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REPORT**

Minimizing Mercury Emissions in Biosolids Incinerators

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MINIMIZING MERCURY EMISSIONS IN BIOSOLIDS INCINERATORS

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Frontier GeoSciences, Inc.

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ABSTRACT AND BENEFITS

The U.S. Environmental Protection Agency (U.S. EPA) has a goal to reduce levels of persistent bio-accumulative toxicants in the environment. Mercury is classified as such. Proactively, the Water Environment Research Foundation funded research related to mercury characterization, measurement, and minimization in publicly owned treatment works (POTWs) that practice biosolids incineration in the United States. In this study, surveys of POTWs determined analytical techniques employed for all matrices, biosolids incinerator design and operational parameters, testing frequency, and historical data. A comprehensive literature review gathered information to summarize current understanding of mercury speciation in combustion gas. This is a critical piece of information needed to develop any mercury minimization strategy. Technology applied to other mercury emission sources (i.e., coal-fired utilities, municipal waste combustors, medical waste incinerators, hazardous waste combustors, crematories, and industrial boilers) is presented in this report. Only limited information is available concerning mercury speciation cycling throughout a biosolids incinerator facility. A more complete understanding of mercury speciation will allow designers and operators to better control mercury. Mass balance studies are an important component of understanding mercury cycling in biosolids incineration, but few studies exist. Therefore, guidance for mass balance study design and application is also included in this report. Overall, the study showed that relative to other sources of mercury emissions (e.g., coal-fired utilities) in the United States, biosolids incinerators emit much lower quantities and are a minor source.

Benefits:

- ◆ Presents up-to-date information regarding current analytical methods used by the wastewater industry.
- ◆ Provides a detailed explanation of mercury speciation in combustion gases and how mercury speciation drives the efficacy of control technology.
- ◆ Evaluates control technology applied to related industries for mercury abatement.
- ◆ Surveys and evaluates next-generation methods for mercury monitoring in combustion gas.
- ◆ Provides step-by-step instructions for mass balance studies necessary to evaluate biosolids incinerators and identify likely control technology.

Keywords: Mercury, biosolids, control technology, emissions, mass balance, incineration.

TABLE OF CONTENTS

Acknowledgments.....	iii
Abstract and Benefits.....	iv
List of Tables.....	viii
List of Figures.....	x
List of Acronyms.....	xiii
Executive Summary.....	ES-1
1.0 Introduction.....	1-1
1.1 Background.....	1-1
1.2 Mercury Emissions.....	1-4
2.0 Mercury in a Biosolids Incinerator.....	2-1
2.1 Combustion Chemistry of Mercury in Coal-Fired Flue Gas Compared to Biosolid Incinerators.....	2-1
2.1.1 Coal Combustion.....	2-1
2.1.2 Biosolids Incineration.....	2-4
2.2 Mercury in Biosolids Incinerators.....	2-5
2.2.1 Source Control.....	2-6
2.2.2 Parameters Affecting Mercury Speciation in a Biosolids Incinerator.....	2-7
3.0 Air Pollution Control Devices in a Biosolids Incinerator.....	3-1
3.1 Air Pollution Control Devices.....	3-1
3.1.1 Venturi Scrubber.....	3-1
3.1.2 Impingement Tray Scrubber.....	3-3
3.1.3 Common Trays.....	3-4
3.2 Combination Systems.....	3-4
3.3 Baghouse.....	3-4
3.4 Electrostatic Precipitators.....	3-6
3.5 Impact of Mercury Speciation on Co-Benefit Removal by Existing APCDs.....	3-7
4.0 Current Practices for Reduction of Mercury Emissions Beyond APCD Co-Benefit.....	4-1
4.1 Mercury Control in Coal-Fired Electric Generating Units.....	4-1
4.1.1 Enhancing Wet Scrubbers for Mercury Capture.....	4-2
4.1.2 Methods to Capture Hg ⁰ and/or Sequester Captured Hg ^{II} in Wet Scrubbers.....	4-3
4.1.3 Mercury Capture by Spray-Dryer Adsorbers and Fabric Filters.....	4-4
4.1.4 Halide Addition.....	4-4
4.1.5 Mercury Capture by Activated Carbon Injection in Coal-Fired Utilities.....	4-4
4.1.6 Mercury Capture by Activated Carbon in Biosolids Incinerators.....	4-6
4.1.7 Mercury Capture in Coal-Fired Utilities by Novel Methods.....	4-7
4.1.8 Other Incineration or Combustion Processes.....	4-8

4.2	Municipal Waste Combustors	4-9
4.3	Medical Waste Incinerators	4-11
4.4	Hazardous Waste Combustors	4-11
4.5	Commercial, Industrial, and Residential Boilers	4-11
4.6	Crematories	4-12
4.7	Enersludge™ Process	4-12
5.0	Mercury Test Methods Available to Biosolids Incinerators	5-1
5.1	Analytical Methods for the Determination of Mercury in a Biosolids Incinerator Mass Balance.....	5-1
5.1.1	Sample Collection (Clean Technique)	5-1
5.1.2	Sample Processing	5-2
5.2	Method Detection Limit versus Reporting Limit, Method Quantitation Limit or Practical Quantitation Limit	5-3
5.3	Analysis of Liquids	5-3
5.3.1	Cold Vapor Atomic Absorption Spectroscopy (CVAAS) for Determination of Mercury in Aqueous Matrix	5-5
5.3.2	Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for Determination of Mercury in Aqueous Matrix	5-6
5.3.3	Inductively Coupled Plasma for Determination of Mercury in Aqueous Matrix	5-7
5.3.4	Future Methods to Consider for Mercury Determination in Liquids.....	5-8
5.4	Analysis of Solids	5-9
5.5	Mercury in Air and Flue Gas	5-11
5.5.1	Introduction and Speciation Considerations	5-11
5.5.2	Sorbent Trap Collection.....	5-12
5.6	Flue Gas Emissions.....	5-13
5.6.1	Sorbent Trap Analysis.....	5-13
5.6.2	Impinger-based Collection.....	5-14
5.6.3	Impinger-based Analysis	5-14
5.6.4	Continuous Emissions Monitor.....	5-15
5.7	Gas Sampling Techniques.....	5-16
5.7.1	Electrochemical Resistance for Determination of Elemental Mercury Detection in a Gas Matrix	5-16
5.7.2	Zeeman CVAAS for Determination of Elemental Mercury Detection in a Gas Matrix	5-16
5.7.3	U.S. EPA Method I-05 for Determination of Vapor Phase and Particulate Mercury in Ambient Air	5-17
5.7.4	Continuous Monitoring of Speciated Mercury in Ambient Air Using Manual and Automated Techniques.....	5-17
5.8	Current U.S. EPA-approved Test Methods for Regulatory Monitoring	5-17
5.9	Future Considerations	5-18
6.0	Recommended Approach for Conducting a Mass Balance Around a Biosolids Incinerator.....	6-1
6.1	Material Balances – Introduction.....	6-1
6.2	Designing a Mass Balance for a Biosolids Incinerator.....	6-2

6.2.1	Project Team	6-3
6.2.2	Data Quality Objectives	6-4
6.2.3	Measurement Quality Objectives	6-10
6.2.4	The Quality Assurance Project Plan	6-13
Appendix A: Project Survey 2006		A-1
Appendix B: Frontier Sorbent Trap Method Sorbent Gas Sampling		B-1
Appendix C: Clean Sampling Techniques		C-1
Appendix D: Palo Alto Regional Water Quality Control Plant Mercury Mass Balance		D-1
Appendix E: Northeast Ohio Regional Sewer District Southerly Wastewater Treatment Center Mercury Mass Balance		E-1
Appendix F: Description of Quality Control Samples		F-1
Appendix G: Biosolids Incinerators Locations (2004)		G-1
Appendix H: A Primer on Biosolids Management and Incineration		H-1
References		R-1

LIST OF TABLES

1-1	Mercury Emissions (Metric Tons) in the United States Classed as Point Source Type and Mercury Form of Emission.....	1-1
1-2	Estimated Mercury Emissions in U.S. Tons Assuming No Co-Benefit Capture.....	1-3
2-1	Mercury Species Potentially Present after a Combustion Process.....	2-1
2-2	A Chemical Content Comparison of a Coal Type and Two Biosolids Samples	2-6
3-1	Categories of Air Pollution Control Devices Reported by the 31 Respondents in the Project Survey	3-1
3-2	Baghouses Come in Four Main Design Classifications Based on How the Dust Cake Accumulation is Removed and “Managed”	3-6
3-3	Co-Benefit Removal of Air Pollution Control Devices in the Coal-fire Utility Industry	3-9
3-4	Speculated Mercury Species Co-Benefit Removal of the Air Pollution Control Devices Discussed	3-9
4-1	Shown is a Summary of the Average Percentage Mercury Capture by Coal Rank and Air Pollution Control Device Configuration as Reported by the U.S. EPA 1999 ICR for Coal-Fired Electric Generating Units	4-2
4-2	Mercury Removal Calculated from Data Reported from the Ypsilanti, Michigan, Biosolids Incinerator.....	4-6
4-3	Capital and Operating Expense Considerations for Adopting Mercury Removal Technology	4-9
4-4	Reported Mercury Removal Rates and Costs for Several Air Pollution Control Devices Technologies in MWCs	4-10
4-5	Mercury Removal Efficiencies by Air Pollution Control Devices in Municipal Waste Incinerators	4-10
5-1	Published Methods for the Determination of Mercury in Aqueous Liquids	5-4
5-2	Methods Reported by the Surveyed POTWs for Analyzing Mercury in Influent and Effluent	5-4
5-3	Preparation Reagents for Mercury in Solids in 31 POTWs Survey Responders	5-10
5-4	Preparation Methods for Mercury in Solids in 31 POTWs Survey Responders	5-10
5-5	Published Methods and Instruments for the Determination of Mercury in Gases.....	5-12
5-6	Methods Reported by Surveyed POTWs for Mercury in Gas	5-15
5-7	Gas Emission Concentrations Reported by the Surveyed POTWs.....	5-15
5-8	Summary of Recommended Air Testing Methods	5-18
A-1	Influent Flow Rates.....	A-41
A-2a	Biosolids Incinerators, Type and Dewatering Devices.....	A-42
A-2b	Mass of Biosolids Incinerated per Year and the Percentage Solids.....	A-43
A-3	Supplemental Fuel Used, Reported on a Giga British Thermal Unit Basis.....	A-44

