have sufficient space for complete written responses. The questionnaire should be as short as possible; lengthy questionnaires are intimidating. Also, shorter questionnaires reduce postal costs.

The ultimate use of the data should always be considered when determining the information to request on the questionnaire. For point sources, process information should also be requested, in addition to emission rates and general source information such as location, ownership, and nature of business. An effort should be made to request activity level data for the appropriate inventory year and inventory season. If data for the appropriate time period cannot be obtained, questions should be included that will collect the information needed to derive temporal adjustment factors as accurately as possible. Control device information is also helpful for determining potential reductions in emissions from applying various control strategies.

Finally, any information that is needed to make corrected or adjusted emissions estimates should be solicited. For example, because emissions from petroleum product storage

and handling operations are dependent on a number of variables, including temperature, tank conditions, and product vapor pressure, the questionnaire should include requests for appropriate values for these variables. If seasonal adjustments are considered, special emphasis should be given to variables such as activity levels, temperature, and wind speed that cause seasonal variations in emissions.

Each questionnaire should be accompanied by a cover letter stating the purpose of the inventory and citing any statutes that require a response from the recipient. Cooperation in filling out and returning the questionnaire should be respectfully requested. In addition, each questionnaire should be accompanied by a set of general procedures and instructions telling the recipient how the questionnaire should be completed and the date it should be returned to the agency. In lieu of a specific reply date, a specific number of calendar or working days in which to respond can be indicated. In this manner, delays in mailouts will not require changing the reply date.

If a more general questionnaire is sent out, the instructions should carefully explain that the questionnaire has been designed for a variety of operations and that some questions or sections of the questionnaire may not apply to a particular facility. In all cases, a contact name, telephone number, and mailing address should be supplied in case a recipient has questions. The cover letter and instructions can be combined in some cases, but this should only be done when the instructions are brief.

5.7 Mailing and Tracking the Questionnaires

After the final mailing list has been compiled and the appropriate questionnaire packages are assembled (including mailing label, cover letter, instructions, questionnaires, and self-addressed stamped envelope), an agency should proceed with the mailout activities. The mailing of the questionnaires can be performed in two ways. The first method is by registered mail, which serves to inform the agency when a questionnaire is received by the company. This does not guarantee that the company will return the form, but the response rate will probably be somewhat greater than if the questionnaires are sent by first-class mail. However, the slight

increase in response may not justify the added expense of sending every company a registered letter. As a compromise, registered mail may be used to contact only larger sources.

The second method is to send the questionnaires by conventional first class mail. This method has proven to be effective if the mailing address includes the name of the plant manager or if "ATTENTION PLANT MANAGER" is printed on the outside of the envelope. This directs the envelope to the proper supervisory personnel and reduces the chances of the questionnaire package being discarded. It is highly recommended that a stamped envelope be included with each questionnaire because the questionnaire is then more likely to be returned.

Incorrect mailing addresses are a large part of unreturned questionnaires; therefore, the extra effort applied to obtaining correct addresses will be rewarded. Also, it is important to distinguish between facility physical location and mailing address. Identifying the mailing address can have a critical effect on the questionnaire response rate.

Responses may begin arriving within a few days after mailing. Many of the early returns may be from companies that are not sources of emissions. Also, some of the questionnaires will be returned to an agency by the postal service because either the establishments are out of business or the company is no longer at the indicated mailing address. New addresses for companies that have moved can be obtained by calling the establishments, looking up their addresses in the telephone book, or contacting an appropriate state or local agency, such as the tax or labor departments.

A simple computer program can be helpful in mailing and logging in the questionnaires. Such a program should be designed to produce a number of duplicate mailing labels for each source sent a questionnaire. One label is attached to the outside of the envelope containing the questionnaire materials. A second label is attached to the cover letter or instruction sheet of the questionnaire. This facilitates the identification of the questionnaires as they are returned, as well as name and mailing address corrections. Additional mailing labels may be used for other administrative purposes or to recontact those sources whose responses are inadequate. Information for an example label is shown below:

Example 5-3

0000 (CMAP Code)
0000 (Plant Number)

INDIVIDUAL'S NAME and TITLE (or PLANT MANAGER)
COMPANY NAME
STREET
MUNICIPALITY, STATE, ZIP CODE

As shown above in the example label, it may be helpful to print the CMAP code and the assigned facility identification number on the upper right corner of the labels. The identification (ID) number can be used to group records of all correspondence with one company. If the study area is large, a municipality identification number may also be included on the mailing label. Be careful to separate the internal coding information from the address so that the Post Office does not confuse these items with the address.

It is important to develop a tracking system to determine the status of each facet of the mail survey. Such a tracking system should tell an agency: (1) to which companies questionnaires were mailed; (2) the dates the questionnaires were mailed and returned; (3) corrected name, address, and CMAP information; (4) information on the type of the source; (5) whether recontacting is necessary; and (6) the status of the follow-up contact effort. Tracking can be accomplished manually through the use of worksheets or through the use of a simple computer program. A computer printout of the mailing list can be formatted for use as a tracking worksheet.

As soon as the questionnaires are returned, some useful analyses can be performed. One activity that can help enhance the timely completion of the mail survey, as well as assist in estimating the amount of resources that will be subsequently needed in the inventory effort, is to classify each response in one of the five categories listed below:

P = point source
A = area source

N = no emissions (non-source)
C = closed/out of business
R = recontact for reclassification

In addition, an agency can begin performing emissions calculations for sources that have responded, and the resulting source and emissions information can begin to be loaded into the inventory files. All responses should then be filed by CMAP code, source category, geographic location, alphabetical order, or any other criteria that provide orderly access for additional analysis.

5.8 Recontacting

The agency may have to recontact a company if it does not return the questionnaire or if the response provided is inadequate. If a company does not return the questionnaire as requested, a more formal letter citing statutory reporting requirements for completing the questionnaire should be sent via registered mail. When the number of companies to be recontacted is small, the information can be obtained through telephone contacts or plant visits.

Recontacting activities should begin two to four weeks after the questionnaires are mailed. Telephone calls are advantageous when recontacting companies in that direct verbal communication is involved and additional mailing costs can be avoided. A second follow-up mailing may be necessary if a large number of companies must be recontacted. In either case, recontact should be completed 8 to 12 weeks after the first mailing.