A-4	Air Pollution Control Devices in Service	A-45
A-5	Scrubber Water Quality and End Use.....	A-46
A-6a	Digestion and Analytical Methods for Biosolids.....	A-47
A-6b	Digestion and Analytical Methods for Ash	A-48
A-6c	Analytical Methods for Influent and Effluent.....	A-49
A-7	Mercury Concentrations in Biosolids	A-50
A-8	Mercury Concentrations in Influent.....	A-51
A-9	Mercury Concentrations in Effluent	A-52
A-10	Test Date, Methods and Hg Emission Concentrations	A-53
C-1	Equipment Used for Collecting Sewage Sludge Samples	C-3
C-2	Sampling Scheme Used in Their Mercury Mass Balance of Their Treatment Plant and Biosolids Incinerator	C-4

LIST OF FIGURES

1-1	The Mercury Biogeochemical Cycle	1-5
2-1	Schematic of the Chemisorption of Mercury on Carbon-Based Particulate Matter in Coal Combustion Flue Gas	2-2
2-2	Predicted Mercury Capture as a Function of Chlorine Coal Content with Varying Coal Sulfur Concentrations for Two Emission Control Systems	2-3
2-3	Reduction of Mercury Capture Efficiency with Increasing Coal Sulfur Content.....	2-3
2-4	Mercury and Its Compounds In Biosolids Incineration Plants	2-5
3-1	Basic Schematic of a Venturi Scrubber without Associated De-Misting Section	3-2
3-2	Basic Schematic of an Impingement Tray Scrubber.....	3-3
3-3	Combination Wet Scrubber System for Optimum Particulate Removal	3-5
3-4	Basic Schematic of a Bag Filter Using Reverse Air System to Clean.....	3-5
3-5	Basic Schematic of an Electrostatic Precipitator	3-7
3-6	Effect of Mercury Species on Co-Benefit Mercury Removal Through Flue Gas Treatment Units	3-8
3-7	Determining the Co-Benefit of Mercury Removal of a Unit.....	3-10
4-1	Schematic of Existing Pollution Control Devices in Coal-Fired Electric Generating Units Used to Capture Mercury and Options For Enhancement by Increasing the Oxidized Mercury Fraction	4-2
4-2	Mercury Emissions Calculated as a Function of Activated Carbon Injected at the St. Paul, Minnesota, Biosolids Incinerator.....	4-7
5-1	Effect of Clean Techniques on Mercury Determinations in the Freeport Marina, New York.....	5-2
6-1	Example of a Process Scheme for Developing a Mass Balance	6-3
6-2	Simplified Schematic of the Metropolitan Sewer District of Greater Cincinnati Biosolids Incinerator and the Potential Mercury-Containing Feed and Product Streams.....	6-5
6-3	A Simplified Schematic for a Mass Balance Study of a Biosolids Incinerator.	6-7
6-4	Effect of Flue Gas Flow on Mercury Detection Limit.....	6-8
6-5	Example of a Process Scheme for Choosing the Analytical Methods to Be Used in the Mass Balance	6-12
A-1	Daily Flow in Millions of Gallons Per Day (MGD) as a Function of POTW ID.....	A-2

A-2	Daily Flow in Millions of Gallons Per Day (MGD) as a Function of POTW ID.....	A-3
A-3a	Types of and Numbers of Incinerators Used as a Function of Location	A-4
A-3b	The Distribution of Multiple Hearth Incinerators	A-5
A-3c	The Distribution of Fluidized Bed Incinerators	A-6
A-3d	Distribution of Fluidized Beds Verses Multiple Hearth Incinerators	A-7
A-4	Conditioning Methods for Biosolids.....	A-8
A-5	Dewatering Methods	A-9
A-6a	Mass of Biosolids Incinerated as a Function of Location and Year	A-10
A-6b	Percent Solids of Biosolids Incinerated as a Function of Location and Year.....	A-11
A-7	Burning Zone Temperatures as a Function of Location	A-12
A-8a	Use of Natural Gas as a Supplemental Fuel as a Function of Location.....	A-13
A-8b	Use of #2 Fuel Oil as a Supplemental Fuel as a Function of Location.....	A-14
A-8c	Use of Other Fuels as a Supplemental Fuel as a Function of Location	A-15
A-8d	Distribution of Supplemental Fuel Oil as a Function of Location.....	A-16
A-8e	Distribution of Supplemental Fuel Oil as a Function of Year in BTU	A-17
A-9a	Type of Air Pollution Control Device as a Function of Location.....	A-18
A-9b	Distribution of Air Pollution Control Devices.....	A-19
A-9c	Destination of Scrubber Water Effluent	A-20
A-10	Digestion Methods Used for Biosolids and Ash Prior to Analysis.....	A-21
A-11	Analytical Methods Used for Biosolids, Ash, Influent, and Effluent.....	A-22
A-12a	Number of Times Per Year That Biosolids Are Tested for Hg as a Function of Location	A-23
A-12b	Distribution of the Frequency for Testing Biosolids for Hg.....	A-24
A-12c	Average Concentration of Hg in Biosolids as a Function of POTW and Year	A-25
A-12d	Highest Concentration of Hg in Biosolids as a Function of POTW and Year	A-26
A-13a	Number of Times per Year That Ash Is Tested for Hg as a Function of Location	A-27
A-13b	Distribution of the Frequency for Testing Ash for Hg	A-28
A-13c	Average Concentration of Hg in Ash as a Function of POTW and Year	A-29
A-14a	Number of Times Per Year That Influent Is Tested for Hg as a Function of Location...	A-30
A-14b	Distribution of the Frequency for Testing Influent for Hg	A-31
A-14c	Average Concentration of Hg in Influent as a Function of POTW and Year.....	A-32

A-14d	Highest Concentration of Hg in Influent as a Function of POTW and Year	A-33
A-15a	Number of Times per Year That Effluent is Tested for Hg as a Function of Location...	A-34
A-15b	Distribution of the Frequency for Testing Effluent for Hg.....	A-35
A-15c	Average Concentration of Hg in Effluent as a Function of POTW and Year	A-36
A-15d	Highest Concentration of Hg in Effluent as a Function of POTW and Year	A-37
A-16a	Popularity of Emission Test Methods.....	A-38
A-16b	Concentration of Hg Measured in Stack Emission Gas as a Function of Year	A-39
A-16c	Concentration of Hg Measured in Stack Emission Gas as a Function of Year	A-40
B-1	Gas Sampling Console Control Panel Faceplate	B-5
H-1	Cross Section of a Multiple Hearth Incinerator	H-3
H-2	Cross Section of a Fluidized Bed Incinerator	H-4

LIST OF ACRONYMS

ACI	activated carbon injection
APCD	air pollution control device
ASTM	American Society for Testing and Materials
BMP	Best Management Practices
CAAA	Clean Air Act Amendments
CAMR	Clean Air Mercury Rule
CCV	Continuing Calibration Verification
CEM	continuous emission monitor
CESP	Cold Electrostatic Precipitator
CFPP	coal-fired power plant
CRM	Certified Reference Material
CVAAS	cold vapor atomic absorption spectroscopy
CVAFS	cold vapor atomic fluorescence spectroscopy
CVI	Cuyahoga Valley Interceptor
DOE	Department of Energy
DMHg	dimethyl mercury
DI	Deionized Water
DQO	data quality objectives
ECR	Electro-Chemical Resistance
EGU	electric generating utility
ESP	electrostatic precipitator
FF	fabric filters
FGD	flue gas desulfurization
FSTM	Frontier Sorbent Trap Method
H ₂ SO ₄	sulfuric acid
HAP	hazardous air pollutants
HBr	hydrobromic acid
HCl	hydrochloric acid
HF	hydrofluoric acid
Hg	mercury

Hg ⁰	elemental mercury
Hg ^{II}	oxidized mercury (or ionic mercury)
Hg ^P	particulate mercury
HNO ₃	nitric acid
HWC	Hazardous Waste Combustor
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICV	Initial Calibration Verification
KMnO ₄	potassium permanganate
LCS	Laboratory Control Standard
MDL	method detection limit
MeHg	methyl mercury (also called monomethyl mercury)
MMHg	monomethyl mercury (also called methyl mercury)
MQO	measurement quality objective
SQL	Method Quantitation Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MWI	Medical Waste Incinerator
MWC	municipal waste combustor
NACWA	National Association of Clean Water Agencies
NEMI	National Environmental Methods Index
NEORS	Northeast Ohio Regional Sewer District
NESHAP	National Emission Standards for Hazardous Air Pollutants
NIST	National Institute of Standard Technology
NPDES	National Pollutant Discharge Elimination System
PBT	Persistent Bio-Accumulative Toxicant
PCB	Polychlorinated Biphenols
PM	Particulate Matter
POTWs	publicly owned treatment works
PQL	practical quantitation limit
QA	quality assurance
QAPP	quality assurance protection plan

QC	quality control
RATA	Relative Accuracy Test Audit
RCRA	Resource Conservation and Recovery Act
RGM	reactive gaseous mercury
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Difference
RWQCP	Regional Water Quality Control Plant
SCR	Selective Catalytic Reduction
SDA	Spray Dryer Adsorption
SOP	Standard Operating Procedure
SRM	Standard Reference Material
SSI	Sewage Sludge Incinerators
SWWTC	Southerly Wastewater Treatment Center
TGM	total gaseous mercury
THg	total mercury
U.S. EPA	U.S. Environmental Protection Agency
WERF	Water Environment Research Foundation
WESP	Wet Electrostatic Precipitator
WWTP	Wastewater Treatment Plant
Z-CVAFS	Zeeman-Cold Vapor Atomic Fluorescence Spectroscopy

EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency has listed mercury compounds as one of the 33 air toxics of greatest concern in urban areas as required under Clean Air Act Section 112(k). This study identifies practices and control technologies that can be used to cost-effectively reduce mercury emissions from biosolids (sewage sludge) incinerators.