5.9 Accessing Agency Air Pollution Files

An agency may have special files or databases that can be accessed for use in emissions inventory development. These files may include permit files, compliance files, or emissions statements. Permits are typically required for construction, startup, modifications, and continuing operation of an emissions source. Permit applications generally include enough information about a potential source to describe the nature of the source and to estimate the

magnitude of emissions that will result from its operations. Some permits also include source test data.

Some agencies may also maintain a compliance file, which records the agency's interaction with each source on enforcement matters. For example, a compliance file might contain a list of air pollution regulations applicable to a given source, a history of contacts made with that source on enforcement matters, and an agreed-upon schedule for the source to effect some sort of control measures.

5.10 Scaling Up the Survey Results

A properly designed area source survey effort will also include a mechanism for "scaling up" the survey results. By the nature of the source type, it may not be possible to survey the universe of sources covered by the category. The method for scaling the results will depend on the type of source that is included in the survey effort. Two examples are provided below.

In the simplest sense, the survey results could be scaled up by applying the average material usage (or emissions) determined from the survey effort to the population of sources. From an emissions perspective, this approach assumes that the population of sources is size independent. For example, a survey of residential LPG usage could be performed to more precisely estimate the amount of this fuel consumed on a residential level. Surveying each home is not practical; therefore, a subset of population would be surveyed and the results scaled to the entire population. For this hypothetical example, the average amount of LPG used per household would be determined through the survey with the average value applied to the total number of households in the region. A simple example follows:

Example 5-4:

Based on a survey of a subset of the households using LPG, the average annual use of LPG is 1,000 liters/yr. Available census data indicate that there are 500,000 households in the region and that 90% of them use LPG as a residential fuel. Estimate the total NO_x emissions from household use of LPG in the region.

Q_{LPG} = 1,000 liters/household/yr x 500,000 households x 90%
= 450 million liters/yr

EF_{NOx} = 1.7 kg/1,000 liters (AP-42, Section 1.5)

E_{NOx} = Q_{LPG} x EF_{NOx}
= (450 x 10^6 liter/yr) x (1.7 kg/1,000 liters)
= 765,000 kg NO_x/yr

If the material usage is expected to vary by source size, then a more complex approach is required. For example, the amount of coating material used in wood coating operations will vary based on the production level of the facility. The survey design must include questions that collect sufficient information that can be used to scale the results to other facilities that were not included in the survey effort. These data can consist of such things as the number of employees, or economic parameters such as the value of goods or services produced. The key is to think ahead and identify appropriate parameters that can be used to scale the inventory results to other sources. A simple example follows:

Example 5-5:

Based on a survey of a subset of the facilities manufacturing wood products, the average coating usage per employee is 30 liters/yr. The total number of employees in the region involved in wood products manufacturing is 1,050 based on data from CANACINTRA. Additionally, the survey results indicate that the average coating has a density of 1.4 kg/liter and is 45% VOC by weight. Estimate the total VOC emissions from wood products manufacturing in the region.

$Q = 30 \text{ liter/employee/yr} \times 1{,}050 \text{ employees}$
$= 31{,}500 \text{ liter/yr}$

$EF_{VOC} = 1.4 \text{ kg/liter} \times 45\%$
$= 0.63 \text{ kg/liter}$

$E_{VOC} = Q \times EF_{VOC}$
$= 31{,}500 \text{ liter/yr} \times 0.63 \text{ kg/liter}$
$= 19{,}845 \text{ kg VOC/yr}$

6.0 EMISSION FACTORS

Emission factors are commonly used to calculate emissions when site-specific stack monitoring data are unavailable. An emission factor is a ratio that relates the quantity of a pollutant released to the atmosphere to a unit of activity. Emission factors can generally be classified into two types: process-based and census-based. Process-based emission factors are commonly used to develop point source emission estimates, and are often combined with the activity data collected from a surveying or material balance approach. Census-based emission factors, on the other hand, are widely used to develop area source emission estimates (see Figure 6-1).

6.1 Process-Based Emission Factors

Various source sampling programs have been conducted to measure emission rates from certain devices or processes known to be air emission sources. Since source testing of every individual emission source is often not required or economically feasible, the source test results from "representative sources" are used to develop process-based emission factors for similar device types or processes. These process-based emission factors are expressed in the general form of mass of pollutant emitted/process unit. Some common process units are energy input, material throughput, production units, operating schedule, or number of devices, or device characteristic (e.g., lb/MMBtu, lb/gal, lb/batch, lb/hr, lb/flanges or lb/sq ft [surface area]).

The most comprehensive source for U.S.-specific process-based emission factors is *AP-42 Compilation of Air Pollutant Emission Factors* (U.S. EPA, January 1995a). The primary reference for toxic air pollutant emission factors is the FIRE data system (U.S. EPA, 1995b).

Non-U.S.-specific emission factors for various source aggregates are available from the *Rapid Source Inventory Techniques* guidance document developed for the WHO (Economopoulos, 1993) and various GHG inventory guidance documents (Intergovernmental Panel on Climate Change [IPCC], 1993a and b).

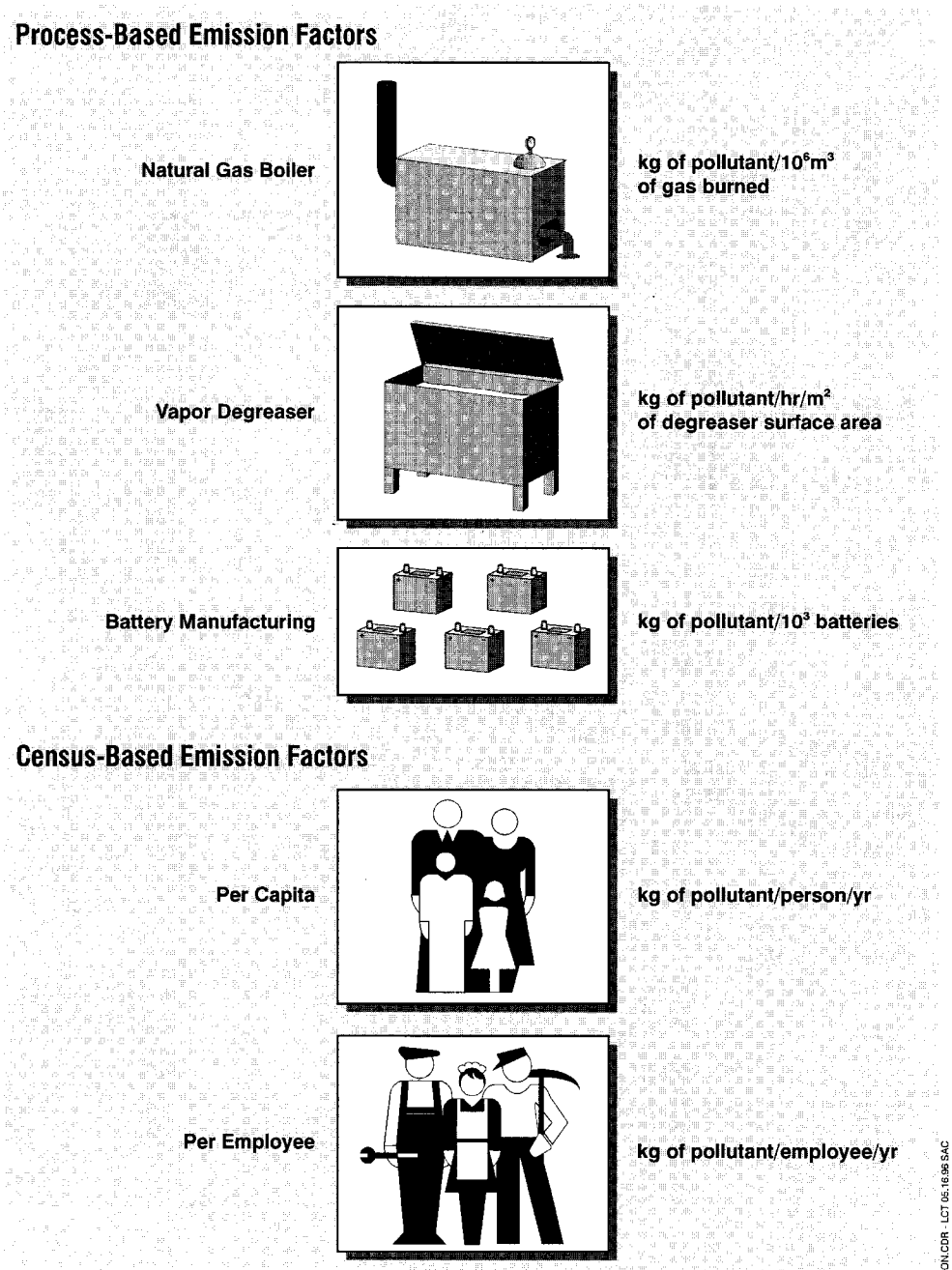

Figure 6-1. Examples of Emission Factors

Below are a few sample calculations of emission estimates developed using process-based emission factors. Volume IV - Point Sources provides more detailed guidance on developing point source emission estimates.

Example 6-1:

Calculate the annual NO_x emissions from an uncontrolled utility boiler (> 100 million Btu/hr heat input) burning natural gas. The annual throughput of natural gas is 50 million cubic meters.

EF_{NOX} = 8800 kg/$10^6 m^3$ (From AP-42, Table 1.4-2)
Q_{fuel} = 50 $10^6 m^3$/yr

E_{NOX} = EF_{NOX} x Q_{fuel}
= 8800 x 50
= 440,000 kg/yr

Example 6-2:

Calculate the annual VOC emissions from an uncontrolled open-top vapor degreaser. The solvent used is 100 percent VOC. The degreaser has a surface area of 5 cubic meters and operates 8 hours/day, 5 days/week, 52 weeks/year.

EF_{VOC} = 0.7 kg/hr/m^2 (From AP-42, Table 4.6-2)
A = 5 m^2
T_{hours} = 8 hrs/day x 5 days/wk x 52 wks/yr
= 2080 hrs/yr

E_{VOC} = EF_{VOC} x A x T_{hours}
= 0.7 x 5 x 2080
= 7,280 kg/yr

Example 6-3:

Calculate the PM emissions from the grid casting step of the production of lead acid storage batteries. Twenty thousand batteries are produced each month.

EF_{PM}	=	1.42 kg/10^3 batteries	(From AP-42, Table 7.15-1)
$Q_{product}$	=	20,000 batteries/month x 12 months/yr	
	=	240,000 batteries/yr	
E_{PM}	=	EF_{PM} x $Q_{product}$	
	=	1.42 x 240	
	=	341 kg/yr	

6.2 Census-Based Emission Factors

Sources in certain area source categories are difficult to inventory by any of the previously discussed methodologies. The use of census-based emission factors is an efficient method for dispersed and numerous emission source types that cannot be readily characterized by a knowledge of process rates, fuel consumption rates, and/or material feed rates. Compared to the other emission estimating techniques, the use of census-based emission factors is the most "user-friendly" and cost-effective choice, since census data are readily available in most emission inventory regions. In Mexico, population and housing data, and employment data by economic sector and municipality are available in printed and electronic format from the INEGI.

The disadvantage of using existing census-based emission factors is that most of them were developed in the U.S. or Europe and may not account for the socioeconomic conditions and control practices in Mexico. The Department of the Federal District (DDF) has begun to develop Mexico-specific census-based emission factors. For example, the U.S. per capita emission factor for consumer solvents is 6.3 pounds/person/year (i.e., 2.86 kilograms/person/year). For the Mexico City area source inventory, DDF has recently reduced the aerosol contribution from 0.36 kg/person/yr to 0.05 kg/person/yr, thus adjusting the overall consumer solvents per capita emission factor to 2.55 kilograms/person/yr.