ES.1 Regulatory Structure

Publicly owned treatment works (POTWs) that practice incineration are subject to the National Emission Standards for Hazardous Pollutants standard of 3200 g Hg/24 hr as a plant-wide ceiling. Actual mercury emissions from each of these POTWs are < 200 g/24 hr. This is primarily because of the fact that concentrations in biosolids are typically less than 1 mg Hg/dry kg. Applying these results to available emission inventory estimates would reduce the stated impact of biosolids incinerators even more.

The Municipal/Industrial Pretreatment Program requires POTWs to control pass-through and interferences attributable to industrial sources of pollution that interfere with the wastewater plant's ability to successfully operate its processes, particularly biological processes. These include selected biosolids management and disposal practices. A minimization plan is usually implemented. If there are no applicable categorical industrial discharge pretreatment standards, typical remedies include permit changes requiring stricter emission standards, and often, as a first step, implementation of best management practices for the source industries.

Because not all mercury originates from non-residential point and area sources, additional measures may be needed for the POTW to achieve continuous permit compliance with effluent limits and air pollution emission limits.

ES.2 Findings and Recommendations

The research revealed that the 234 biosolids incinerators located in the United States are a very minor source of mercury. For example, conservative (high) estimates show these units collectively emit less than 0.9 metric tons (1 U.S. ton) of mercury to the atmosphere each year, which is roughly 0.5% of the total amount of mercury annually emitted to the atmosphere in North America.

In general, it is recommended that POTWs that practice incineration should consider the following series of actions:

- ◆ Conduct a mercury mass balance for their plants, including a specific mass balance around their incinerators, using standardized test methods and techniques.
- ◆ Determine the industrial and non-industrial sources of mercury entering their plant, which could include dental amalgams, other industrial discharges, or background concentration in soil, etc.

- ◆ Implement source control measures, through Municipal/Industrial Pretreatment Program modifications. These may include regulatory changes, and implementation of best management practices for significant sources of mercury to the system (e.g., dentists and dental laboratories).
- ◆ If source control measures prove insufficient to reduce mercury emissions to the needed level, a POTW could consider installing additional air pollution control devices (APCDs). Systems include activated carbon injection systems with a baghouse and activated carbon polishing. Such systems are costly to procure, install, operate, and maintain.

ES.3 Background Information

The Water Environment Research Foundation (WERF), the National Association of Clean Water Agencies, and the Central Contra Costa Sanitary District provided funding for a study related to mercury characterization, measurement, and minimization at POTWs that use incineration to manage their biosolids.

The study focused on

- ◆ Examination of analytical techniques currently used by POTWs to quantify mercury content of their various process streams (e.g., influent, effluent, biosolids, biosolids incinerator ash, incinerator scrubber water influent and effluent, air emissions, etc.),
- ◆ Identification of analytical testing protocols/methods to improve mercury-related data quality, and to increase understanding of mercury cycling within the biosolids incineration facility,
- ◆ Investigation of mercury control practices and mercury-specific minimization technology being used at POTWS and other combustion industries, and
- ◆ Identification of cost-effective strategies to minimize mercury emissions from biosolids incinerators.

ES.4 Chemistry of Mercury in Exhaust Gases

Mercury in the exhaust gases from combustion sources are partitioned into three general species (forms): elemental (Hg^0), oxidized (Hg^{II}) (ionic), and particulate bound (Hg^{P}).

It is not possible to predict mercury speciations on biosolids incinerator exhaust gases solely, because exhaust gas systems are rarely at equilibrium. Therefore, mercury (chemical) speciation depends on the following kinetic considerations:

- ◆ Humidification of exhaust gases can lower temperatures, but this high water content can inhibit mercury oxidation or mercury adsorption onto particulate material.

- ◆ Excess oxygen provided post-combustion pushes the system towards oxidative conditions. Chlorine influences the formation of metallic chlorides, and high chloride content drives production of HgCl_2 .
- ◆ In the presence of sulfur, mercury can form stable compounds such as HgS or HgSO_4 . This bonding of mercury with sulfur inhibits the formation of soluble mercury species through competition.
- ◆ Carbon in biosolids can inhibit mercury evolution during incineration, with higher carbon concentrations relating to lower mercury emissions; unburned carbon in ash can adsorb mercury.
- ◆ The presence of other chemicals can affect mercury emissions. For example, selenium reacts to form the stable compound HgSe .

ES.4 Mercury Emission Control Techniques

Mercury emission minimization strategies typically begin with the consideration of source control as the first measure to reduce mercury entering the process cycle. Source management programs focus on source identification, source reduction and segregation, infrastructure control and maintenance, and pretreatment systems.

Mercury removal in APCDs depends largely on the method of operation of the APCDs and the physical properties of mercury species. For example:

- ◆ Elemental mercury (Hg^0) is a difficult species to capture and presents the greatest challenges for mercury control strategies.

Oxidized mercury (Hg^{II}) is highly water-soluble, allowing removal in any type of wet scrubbing mechanism.

- ◆ Particulate-bound mercury (Hg^{P}) is also removed partially in the wet scrubbing mechanisms, whereas further reduction has been reported through the use of fabric filters and wet electrostatic precipitators.

Wide-ranging mercury removal rates are reported for all types of APCDs, primarily because of variable operational conditions as well as diverse chemical and physical composition of the feedstock. Speculation as to the actual ability of existing technologies to add co-benefit mercury removal needs to begin with solid understanding of speciation throughout the biosolids incinerator.

To date, installation of mercury-specific control systems for biosolids incinerators has been limited to two POTWs that have only recently installed activated carbon-based APCDs for mercury control.

Ypsilanti, Michigan, installed an activated carbon fixed-bed polishing system in 2005 to remove mercury from its fluidized bed incinerator's exhaust gases. Ypsilanti's air pollution control train consists of a Venturi/impingement tray scrubbing system, wet electrostatic precipitator, and followed by an activated carbon fixed-bed polishing system. Ypsilanti personnel have reported mercury removal efficiencies across the air pollution control train in excess of 99%.

Considering multiple APCDs and lack of information on the test methods/techniques used, the authors were unable to verify the reported removal efficiencies or determine the mercury removal efficiencies across the activated carbon fixed bed polishing system.

St. Paul, Minnesota, installed three new fluidized bed incinerators, placing them into service in 2004. The air pollution control train consisted of an activated carbon injection system, fabric filter (baghouse) Venturi/impingement tray scrubbing system, and, finally, a wet electrostatic precipitator. Plant personnel have reported mercury removal efficiencies across activated carbon injection system/fabric filter of 94%, whereas an additional 4% reduction occurs across the wet electrostatic precipitator. Staff also noted that increasing the carbon injection rate did not increase mercury capture as expected. This suggests that the fabric filter (baghouse) may be the dominant capture mechanism.

Analyzing these multiple APCDs and lack of intermediate information on the test methods/techniques/sites used, the authors were unable to verify the reported removal efficiencies or determine the mercury removal efficiencies across the separate APCDs.

ES.5 Summary

This WERF-sponsored study provides a technical background to recognize, sample, analyze, and evaluate multiple mercury species, and, further, to use this increased understanding as a basis to specify and design effective mercury minimization systems and processes.

Comparison of reported data in regard to mercury removal efficiencies is extraordinarily difficult, given the use of numerous test methods for different target species, and varied sampling and analytical techniques used by POTWs. For example, reported mercury control efficiencies from the 31 POTW participants in the WERF survey (see Appendix A) ranged from a low of -5.0% to a high exceeding +99%. Although all may be correct with respect to total mercury, these data provide little insight to confirm removal mechanisms.

POTWs clearly need to perform additional testing using standardized test methods and techniques to determine the actual fate of the mercury being incinerated at their plant to better understand the removal mechanisms. Determination of the species of mercury in biosolids incinerator exhaust gases is necessary for all additional testing identified and proposed.

CHAPTER 1.0

INTRODUCTION

1.1 Background

The U.S. Environmental Protection Agency (U.S. EPA) has established a goal of reducing all persistent bio-accumulative toxicants in the environment. Mercury, one of the persistent bio-accumulative toxicants of concern, is receiving much of the U.S. EPA's attention. Mercury is of particular concern because it occurs in a variety of chemical forms, or species, which differ widely in their chemical and physical properties.¹ This report identifies practices and control technologies to cost-effectively reduce mercury emissions from biosolids incinerators.

It is estimated that 144-189 metric tons (158-207 U.S. tons) of mercury are emitted annually into the atmosphere by anthropogenic (derive from human activities) sources in the United States,² and that biosolids incinerators are responsible for less than 0.9 metric tons/year (1 U.S. ton/year) or approximately 0.5% of the total.

Approximately 87% of the mercury is from combustion-point sources (where a point source is defined as an anthropogenic mercury emitter associated with a fixed location) and 10% from manufacturing-point sources. The combustion-point sources can primarily be broken down further into four classes, coal-fired utility boilers, municipal waste incinerators, commercial/industrial boilers and medical waste incinerators (Table 1-1).

Table 1-1. Mercury Emissions (Metric Tons) in the United States Classed as Point Source Type and Mercury Form of Emission.

Sources	Elemental Mercury (Hg ⁰)	Oxidized Mercury (Hg ^{II})	Particulate Mercury (Hg ^P)	Total Mercury
Coal burning	38	23	15	76 (45%)
Incinerators (all types)	11	33	11	55 (33%)
Other point sources	24	4	2	30 (18%)
Area sources	7	0	0	7 (4%)
Total	80 (48%)	60 (36%)	28 (16%)	168

Future trends in mercury emissions are dependent on how utilities and industries address the Clean Air Act rules that the U.S. EPA promulgates. U.S. EPA is working to regulate and reduce emissions from both municipal waste and medical waste incinerators, and state agencies are implementing regulations requiring discharge levels even lower than those federally mandated.

¹ Bloom, N.S., Prestbo, E.M. (1994)

² U.S. EPA. (1997a)

Biosolids Incinerator Regulation

Air emissions from biosolids incinerators are regulated under Subpart E of U.S. EPA's Biosolids Regulation (40 CFR Part 503) and the Clean Air Act Amendments of 1990. The Part 503 Rule requires that the firing of biosolids in an incinerator must not violate the requirements in the National Emission Standard for Hazardous Air Pollutants (NESHAP) for mercury contained in Subpart E of 40 CFR Part 61 of 3200 g/24 hr. This limit covers the mercury from all of the air emissions units located at the publicly owned treatment work (POTW.)