Also, it is important to remember that census-based emission factors are more accurate when applied to the entire region for which the emission factor was developed than when applied to smaller regions. For example, the Mexico-specific per capita emission factor for aerosols developed by DDF is an "average" emission factor for the entire country (i.e., it was based on national population and aerosol usage data). The accuracy of this emission factor decreases as it is applied to smaller regions. For example, if the per-capita consumption of aerosols in Xochimilco is higher than the national average, then use of the "average" emission factor will result in an underestimation of emissions for Xochimilco).

Per-employee emission factors are generally more accurate than per capita emission factors, since higher levels of employment reflect economic growth and, more specifically, tend to reflect rises in pollution-generating activity levels. However, care should be taken to eliminate employment data that are associated with non-manufacturing (e.g., administrative and clerical) jobs, whenever possible, since they are not likely to contribute significantly to pollution-generating activity levels. At a minimum, an effort should be made to eliminate employment data associated with company locations that are administrative offices rather than production plants.

6.2.1 Per Capita Emission Factors

Solvent evaporation from consumer and commercial products such as waxes, aerosol products, and window cleaners cannot be routinely determined for many local sources by the local agency. In addition, it would probably be impossible to develop a survey that would yield such information. Using per capita factors assumes that emissions in a given area can be reasonably associated with population. This assumption is valid over broad areas for certain activities such as dry cleaning, architectural surface coatings, small degreasing operations, and solvent evaporation from household and commercial products.

Per capita emission factors should not be developed and used indiscriminately for sources whose emissions do not correlate well with population. For example, large, concentrated

industries, such as petrochemical facilities, should not be inventoried using per capita emission factors.

U.S.-specific per capita emission factors for various activities are available from several sources including the U.S. EPA's FIRE emission factor database, *AP-42 Compilation of Air Pollutant Emission Factors*, and *Procedures for the Preparation of Emission Inventories for Carbon Monoxide and Precursors of Ozone*, (U.S. EPA, 1991b).

Below is a sample calculation of an emissions estimate developed using per capita emission factors. Volume V - Area Sources provides more detailed guidance on developing area source emission estimates.

Example 6-4:

Calculate the 1990 VOC emissions from consumer aerosol usage in Xochimilco (D.F.). Assume that aerosols are 69% VOC. The 1990 population was estimated to be 642,753 people.

EF_{VOC} = 0.046 kg/person/yr x 69% VOC (From DDF, 1995)
= 0.032 kg/person/yr
$P_{Xochimilco}$ = 642,753 people

E_{VOC} = EF_{VOC} x $P_{Xochimilco}$
= 0.032 x 642,753
= 20,568 kg/yr

6.2.2 Per-employee Emission Factors

This approach uses employment rather than population as the surrogate activity level indicator. Per-employee emission factors are usually used to estimate emissions for those source categories for which a CMAPP has been assigned and for which employment data (typically by CMAP) are available at the local level. Generally, this involves manufacturing the appropriate CMAP categories. In most cases, a large fraction of VOC emissions within CMAP

will be covered by point source procedures, so the per-employee emission factor approach can be considered a secondary procedure to cover emissions from sources that are below the point source cutoff level. Point source reconciliation is discussed in more detail in the Area Sources Manual (Volume V).

The following sample calculation presents an emissions estimate developed using per capita emission factors. The Area Sources Manual (Volume V) provides more detailed guidance on developing area source emission estimates.

Example 6-5:

Calculate the annual VOC emissions from commercial dry cleaners in Mexico City (D.F.) for the area source inventory. Assume the dry cleaning solvents are 100% VOC. Assume that employment records for Mexico City show that there are 3,000 employees in the appropriate CMAP. Assume that 1,000 of these employees work at facilities that are included in the point source emissions inventory.

EF_{VOC} = 2,937 kg/employee/yr (EPA-450/4-91-016)
$E_{dry\ clean}$ = 3,000 total employees - 1,000 point source employees
= 2,000 area source employees

E_{VOC} = EF_{VOC} x $E_{dry\ clean}$
= 2,937 x 2,000
= 5,874,000 kg/yr

7.0 MATERIAL BALANCE

The material balance (also known as a mass balance) is a method commonly used for estimating emissions from many source categories. The material balance method can be used where source test data, emission factors, or other developed methods are not available. In fact, for some sources, a material balance is the only practical method to estimate emissions accurately. For example, source testing of low-level, intermittent, or fugitive VOC exhaust streams can be very difficult and costly in many instances.

Use of a material balance involves the examination of a process to determine if emissions can be estimated solely on knowledge of specific operating parameters and material compositions. Although the material balance is a valuable tool in estimating emissions from many sources, its use requires that a measure of the material being "balanced" be known at each point throughout the process. The material balance is most appropriate to use in cases where accurate measurements can be made of all but the air emission component. If such knowledge is not available, and is therefore, assumed, serious errors may result.

In the VOC emissions inventory, a material balance is generally used to estimate emission from solvent evaporation sources. This technique is equally applicable to both point and area sources. Point sources may use a material balance approach at the device or facility level, whereas area sources may use a material balance approach at the regional or national level.

Figure 7-1 illustrates a few examples of using a material balance approach for point sources. The simplest method of material balance is to assume that all solvent consumed by a source process evaporates during that process. For instance, it is reasonable to assume that during many surface coating operations, all of the solvent in the coating evaporates to the atmosphere during the drying process. In such cases, emissions are simply equal to the amount of solvent applied in the surface coating (and added thinners) as a function of time. As another example, consider a dry cleaning plant that uses Stoddard solvent as the cleaning agent. To estimate emissions, the agency needs only to elicit from each plant the amount of solvent

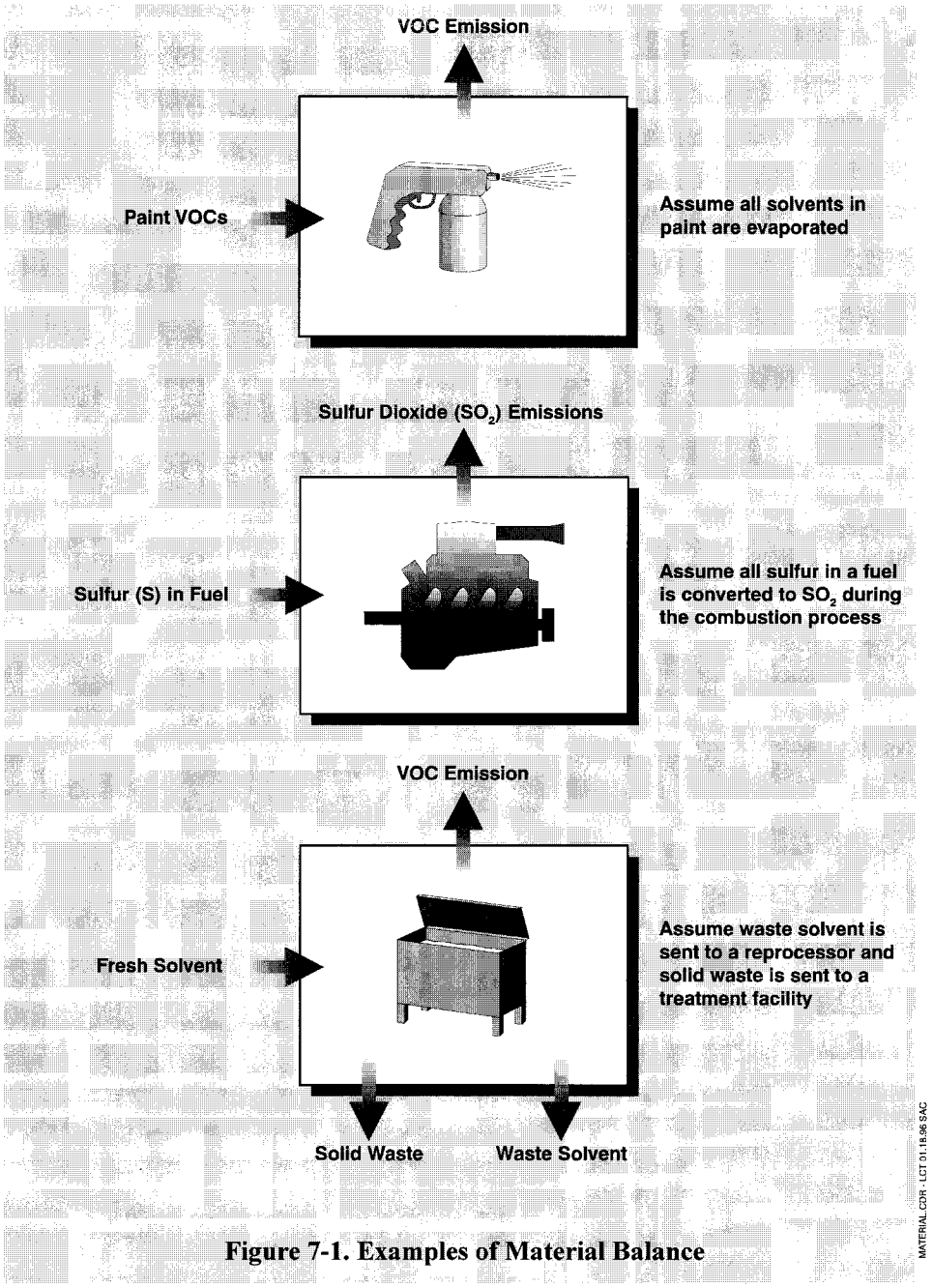

Figure 7-1. Examples of Material Balance

purchased during the time interval of concern, because the emissions are assumed equal to the quantity of solvent purchased.

The assumption that makeup solvent equals emissions also holds in certain more complicated situation. If a nondestructive control device such as a condenser or adsorber is employed, this assumption is valid to the extent that the captured solvent is returned to the process. Similarly, if waste solvent reclamation is practiced by a plant, by distillation or "boildown," this assumption will be applicable. Both of these practices simply reduce the makeup solvent requirements of an operation, and therefore, the quantity of solvent lost to the atmosphere.

Available test methods are published through the American Society for Testing and Materials (ASTM) and have focused on providing information on material balance and gravimetric determinations for various industrial processes (ASTM, Volumes 06.01 and 15.05). The use of a mass or material balance to determine total emissions from a process is usually simple and affordable. Total VOC emitted from a batch paint mixing process, for example, would be calculated as follows (according to ASTM Method D 2369):

$$\mathbf{VOC_{in}\ (lb/gal) - VOC_{mixed\ paint}\ (lb/gal) = VOC_{emitted}\ (lb/gal)} \qquad (7\text{-}1)$$

As another example, fuel analysis can be used to predict emissions based on application of conservation laws. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes toxic elements such as metals found in coal as well as other elements such as sulfur which may be converted to other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is:

$$E = Q_f \text{ x Pollutant concentration in fuel x } \left(\frac{MW_p}{MW_f}\right) \quad (7\text{-}2)$$

Where:
Q_f = Throughput of the fuel, mass rate (e.g., kg/hr)
MW_p = Molecular weight of pollutant emitted (lb/lb-mole)
MW_f = Molecular weight of pollutant in fuel (lb/lb-mole)

For instance, SO_2 emissions from oil combustion can be calculated based on the concentration of sulfur in the oil. This approach assumes complete conversion of sulfur to SO_2. Therefore, for every pound of sulfur (MW = 32 g) burned, two pounds of SO_2 (MW = 64 g) are emitted.

Example 7-1:

Calculate the hourly SO_x emissions (reported as SO_2) from an internal combustion engine burning diesel fuel, based on the fuel analysis data (i.e., sulfur content). The fuel throughput is estimated to be 150 liters/hr. The density of diesel is 0.85 kg/liter (7.1 lb/gal). The sulfur content of the diesel is 0.05% by mass.

Q_{fuel} = 150 liters/hr x 0.85 kg/liter
= 127.5 kg/hr
C_S = 0.05/100
= 0.0005
E_{SO2} = Q_{fuel} x C_S x (MW_p /MW_f)
= 127.5 x 0.0005 x (64/32)
= 0.13 kg/hr

In the above examples, the material balance is simplified, because of the assumption that all of the material being balanced is emitted to the atmosphere. Situations exist where this assumption is not always reasonable. For example, if a destructive control device such as an afterburner, incinerator, or catalytic oxidation unit is employed on the process exhaust, any VOC emissions will be either destroyed or so altered, that one could not reasonably assume, without testing the exhaust downstream of the device, the characteristics and quantities of any

remaining VOC material. As another example, degreasing emissions will not equal solvent consumption if the waste solvent is sold to a commercial reprocessor. In such a situation, emissions will be the difference of solvent consumed and solvent in the waste sent to the reprocessor. As still another example, some fraction of the diluent used to liquify cutback asphalt is believed to be retained in the pavement rather than evaporating after application.