As a general rule, biosolids incinerator facilities have been able to meet these requirements because of the low or negligible levels of mercury in their incinerated biosolids [normally 1 mg (Hg)/dry kg (biosolids)]. Actual mercury emissions from POTWs that practice incineration are less than 200 g/24 hr, which is less than 6% of the mercury NESHAP.

Under U.S. EPA's Urban Air Toxics Strategy [Section 112(k) of the Clean Air Act Amendments], the agency is developing standards to control toxic air pollutants from area sources. "Area" sources are defined as those sources that emit less than 10 tons annually of a single hazardous air pollutant or less than 25 tons or more annually of a combination of hazardous air pollutants.

The Clean Air Act requires U.S. EPA to identify a list of at least 30 air toxics that pose the greatest potential health threat in urban areas. For the Strategy, U.S. EPA identified a list of 33 air toxics.

The Clean Air Act also requires U.S. EPA to identify and list the area source categories that represent 90% of the emissions of the 30 urban air toxics associated with area sources and subject them to standards under Section 112(d). Through three separate listings (including a list in the Urban Air Toxics Strategy), U.S. EPA has identified a total of 70 area source categories that represent 90% of the emissions of the 30 listed air toxics. Of these 70 area source categories, 28 had been regulated by June 2007 with the remaining area source standards under development. The U.S. EPA was recently put on a court-ordered schedule to issue the area source rules listed under the Urban Air Toxics Strategy. Court orders from 2003 and 2006 resulted in the deadlines listed below.

U.S. EPA is also in the process of reconsidering whether to regulate biosolids incinerators under the Urban Air Toxic rule contained within Section 112(k) of the Clean Air Act Amendments or the Other Solid Waste Incinerator rule contained within Section 129 of the Clean Air Act Amendments.

Major sources of air emissions are defined in Section 112 of the Clean Air Act as those that could emit 9 metric tons (10 U.S. tons) or more per year of any of 189 identified hazardous air pollutants (HAPs) or 23 metric tons (25 U.S. tons) or more per year of any combination of HAP. U.S. EPA has determined that biosolids incinerators are not a major source of HAP emissions. However, biosolids incinerators that do not qualify as a major source of HAP emissions may still be regulated for emission of 30 selected pollutants, one of which is mercury. In an ideal situation, mercury would be absent from the raw materials used in the processes described above, thus negating the concern of mercury emission. Unfortunately, it is not currently feasible to remove the trace mercury from biosolids before the incineration process.

Table 1-2. Estimated Mercury Emissions in U.S. Tons Assuming No Co-Benefit Capture. Calculations are Made from the Data Received from the Project Survey and Based on 234 Active Biosolids Incineration Units.

Year	Estimated Mercury Emissions (U.S. Tons)					
	Mean	Median	Min	Max	25th Percentile	75th Percentile
2002	0.95	0.68	0.022	3.0	0.24	0.98
2003	1.3	0.85	0.15	4.4	0.36	1.7
2004	1.1	0.68	0.15	3.0	0.36	1.9
2005	0.90	0.43	0.066	4.8	0.21	1.3

Even though biosolids incinerators are a negligible source of mercury (Table 1-2), WERF has stated that the time is right for the water quality community to actively research methods that can cost-effectively be used to minimize mercury emissions from biosolids incinerators.

U.S. EPA has listed mercury compounds as one of the 33 air toxics of greatest concern in urban areas as required under Clean Air Act Section 112(k).³ In that notice, U.S. EPA listed biosolids incinerators as a source category of concern and, in 2002, added biosolids incinerators to its list of source categories that will be regulated under the 112(k) program.^{4,5} Documentation in the record supporting U.S. EPA's listing shows biosolids incinerators as contributing 0.6% of the total urban area emissions of mercury, where this percentage is based on best point estimates of 1994-1995 and recorded as having a high degree of uncertainty ($\pm 50\%$). The 1997 U.S. EPA Mercury Study Report to Congress briefly addresses biosolids incinerators (they use the term sewage sludge incinerators). The report indicates that, as of 1994, the 116 biosolids incinerator locations⁶ in the United States account for 0.86 Mg/yr (0.94 tons/yr, 0.00086 kg/yr) of mercury emission, $\sim 0.5\%$, a reduction when compared to the 1990 data. However, the report states that the average emission factors were calculated based on limited understanding of the effect of emission control equipment on mercury emission concentrations at biosolids incinerators in the United States. No direct measurements of mercury emissions were made.

POTWs that practice incineration need a complete understanding of the actual emissions of mercury from their incinerators and the methods for controlling those emissions to effectively respond to any proposed or new requirements.

New Clean Air Act requirements addressing mercury emissions are expected for biosolids incineration in the next 2 years. In 1997, U.S. EPA proposed to regulate biosolids incinerators under Section 129 of the Clean Air Act with medical waste, hazardous waste, and municipal solid waste incinerators. On the basis of information provided by the Association of Metropolitan Sewerage Agencies (now known as the National Association of Clean Water Agencies, or NACWA) and other interested parties, U.S. EPA announced in November 2000 that it would not be regulating biosolids incinerators under Section 129. However, in 2006, U.S. EPA formally requested comments on whether biosolids incinerators should be covered under Section 129, because it had neglected to provide an opportunity for public comments in 2000. After reviewing all comments received, U.S. EPA announced in January 2007 that it would not be

³ U.S. EPA. (1999a)

⁴ U.S. EPA. (2002)

⁵ U.S. EPA has not promulgated 112(k) regulations for biosolids incinerators leaving open the possibility that they will be regulated with the other solid waste incinerators under Section 129 of the Act.

⁶ As of 2004, 120 POTWs operated 234 incinerators (National Association of Clean Water Agencies, 2007) in 120 locations (Appendix G).

regulating biosolids incinerators under Section 129. A subsequent court decision has U.S. EPA reconsidering its approach to incinerator regulation, including biosolids incinerators.

POTWs using incineration to manage their biosolids are currently subject to a national emission standard for hazardous pollutants (NESHAPs) for mercury of 3200 g/24 hr. This is a site-wide limit that covers combined mercury emissions for all biosolids incinerators located at a POTW. However, POTWs report that they are voluntarily achieving lower mercury emissions from biosolids incinerators.

Over the years, only a limited amount of data have been collected concerning the percentage of mercury in the biosolids incinerated at POTWs that passes through the air pollution control system and is emitted to the atmosphere. Mercury volatilizes at a much lower temperature than other metals regulated under U.S. EPA's Biosolids Regulation (40 CFR Part 503), so it is possible that some of the mercury is volatilized by the incinerators and emitted to the atmosphere through the exhaust stacks in the absence of mercury-specific control technologies.

U.S. EPA is updating its national mercury emissions inventory, and requested NACWA members to provide mercury emissions data for biosolids incinerators. All of the NACWA members surveyed reported their current emissions are substantially below the 3200 g/24 hr national emission standard. Reported emissions are primarily based on the mercury concentrations detected in biosolids samples and a conservative 0% mercury control efficiency assumption for particulate air pollution control systems. This conservative method for determining mercury emissions from biosolids incinerators has been approved by U.S. EPA.

The members reported their calculated mercury emissions, assuming no mercury controls in place, to be less than 200 g/24 hr (less than 6% of the NESHAPs limit). A limited number had test data and noted that their mercury control efficiencies was anywhere from -5% to +80%. The test results varied greatly in part because of the use of a variety of test methods in the absence of a standardized methodology that accurately accounts for all phases of mercury during measurement.

1.2 Mercury Emissions

The effluents and emissions of many industrial processes often contain levels of trace metals, of which many must be monitored before discharge to the environment. Mercury is a particular concern in this regard, because it occurs in a variety of chemical forms, or species, which differ widely in their chemical and physical properties,⁷ and because one mercury species, methyl mercury (MeHg), is a persistent bio-accumulative toxicant.

Mercury in the environment is constantly cycled and recycled through what is known as a biogeochemical cycle (Figure 1-1). Mercury cycles in the environment as a result of natural and anthropogenic activities. Both these natural and human activities release mercury into the atmosphere. Once in the atmosphere, the mercury vapor can circulate for up to a year, and hence become widely dispersed. The elemental mercury vapor can then undergo chemical and physical

⁷ Bloom, N.S, Prestbo, E.M. (1994)

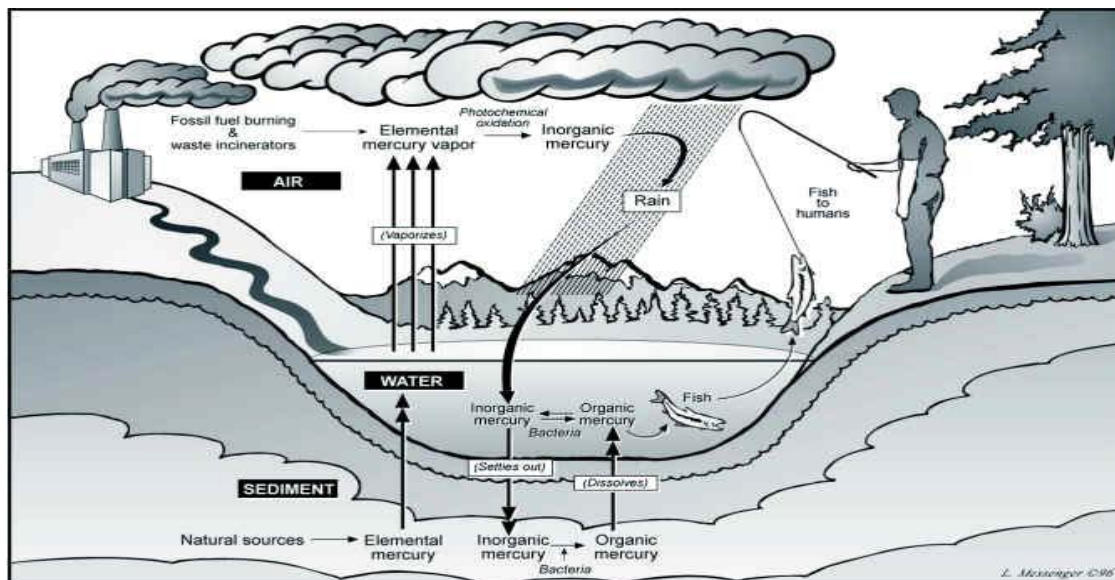


Figure 1-1. The Mercury Biogeochemical Cycle.

reactions, being re-deposited in rain. In soil, the mercury accumulates until a physical event, such as a forest fire, causes it to be released again. In water, inorganic mercury can be converted into insoluble mercury sulfide that settles out of the water and into the sediment, or it can be converted by bacteria⁸ that process sulfate into methyl mercury.⁹ The methyl mercury is consumed by an organism and passed up the food chain. This continues as small fish/organisms get eaten by progressively bigger and bigger fish until the fish are finally eaten by humans or other animals.