Example 7-2:

Calculate monthly VOC emissions from a vapor degreaser. Each month, 100 liters of solvent is added at the beginning of the month. During the month, an additional 20 liters are added to replenish losses. At the end of the month, 100 liters of waste solvent is sent to a recycler and 0.2 kg of solid waste is collected for disposal. The solvent is 100% VOC. The waste solvent is 98% VOC. The solid waste is 5% VOC. The solvent density is 1.5 kg/liter.

$Q_{solvent}$ = (100 liters/month + 20 liters/month) x 1.5 kg/liter
= 180 kg/month

Q_{waste} = (100 liters/month x 1.5 kg/liter x 98% VOC) + (0.2 kg/month x 5% VOC)
= 147 kg/month + 0.01 kg/month
= 147 kg/month

E_{VOC} = $Q_{solvent}$ - Q_{waste}
= 180 - 147
= 33 kg/month

The above example shows that, in some cases, assuming total evaporation of all consumed solvent would result in an overestimation of emissions. Therefore, material balances can also be used in conjunction with process-based emission factors (see Section 6.1) to estimate emissions, such as those based on the difference between the raw material and the product when the emission factor for a process is per unit of material consumed.

For example, material balances could be performed for area source emission calculations involving fuel manufacture, distribution, and consumption (see Figure 7-2). A material balance for fuel distribution and consumption was recently applied in the United States

(De Luchi, 1993). A national material balance for solvents for surface coating materials may also be the best method for estimating VOC emissions from these source categories or pesticide application.

Several other situations can complicate the material balance. First, not all of the solvent losses from certain operations such as dry cleaning or degreasing occur at the plant site. Instead, significant quantities of solvent may be evaporated from the waste solvent disposal site, unless the waste solvent is incinerated or disposed of in a manner that precludes subsequent evaporation to the atmosphere. Generally, one can assume that much of the solvent sent to disposal sites will evaporate. The agency should determine whether some solvent associated with various operations evaporates a the point of disposal rather than at the point of use, since these losses may occur outside of the area covered by the inventory.

Material balances cannot be employed in some evaporation processes because the amount of material lost is too small to be determined accurately by conventional measurement procedures. As an example, applying material balances to petroleum product storage tanks is not generally feasible, because the breathing and working losses are too small relative to the total average capacity or throughput to be determined readily from changes in the amount of material stored in each tank. In these cases, AP-42 emission equations (i.e., models), developed by special procedures, should be applied.

In summary, with the exception of a few source types such as fuel and solvent use examples presented above, a material balance approach is not recommended as the primary method for estimating emissions. Rather, material balances may be more widely used as a top-down method to evaluate the reasonableness of emission estimates generated using other techniques.

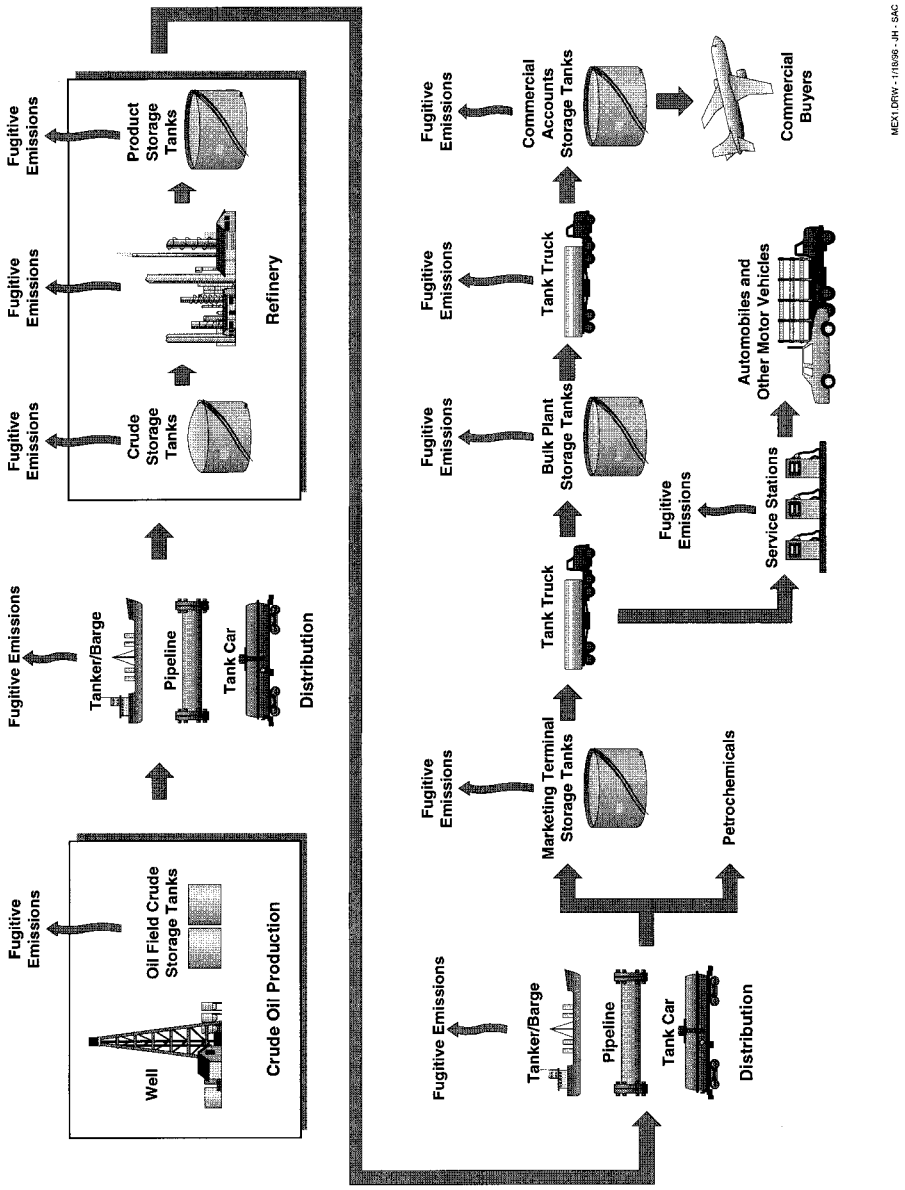

Figure 7-2. Example of Material Balance Highlighting Fugitive Emissions

8.0 EXTRAPOLATION

Extrapolation techniques can be used to calculate emissions directly and to verify the emission estimates calculated using another approach. Figure 8-1 illustrates the general concept of emissions extrapolation. Extrapolation of emissions from one geographic region to another is generally considered the least desirable approach for emissions estimation. Such an approach may not properly account for important differences between two regions and may propagate biases from one inventory to another.

When combined in a modeling framework, however, extrapolation will be a practical and cost effective approach to develop emission estimates for regions where there is insufficient information to support more rigorous emissions estimating methodologies. The rest of this section presents some examples of how an extrapolation approach may be used to develop emission estimates.

First, emissions data from one type of process or one facility may be extrapolated to similar source types or facilities. This type of extrapolation would be used to develop point source emission estimates.

In other cases, if it can be argued that the socioeconomic conditions between two or more geographical regions are comparable, then the available area source emissions data for one region can be extrapolated to the remaining regions based on population/employment data. Emissions inventories compiled in the U.S. and in Europe can be used in this manner. Within Mexico, emissions inventories that have been compiled for Mexico City and that are being developed for other areas (e.g., Monterrey metropolitan area) may be used as a basis for QA and/or development of portions of the emissions inventories for other regions.

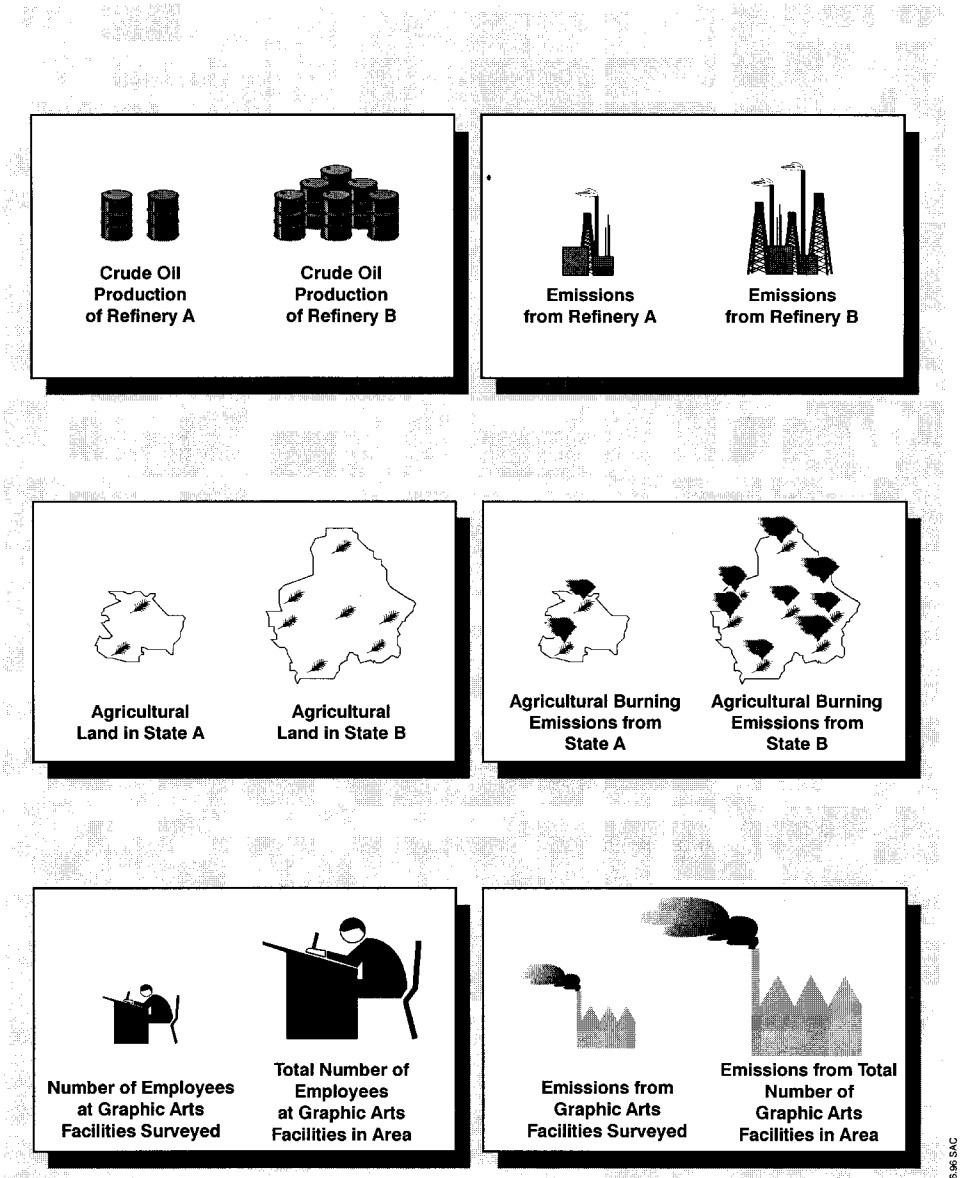

Figure 8-1. Examples of Extrapolation

Example 8-1:

Based on detailed emissions calculations for Refinery A, the total annual VOC emissions are estimated to be 100 tonnes (metric). The company has just purchased a smaller facility, Refinery B, which processes one-half as much crude oil as Refinery A. For a meeting tomorrow, the company president wants an estimate of the total cost that will be associated with permit fees for VOC emissions. Since there is no time for detailed emissions calculations for Refinery B, estimate the VOC emissions by extrapolating from Refinery A based on the refinery capacities (i.e., the amount of crude oil processed).