⁸ Zillioux, E.J., Porcella, D.B., Benoit, J.M. (1993)

⁹ Watras, C.J., Bloom, N.S. (1992)

CHAPTER 2.0

MERCURY IN A BIOSOLIDS INCINERATOR

2.1 Combustion Chemistry of Mercury in Coal-Fired Flue Gas Compared to Biosolid Incinerators

As a result of combusting mercury containing materials, such as coal or biosolids, mercury can be present in the emission-gas in three forms: elemental (Hg^0), oxidized (Hg^{II}), and particulate bound (Hg^{P}) (Table 2-1).

Table 2-1. Mercury Species Potentially Present after a Combustion Process.

Mercury Species	Nomenclature	Boiling Point /Water Solubility	Co-Benefit Removal
Elemental mercury	Hg^0	357 C/ Very slightly sol. (0.002 g/100 mL @ 20 C)	N/A
Reactive gaseous mercury (oxidized)	RGM – HgX_2 , (Hg^{II})	300 – 360 C / Very sol. (0.5-1.0 g/100 mL @ 22 C)	Wet scrubbers
Particulate mercury	Hg^{P}		Particulate removal

2.1.1 Coal Combustion

The chemistry of mercury speciation and capture in coal flue gas is very complex. However, recent and past research has elucidated several key chemical mechanisms.^{10,11,12,13} In general, the concentration and form of sulfur species (SO_2 , H_2SO_4 , SO_3), halogen species (HCl , Cl_2), and active carbon surfaces [native unburned carbon and activated carbon injection (ACI)] will determine the speciation and capture of mercury in coal flue gas. The models^{14,15,16} also suggest the concentration of chlorine is potentially controlled by other gases, including HCl , CO , H_2O , and NO . However, the calculated mercury oxidation predicted by models does not accurately match the values determined in combustion systems. Agarwal and colleagues determined that NO , H_2O , and SO_2 inhibit the homogeneous oxidation of Hg by Cl_2 .¹⁷ Other possible mechanisms for oxidation involve physical and chemical adsorption on flyash or sorbent particles, such as unburned carbon. In addition, most studies on mercury gas-solid partitioning and speciation in coal combustion flue gas have been performed in small to pilot-scale fixed packed-bed reactors instead of in entrained-flow reactors as used in coal combustion.

¹⁰ Senior, C.L., Sarofim, A.F., Mamani-Paco, R. (2000)

¹¹ Zhuang, Y., Thompson, J.S., Zygarlicke, C.J., Pavlish, J.H. (2004)

¹² Olson, E.S., Laumb, J.D., Benson, S.A., Dunham, G.E., Sharma, R.K., Mibeck, B.A., Miller, S.J., Holmes, M.J., Pavlish, J.H. (2003)

¹³ Kolker, A., Senior, C.L., Quick, J.C. (2006)

¹⁴ Sliger, R.N., Kramlich, J.C., Marinov, N.M. (2000)

¹⁵ Niksa, S., Helble, J.J., Fujiwara, N. (2001)

¹⁶ Edwards, J.R., Srivastava, R.K., Kilgroe, J.D. J. (2001)

¹⁷ Agarwal, H., Romero, C.E., Stenger, H.G. (2006)

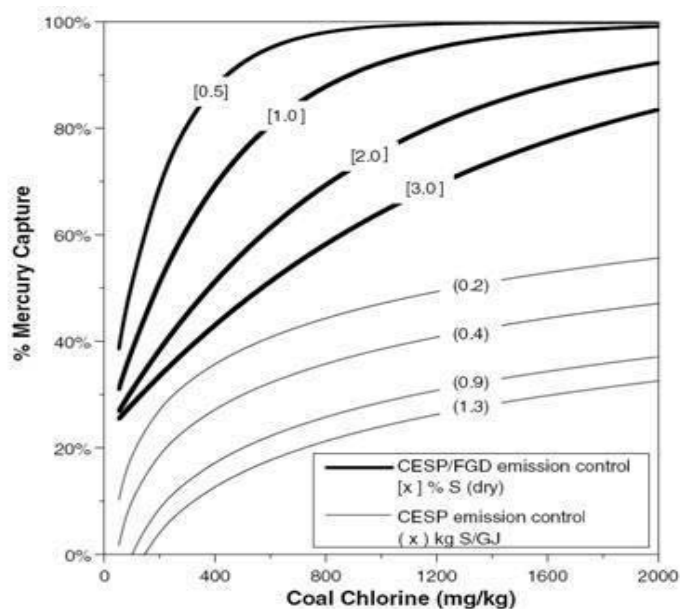


Figure 2-2. Predicted Mercury Capture as a Function of Chlorine Coal Content with Varying Coal Sulfur Concentrations for Two Emission Control Systems.

Reprinted with permission of Kolker et al., 2006; CESP, cold electrostatic precipitator; FGD, flue gas desulfurization.

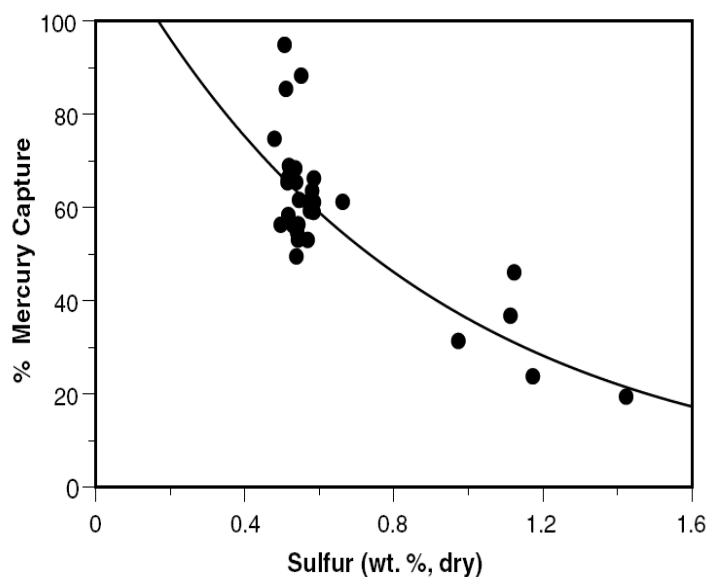


Figure 2-3. Reduction of Mercury Capture Efficiency with Increasing Coal Sulfur Content.

Reprinted with permission of Kolker et al., 2006.

2.1.2 Biosolids Incineration

The mercury combustion chemistry of biosolid incinerator flue gas has not been as thoroughly investigated as coal or municipal waste flue gas. Certainly some of the chemistry of coal and waste incineration flue gas will be applicable to biosolid incineration, but the differences in the composition, Table 2-2, and combustion of the fuel will likely be important for mercury speciation and control technology options. However, with recent developments in pollution control in the European Union, several researchers have begun to examine mercury speciation in biosolids incinerators.²² The model that they are developing (Figure 2-4) partially represents proposed coal-fired utility models, however matrix component concentrations and operating conditions result in different mercury speciation distributions in the two systems. In addition, the model is a collective of individual bench-top experiments that have been collated in a speculative manner rather than uniform empirical demonstrations.

Although the sulfur content of biosolid fuel is similar to coal (biosolids 1-3.5%wt sulfur, coal 0.25-4%wt sulfur), the nitrogen and oxygen content in biosolids is much larger.^{23,24} More relevant to mercury speciation and control, the chlorine content of biosolids is fairly low in comparison to coal or municipal waste,^{25,26,27} and this lower content of chlorine may lead to the fraction of oxidized mercury being lower than expected when direct comparisons with coal-fired utility flue gas is made.^{28,29} This is further reinforced by Saenger and Werther where the decrease in chloride results in a decrease in oxidized mercury.³⁰ This trend correlates with the coal-fired utility industry, where mercury removal increases with chloride concentration, when using a wet scrubber, explained by the assumption that more water soluble oxidized mercury is being formed (Figure 2-4).

The high content of moisture and volatile matter of wet biosolids have an influential effect on the combustion characteristics of the biosolids, and thus the design of dryers and incinerators for biosolids drying and combustion, respectively. Compared to a coal-fired facility the drying and devolatilization processes are interrelated, although the location of drying, and the release and combustion of volatiles determines the temperature distribution in a biosolids combustion furnace, especially if the combustion is carried out in a multiple hearth or fluidized bed incinerator. In addition, the high volatile matter content of biosolids dominates the combustion process with the role of the char combustion step playing a less important role. Saenger and Werther also offer that oxidized mercury species are chemically reduced on the surface of hot steel by reaction with SO₂.³¹

²² Saenger, M., Werther, J. (1999)

²³ Werther, J., Ogada, T. (1999)

²⁴ Werther, J., Saenger, M. (2000)

²⁵ Werther, J., Ogada, T. (1999)

²⁶ Werther, J., Saenger, M. (2000)

²⁷ Yao, H., Naruse, I. (2005)

²⁸ Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

²⁹ Werther, J., Ogada, T. (1999)

³⁰ Saenger, M., Werther, J. (1999)

³¹ Saenger, M., Werther, J. (1999).

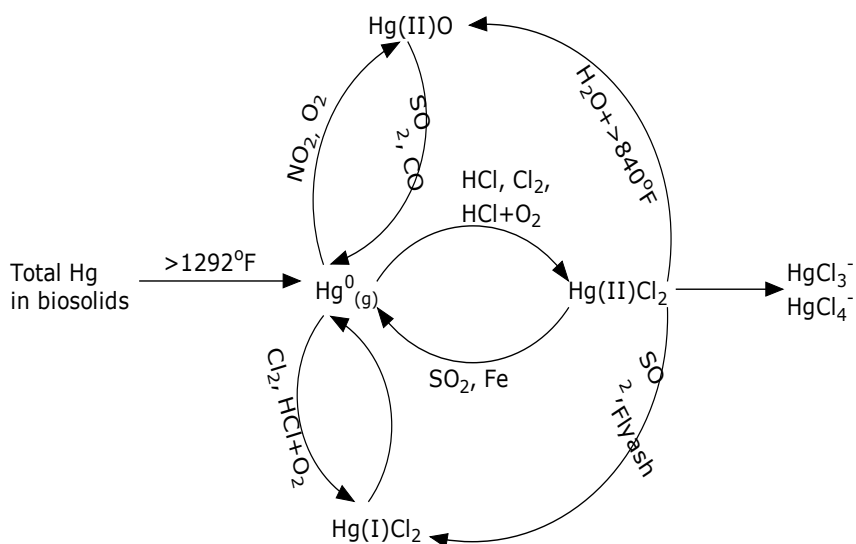


Figure 2-4. Mercury and Its Compounds in Biosolids Incineration Plants.³²

Definite differences in coal and biosolids exist, which affects solids and combustion chemistry. Any information about coal flue gas mercury control technology should be extrapolated cautiously to the biosolids industry. This inability to overlap the two chemistries has been acknowledged by the U.S. EPA.

2.2 Mercury in Biosolids Incinerators

In 2000, NACWA³³ released a report examining the sources of mercury in wastewater entering a POTW. The sources evaluated included common household products and food items, as well as research on mercury contributions from individuals with amalgam fillings.

The report determined that:

- ◆ Mercury is consistently found in strictly domestic wastewater.
- ◆ Common household and toiletry items were found to contain concentrations of mercury. These products individually do not contribute significantly to a total concentration in wastewaters, their cumulative effect accounts for approximately 15% of the mercury concentration in domestic wastewater.
- ◆ Human wastes (feces and urine) from individuals with dental amalgam fillings are believed to deposit >80% of the mercury in the wastewaters.

The report concluded that “based on this information, domestic waste contributes appreciable concentrations of mercury to POTW influent wastestreams and must be considered when addressing mercury control strategies and the likelihood of virtual elimination of mercury.

³² Reprinted with permission of Saenger, M. and Werther, J. (1999). “Mercury emissions from German fluidized bed sludge incinerators.” *Proceedings of the 15th International Conference on Fluidized Bed Combustion*, May 16-19, 1999, Savannah, GA.

³³ National Association of Clean Water Agencies (2000)

Table 2-2. A Chemical Content Comparison of a Coal Type and Two Biosolids Samples.

Component		Bituminous Coal	Biosolids 1	Biosolids 2
Moisture	wt%	2	69	55.4
Carbon	dry wt%	79.2	30.9	29
Hydrogen	dry wt%	4.7	4.6	3.8
Nitrogen	dry wt%	1.8	4.5	3.1
Sulfur	dry wt%	0.9	1.1	0.8
Chlorine	dry wt%	0.7	0.1	0.17
Oxygen	dry wt%	7.6	26.5	17.56
Pb	dry wt ppm (mg/kg)	20	211	369
Cd	dry wt ppm (mg/kg)	<1	2	5
Hg	dry wt ppm (mg/kg)	<2	<2	<20
Zn	dry wt ppm (mg/kg)	15	567	834
Nitrogen	dry wt ppm (mg/kg)	3	32	35
Cu	dry wt ppm (mg/kg)	23	829	487
Cr	dry wt ppm (mg/kg)	<2	62	227
Ash	dry wt ppm (mg/kg)	5	10	20
<u>Ash components</u>				
- Al ₂ O ₃	ash oxides wt%	24.9	15.6	14.3
- CaO	ash oxides wt%	8.1	22.2	19.8
- P ₂ O ₅	ash oxides wt%	1.2	16.7	8.7
- Fe ₂ O ₃	ash oxides wt%	21.1	3.6	6.8
- TiO ₂	ash oxides wt%	0.7	1.3	1.2
- MgO	ash oxides wt%	1.9	2.3	3.2

Notes:

Biosolids 1 is chemically conditioned, centrifuge-dewatered.

Biosolids 2 is thermally conditioned, centrifuge dewatered.

Background mercury concentrations averaging more than 100 parts per trillion can be expected in POTW wastewater influents, even if complete elimination of industrial point source discharges is accomplished.”

2.2.1 Source Control

Mercury is ubiquitous, but its concentration is normally less than 1 mg/dry kg in biosolids (the project survey reports an average of 0.75, 0.82, 0.79, and 0.84 mg/dry kg for 2002, 2003, 2004, and 2005, respectively from across the 31 respondents). Any commentary made on reducing the mercury emissions from biosolids incineration should begin by considering source control of the mercury entering the process cycle. For example, NACWA recently undertook a Mercury Sampling Project Report examining the impact of dental amalgam separators on the mercury loading of 13 POTWs.³⁴ Although the report is currently in draft phase and is not a final statement on the issue addressed, it did find that the use of dental amalgam separators can

³⁴ Dominak, R. (2007)

decrease the amount of mercury entering POTWs, thereby decreasing the amount of mercury that would be removed by plant processes and deposited in the biosolids.

In addition, NACWA conducted monitoring efforts at one POTW that showed that mercury concentrations of samples collected downstream from sewer cleaning operations were one to two orders of magnitude higher than upstream samples.³⁵

Although the most successful source management comes from education of the system stakeholders, the source management programs are often organized around four major components:

1. Source identification
2. Source reduction and segregation
3. Infrastructure control and maintenance
4. Pretreatment systems

Many system stakeholders have found that all four components are needed as part of an ongoing Mercury Management Plan. Control measures include administrative, procedural, and engineered controls. Source reduction, source segregation, infrastructure improvements, and, in some cases, pretreatment may be needed. A valuable step-by-step tool can be viewed in Section 3.0, “Step-by-Step Approach to Discharge Compliance” of the MWRA/MASCO Mercury Work Group, Phase II, End-of-Pipe Subcommittee, *Pretreatment Guidance Manual*, December 1997. This publication may be of use to communicate to the system stakeholders.³⁶

2.2.2 Parameters Affecting Mercury Speciation in a Biosolids Incinerator

2.2.2.1 Temperature

Mercury is typically converted to Hg^0 in the high temperatures of an incinerator, 1470°F +/- 103 °F, (many Hg species decompose at 200-300°C).³⁷ After leaving the combustion chamber, the mercury then partitions into three primary forms as it cools and condenses:³⁸

1. elemental mercury vapor (Hg^0)
2. oxidized or ionic mercury vapor (Hg^{II})
3. particulate mercury (Hg^{P})

As discussed elsewhere in this report, the final speciation depends on temperature and other flue gas components present.^{39,40}

Temperatures of operation across a facility are important because of the highly volatile nature of mercury. The dynamics of volatilization in the incineration chamber and re-condensation in the flue gas stream, and speciation throughout the process can dictate the concentration of mercury emitted or captured.⁴¹ Several studies have included temperature investigations on the impact of volatilization and speciation of mercury in incinerators, biosolids incinerators as well as those in other industries. Unfortunately, predictions of mercury speciation

³⁵ National Association of Clean Water Agencies (2008)

³⁶ Medical Academic and Scientific Community Organization, Inc. (2007)

³⁷ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

³⁸ U.S. EPA. (2005a)

³⁹ Kilgroe, J.D. (1996)

⁴⁰ Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

⁴¹ Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

Minimizing Mercury Emissions in Biosolids Incinerators

are difficult because flue gas systems are rarely at equilibrium, therefore mercury speciation becomes more dependent on kinetic considerations.⁴²

It should be recognized that the manipulation of incineration temperatures performed for other pollutant controls may also adversely affect mercury control. For example, incineration at higher temperatures can decompose dioxins and furans, but could increase mercury emissions as well.⁴³

2.2.2.2 Humidity

Humidifying flue gas can lower its temperature, but high water content can inhibit mercury oxidation or mercury adsorption onto particulate material, both actions shifting the mercury equilibrium towards volatile elemental mercury.

2.2.2.3 Oxygen

The oxygen content of combustion system pushes the system towards oxidation conditions.⁴⁴ In general, mercury will tend to be in ionic form (HgCl_2) under oxidizing conditions.⁴⁵

2.2.2.4 Chlorine

As discussed previously, the presence of chlorine influences the formation of metal chlorides;⁴⁶ high chloride content drives the production of HgCl_2 , which is a simpler species to control by using wet and dry scrubbers. These methods are less effective at removal of elemental mercury.

2.2.2.5 Sulfur

The influence of sulfur on mercury speciation depends on the form of sulfur present in the feedstock. Sulfur can bond with mercury to form stable compounds such as HgS or HgSO_4 .⁴⁷ This bonding of mercury with sulfur inhibits the oxidation of mercury through competition.⁴⁸

It has been reported that mercury emissions are lower in biosolids with high sulfur contents. This is likely because of the mercury and sulfur present in the feedstock being a stable compound to begin with (e.g., HgSO_4), rather than the formation of Hg-S compounds during the incineration process.⁴⁹ It has also been suggested that other metals may have a higher affinity to sulfur than mercury, so presence of other competing metals may reduce the mercury control capacity of sulfur.⁵⁰ In addition, there is also some evidence that SO_2 in flue gas can increase mercury oxidation, which could increase mercury removal rates because ionic mercury is generally more easily removed than elemental mercury;⁵¹ sulfate, however, can inhibit mercury oxidation by competing for active sites.⁵²

⁴² Brown, T.D., Smith, D.N., Hargis, R.A. Jr., O'Dowd, W.J. (1999)

⁴³ Kilgroe, J.D. (1996)

⁴⁴ Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

⁴⁵ Gauthier, R.Y.D., Flamant, G. (2001)

⁴⁶ Chang, M.B., Hsiung, C., Hsiu, J., Wu, T., Yi, H. (2003)

⁴⁷ Yao, H., Luo, G., Xu, M., Kameshima, T., Naruse, I. (2006)

⁴⁸ Yao, H., Luo, G., Xu, M., Kameshima, T., Naruse, I. (2006)

⁴⁹ Yao, H., Luo, G., Xu, M., Kameshima, T., Naruse, I. (2006)