$$E_{VOCb} = E_{VOCa} \times P_{CRUDEb}/P_{CRUDEa}$$
$$= 100 \text{ tonnes/yr} \times 1/2$$
$$= 50 \text{ tonnes/yr}$$

Example 8-2:

Based on a surveying effort, the total annual VOC emissions from agricultural burning in State A are estimated to be 50 tonnes (metric). Resources are not available to fund a similar surveying effort in State B. Since the agricultural conditions are very similar in State B emissions (e.g., similar crops, agricultural methods, climate, etc.), estimate the VOC emissions by extrapolating from State A based on the area of agricultural land in each state. Land use maps show 400,000 m^2 of agricultural land in State A and 50,000 m^2 of agricultural land in State B.

$$E_{VOCb} = E_{VOCa} \times A_{AGb}/P_{AGa}$$
$$= 50 \text{ tonnes/yr} \times 50{,}000/400{,}000$$
$$= 6.25 \text{ tonnes/yr}$$

This approach can also be used when the agency surveys only a fraction of the area sources within a given category. In this case, employment is used as an indicator to "scale up" the inventory to account collectively for emission sources and emissions in the area source inventory. Parameters other than employment, such as sales data or number of facilities, can be used to develop emission estimates. However, employment is generally the most readily available parameter. Scaling up emission estimates is also discussed in Section 5.0 of this manual.

Example 8-3:

A surveying effort is conducted to collect VOC emission estimates from small graphic arts facilities in Coyoacan to use in the area source inventory for Mexico City. Due to resource constraints, the questionnaire is only sent to some facilities in Coyoacan, and not all the facilities that are included in the survey mailing list actually return the questionnaire. The total annual VOC emissions reported on the questionnaires is 100 tonnes (metric). Since resources are not available to survey each small graphic arts facility, estimate the VOC emissions for Coyoacan by extrapolating (i.e., scaling up) the collected VOC emissions based on employment. Available employment records show that 500 people in Coyoacan work in the graphic arts industry and the questionnaires show that a total of 125 people work at the facilities completing the survey forms.

$$E_{VOCcoy} = E_{VOCsur} \times P_{coy}/P_{sur}$$
$$= 100 \text{ tonnes/yr} \times 500/125$$
$$= 400 \text{ tonnes/yr}$$

9.0 REFERENCES

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APPENDIX III-A

SAMPLE CALCULATIONS FOR EMISSIONS MODELS

Sample Calculation—Fugitive Dust

$$M = VKT \times EF \tag{4-12}$$

where:
M = average annual mass emission rate, kg/yr;
VKT = vehicle kilometers traveled, VKT/yr;
EF = emission factor, kg/VKT.

$$EF = k(1.7)\left(\frac{s}{12}\right)\left(\frac{S}{48}\right)\left(\frac{W}{2.7}\right)^{0.7}\left(\frac{w}{4}\right)^{0.5}\left(\frac{365-p}{365}\right) \text{ (kg/VKT)} \tag{4-13}$$

$$EF = k(5.9)\left(\frac{s}{12}\right)\left(\frac{S}{30}\right)\left(\frac{W}{3}\right)^{0.7}\left(\frac{w}{4}\right)^{0.5}\left(\frac{365-p}{365}\right) \text{ (lb/VMT)} \tag{4-14}$$

where:
EF = emission factor;
k = particle size multiplier (dimensionless);
s = silt content of road surface material (%);
S = mean vehicle speed, km/hr (mph);
W = mean vehicle weight, Mg (ton);
w = mean number of wheels;
p = number of days with a least 0.254 mm (0.01 in.) of precipitation per year.

Calculate annual PM_{10} emissions (i.e., using an aerodynamic particle size multiplier of 0.36) from rural dirt roads with an average silt content of 12 percent. Assume the mean vehicle weight is 4 Mg, the mean vehicle speed is 25 km/hr, and the mean number of wheels is four. Also, the mean number of days with greater than 0.254 mm precipitation is 40 and the vehicle kilometers traveled is 3,650,000 km/yr.

$$EF = (0.36)\ (1.7)\left(\frac{12}{12}\right)\left(\frac{25}{48}\right)\left(\frac{4}{2.7}\right)^{0.7}\left(\frac{4}{4}\right)^{0.5}\left(\frac{365-40}{365}\right)$$

$$= 0.3737 \text{ kg/VKT}$$

$$M = (3{,}650{,}000) \times (0.3737)$$

$$= 1{,}364{,}000 \text{ kg } PM_{10}\text{/yr}$$

Sample Calculation—Landfills

$$Q_{CH4} = L_o \times R \times (e^{-kc} - e^{-kt}) \quad (4\text{-}11)$$

where:

Q_{CH4}	=	methane generation rate at time t, m^3/yr;
L_o	=	methane generation potential, m^3CH_4/Mg refuse;
R	=	average annual refuse acceptance rate during active life, Mg/yr;
e	=	base log, unitless;
k	=	methane generation rate constant, yr^{-1};
c	=	time since landfill closure, yrs (c=0 for active landfills); and
t	=	time since the initial refuse placement, yrs.

Calculate annual methane emissions from an active landfill that has been open for 15 years and has accepted refuse at an average rate of 10,000 Mg/yr. Assume a methane generation potential of 125 m^3/Mg and a methane generation rate constant of 0.02/yr

$$Q_{CH4} = (125\ m^3\ Mg) \times (10{,}000\ Mg/yr) \times (e^{-(0.02/yr)\ (0\ yr)}\ e^{-(0.02/yr)\ (15\ yr)})$$

$$= 125 \times 10{,}000 \times (1 - 0.7408)$$

$$= 324{,}000\ m^3\ CH_4/yr$$

Sample Calculation—Fugitive Dust

Sample Calculation—Landfills

Sample Calculation—Storage Tanks

Sample Calculation—Petroleum Products Loading

Sample Calculation—Waste & Wastewater

APPENDIX III-B

HOW TO OBTAIN U.S. EPA AIR EMISSION ESTIMATING TOOLS

APPENDIX III-C

SAMPLE POINT SOURCE QUESTIONNAIRE (I.E., INE'S ENCUESTA INDUSTRIAL)