⁵⁰ Gauthier, R.Y.D., Flamant, G. (2001)

⁵¹ Montgomery, J.L., Whitworth, C.G., Battleson, D.M., Ray, I., Buckley, W., Reynolds, J., Altman, R. (2005)

⁵² U.S. EPA. (2005a)

2.2.2.6 Carbon

As with carbon use in APCDs (such as fixed beds or ACI), carbon present in the biosolids can also influence emissions. Carbon in biosolids can inhibit mercury evolution during incineration with higher carbon concentrations relating to lower mercury emissions⁵³ and unburned carbon in ash can adsorb mercury.⁵⁴

2.2.2.7 Selenium

Selenium can combine with mercury to produce HgSe, a stable compound. The addition of Se to the combustion chamber can reduce mercury emissions.⁵⁵

⁵³ Yao, H., Luo., G., Xu., M., Kameshima, T., Naruse, I. (2006)

⁵⁴ Dajnak, D., Clak, K.D., Lockwood, F.C., Reed., G. (2003)

⁵⁵ Hogland, W.K. (1994)

CHAPTER 3.0

AIR POLLUTION CONTROL DEVICES IN A BIOSOLIDS INCINERATOR

3.1 Air Pollution Control Devices

All biosolids incinerators that were built or modified after June 11, 1973, are required to meet the particulate emission limit of 1.3 lb/ton dry solids incinerated. This equates to approximately 0.03 grains/dscf at 7% oxygen and all biosolids incinerators primarily use wet scrubbers to minimize particulate. In the project survey preceding this report, four categories of APCD were reported to already be in operation (Table 3-1).

Table 3-1. Categories of Air Pollution Control Devices Reported by the 31 Respondents in the Project Survey.

APCD	Devices Used (%)
Impingement tray scrubber only	3 (10)
Venturi scrubber only	6 (19)
Venturi/Impingement tray scrubber	12 (39)
Venturi/Impingement tray scrubber and bag house	1 (3)
Venturi/Impingement tray scrubber and wet electrostatic precipitator	1 (3)
Venturi/Impingement tray scrubber and bag house/Wet electrostatic precipitator	1 (3)
Impingement tray scrubber and other	1 (3)
Venturi/Impingement tray scrubber and other	6 (19)

Although the use of these APCDs was initiated by the control of other potential pollutants, such as particulate material in the flue gas, they do have a co-benefit in the removal of mercury. To understand the co-benefit that may be latently obtained from these systems, two things must be understood: 1) the method of operation of the APCDs, and 2) the physical properties of mercury species. This section outlines the method of operation of the APCDs reported in the project survey. The chemistry of mercury is reviewed in following sections.

3.1.1 Venturi Scrubber

A Venturi scrubber consists of three sections: a converging section, a throat section, and a diverging section. Liquid is introduced either at the throat or at the entrance to the converging section (Figure 3-1). The applied Venturi effect is a case of fluid flow through a tube or pipe with a constriction in it.

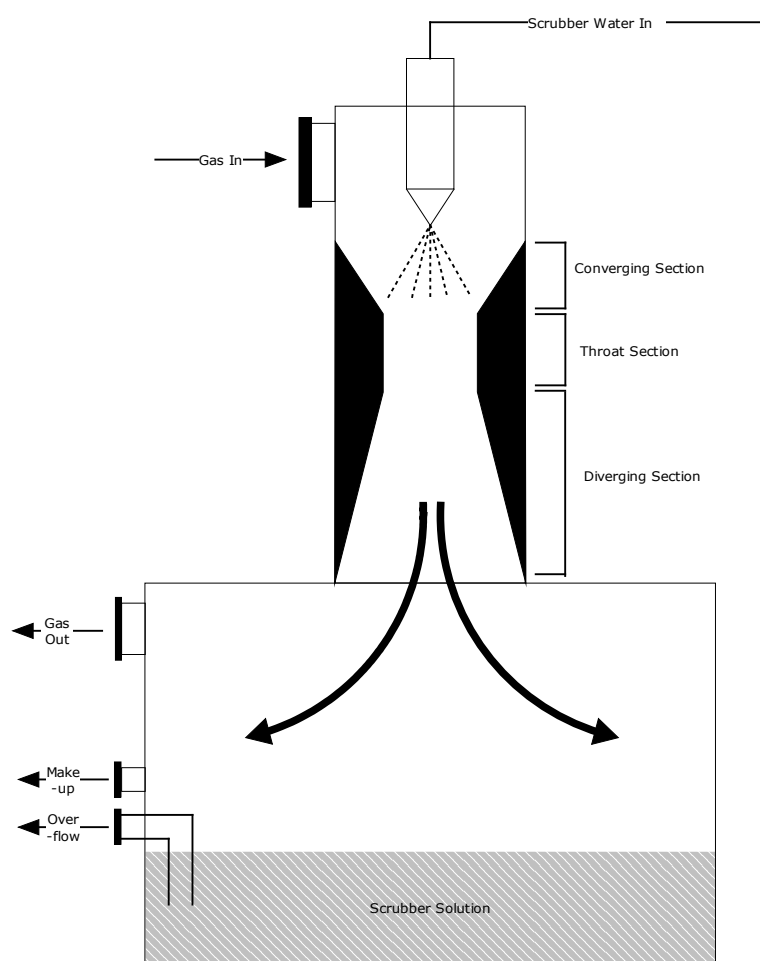


Figure 3-1. Basic Schematic of a Venturi Scrubber Without Associated De-misting Section.

The fluid is forced through the throat by the incoming gas, this increases the fluid velocity, at the same time the system pressure decreases. When the fluid exits the throat the fluid velocity decreases and the pressure increases, the resulting increase in pressure aerosolizes the fluid (the inlet gas, forced to move at extremely high velocities in the small throat section, shears the liquid from its walls, producing an enormous number of very tiny droplets) and mixes it with the incoming gas. This was demonstrated to effectively remove particles from the gas stream.⁵⁶ Particle and gas removal occur in the throat section as the inlet gas stream mixes with the liquid droplets. Generally Venturi scrubbers are selected to control particulate matter and high-solubility gases.

All Venturi scrubbers require some form of entrainment separator because of the fine droplets created by the Venturi action tend to entrain in

to the outlet clean gas stream. These are typically a cyclonic mechanism, but mesh-pad and blade separators are also used. [Biosolids incinerators almost always use the variable Venturi followed by an impingement plate scrubber, followed by blade (vane), mesh (or structured packing) type entrainment separators.]

The high-inlet gas velocities in a Venturi scrubber results in a very short contact time between the liquid and gas phases. This short contact time, in turn, limits gas absorption. If abatement of a gaseous component is the main target of a Venturi, absorption can be maximized by reducing the gas velocity, which increases residence time. The increased residence time allows for a longer contact time between phases, thus better absorption. Most biosolids incinerators use a mechanically variable throat to optimize the contact area and velocity for varying flow conditions and particulate removal.

⁵⁶ Johnstone, H.F., M.H. Roberts. (1949)

3.1.2 Impingement Tray Scrubber

Impingement tray scrubbers are often used where higher gas absorption efficiency is required, with some particulate collection as well. An impingement-plate scrubber is a vertical chamber with plates mounted horizontally inside a hollow shell (Figure 3-2).

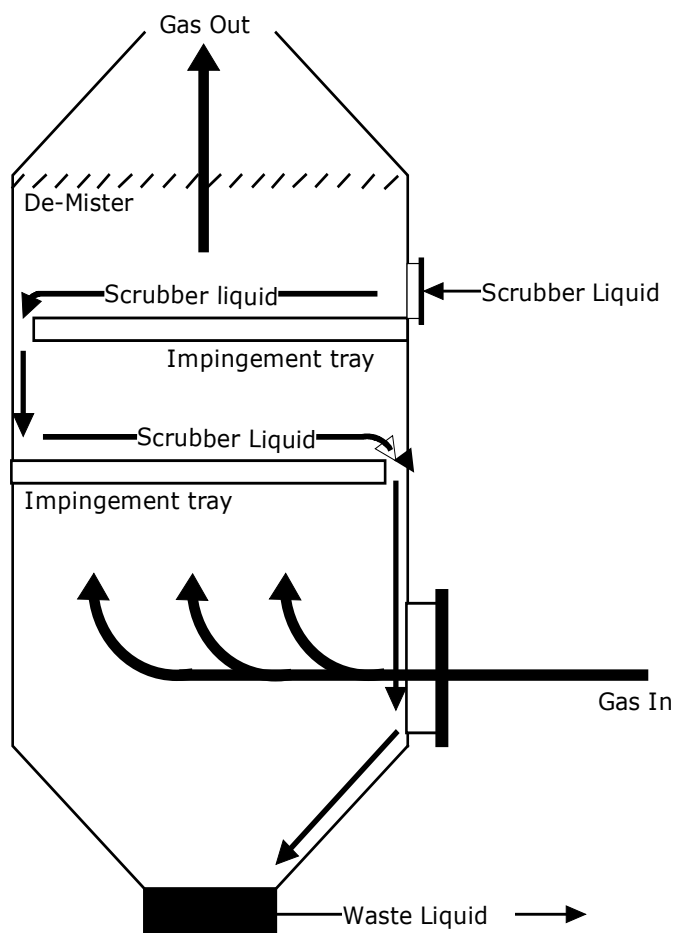


Figure 3-2. Basic Schematic of an Impingement Tray Scrubber.

Impingement-plate scrubbers operate as crosscurrent particulate matter collection devices. The scrubbing liquid flows across the plates, and is distributed down the tower to the next plate while the gas stream flows upward. Contact between the liquid and the particle-laden gas occur on the plates. The plates are equipped with openings that allow the gas to pass through. Some plates are perforated or slotted, whereas more complex plates have valve-like openings. The simplest impingement-plate scrubber is the sieve plate, which has round perforations. In this type of scrubber, the scrubbing liquid flows over the plates and the gas flows up through the holes. The gas velocity suspends the liquid, and thus minimizes the liquid from flowing down through the perforations. Enhanced gas-liquid- particle contact is achieved within the froth generated by the gas jetting (passing) through the liquid

layer; and thus the flowing fluid sweep away (entrains) the particulate. Complex plates, such as bubble cap or baffle plates, increase the effectiveness of collecting particulate matter. The bubble caps and baffles placed above the plate perforations force the gas and particulate to turn and the particulate to be entrained before escaping the layer of liquid. Bubble caps and the like also modify the gas jet pressure drop to help prevent liquid from weeping (flowing down the perforations) if the gas flow is reduced. In all types of impingement-plate scrubbers, the scrubbing liquid flows across each plate and down the inside of the tower onto the plate below. After the bottom plate, the liquid and collected particulate matter flow out of the bottom of the tower.

3.1.3 Common Trays

Impingement tray – A dual layer tray providing high mass transport (large surface area) for the gas and liquid mixing and heat transfer (cooling). The bottom layer takes the gas flow and converts it into small bubbles. The top layer reduces the bubble size further and creates a target area for particulate matter removal. The dual layer also provides effective cooling.

Tubular slot tray – Used for gases with high particulate loading, it effectively cools the gas and removes particulate matter and fibrous matter without plugging

Sieve tray – Primarily used to cool gas, the numerous small orifices convert the gas stream into tiny jets penetrating the scrubber liquid layer.

Valve tray – Essentially this is an adjustable impingement tray that maintains constant efficiency and pressure drop via self-adjusting caps. It provides good cooling and excellent gas adsorption.

3.2 Combination Systems

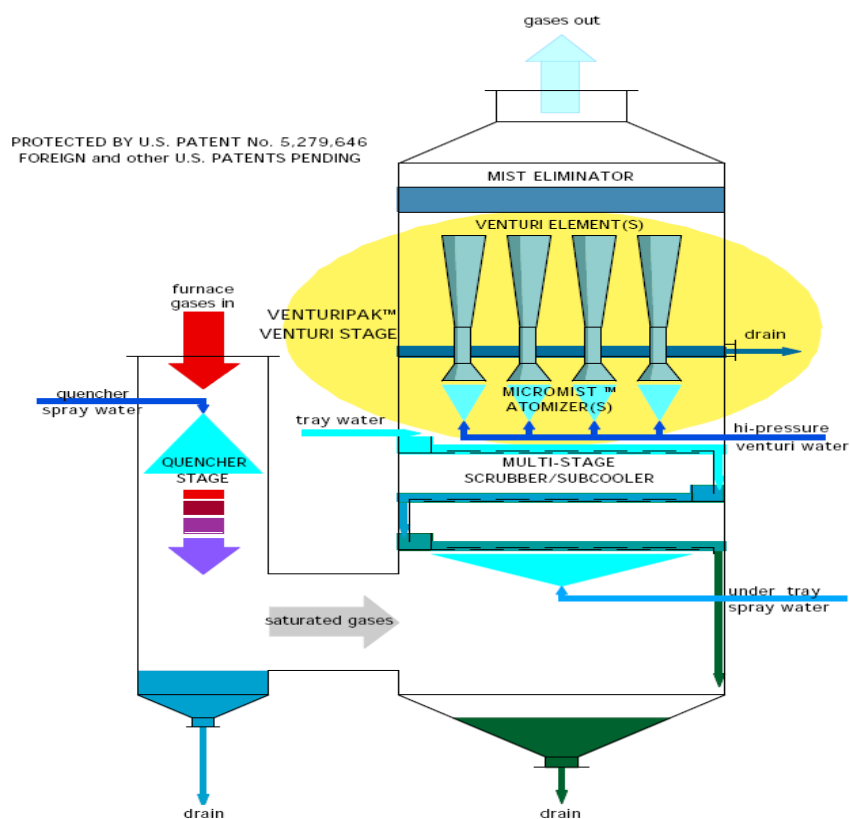
Recently Central Contra Costa Sanitation District, as well as other facilities, have examined the use of a combined quencher/impinger/multiple fixed-throat Venturi scrubber system and found favorable results. The system (Figure 3-3) contacts the flue gas with the three scrubbing stages to remove large particulates first and then subsequently remove smaller particulate material. The low-energy quench/Venturi section is reported to capture most of the ash, sand, and other “coarse” particulate in the entering gas stream. It will also capture all soluble mercury species. The impingement trays remove most particulate 10-micron and larger, and agglomerate and condition submicron particulates and aerosols for removal in the final stage. The final stage is a bank of several “near true” remaining particulate matter (2.5/submicron particulate material, including aerosols and soot), are removed.

3.3 Baghouse

A baghouse is generic name for APCD that is designed around the use of engineered fabric filter tubes, envelopes, or cartridges in the dust capturing, separation, or filtering process.

Baghouses use sieving, impaction, agglomeration, and electrostatic filtration principles to remove solids from a gaseous exhaust stream. They maximize the filtration area by configuring the fabric filter media into a series of long small-diameter fabric tubes referred to as bags (Figure 3-4). They are tightly packed into a housing wherein the dust-laden air moves across the bag fabric thereby removing it from the gas stream and building up a filter cake, which further enhances air cleaning. Large dust particles create a barrier that can capture the incoming fine particles. Fine particles, 1 micron in diameter or less, are very difficult to capture without this cake-layer. As the filter cake builds up on the filter bag, the pressure drop across the bag increases and the gas flow reduces. This means that the bags must be routinely “cleaned” of filter cake (Table 3-2) resulting in a pulse-type cycle of operation. The filter cake is removed to hoppers by various shaking means.

VenturiPak™ Wet Scrubber



57

Figure 3-3. Combination Wet Scrubber System for Optimum Particulate Removal.

⁵⁷ Reprinted with permission of Envirocare.

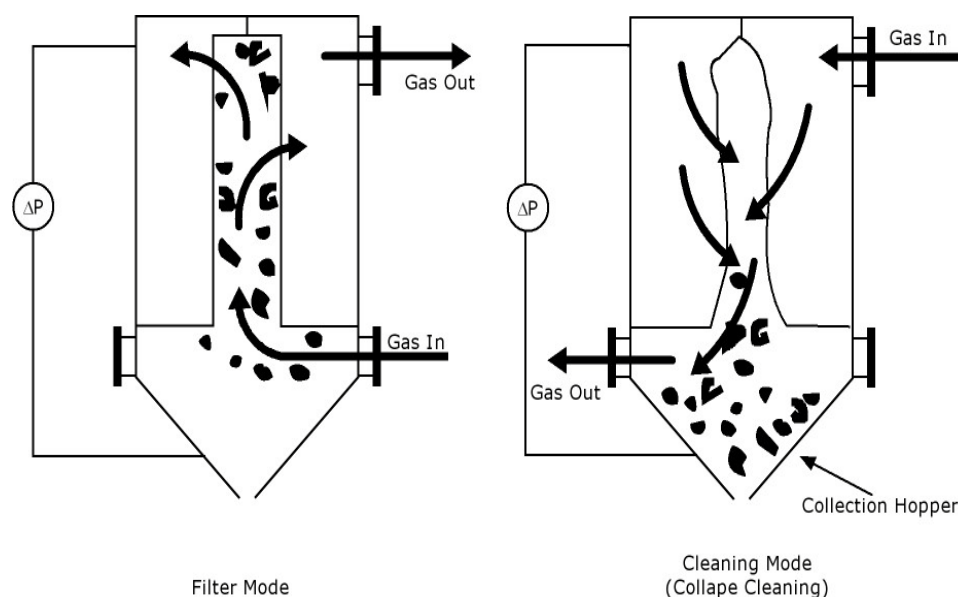


Figure 3-4. Basic Schematic of a Bag Filter Using Reverse Air System to Clean.

Table 3-2. Baghouses Come in Four Main Design Classifications Based on How the Dust Cake Accumulation is Removed and “Managed.”

	Method	Airflow	A/C Ratio
Pulse jet system	High-pressure air directed into the clean side of a filter bag to remove the dust cake from the surface of the media.	on-line cleaning	4-6 to 1
Shaker style system	Physically shakes the bags to mechanically release the dust cake.	off-line cleaning	2-4 to 1
Reverse air system	Physically collapses the bags to mechanically “shear” the dust cake from the bag surface.	off-line cleaning	1-3 to 1
Combinations and variations on the above three	Shaker with reverse air assist	off-line cleaning	
	Traveling manifold reverse air	on-line cleaning	
	Plenum pulse: usually off-line	Usually off-line cleaning	

3.4 Electrostatic Precipitators

The electrostatic precipitator (ESP) is control device that uses gaseous ions (a corona) to charge particles in a gas stream. The particles are then routed past positively charged, or grounded, plates. The negatively charged particles are attracted to the plates, and stay associated to the plates. Particulate material is then removed by “rapping” or washing the plates (Figure 3-5).

In a wire-pipe (tubular) ESP, the exhaust gas flows vertically through many parallel tubes. The electrodes are wires or rigid, narrow tubes suspended from a frame in the upper part of the ESP and run concentric down the central axis of the tube. In a wire-plate ESP, the exhaust

gas flows parallel to vertical plates of sheet metal. The electrodes are weighted wires, or posts, placed between the plates. The plates are placed within a flow path, forcing the gas to pass each wire in turn.

Particle removal efficiency can be affected by a non-charged area at the top of the ESP, because of necessary clearances. Anti-sneakage baffles are used to divert any gas back into the main flow. In addition, the rapping that dislodges the particulate build up on the plates can throw some of the collected material back into the gas stream. This can be avoided in a wet ESP where the particle build up is washed into a sump by water, sprayed near the top of the chamber. Particle resistivity can also reduce the collection efficiency.

To produce the free ions and electric field, high internal voltages are required. Because the collection process does not rely on mechanical processes such as sieving or impaction, but rather electrostatic forces, the internal gas passages within a precipitator are relatively open with small pressure drops and lower energy costs to move the gas stream. High collection efficiencies are possible, but as mentioned collection efficiency may drastically change with changes in operating parameters. The inlet gas stream typically has a high temperature and may require a pretreatment step of spraying water into the flue gas to increase the gas humidity thereby lowering the particle resistivity.

ESPs require a large installation space, they have a high potential for ignition sources, and they have re-entrainment issues and are susceptible to changes in moisture and resistivity. In biosolids incinerator facilities only wet ESPs have been reported as being used and these have the potential of severe corrosion problems as discussed in later sections. However, ESPs also have low pressure drops and air moving costs, have a high affinity for small particles and can operate at high temperatures.

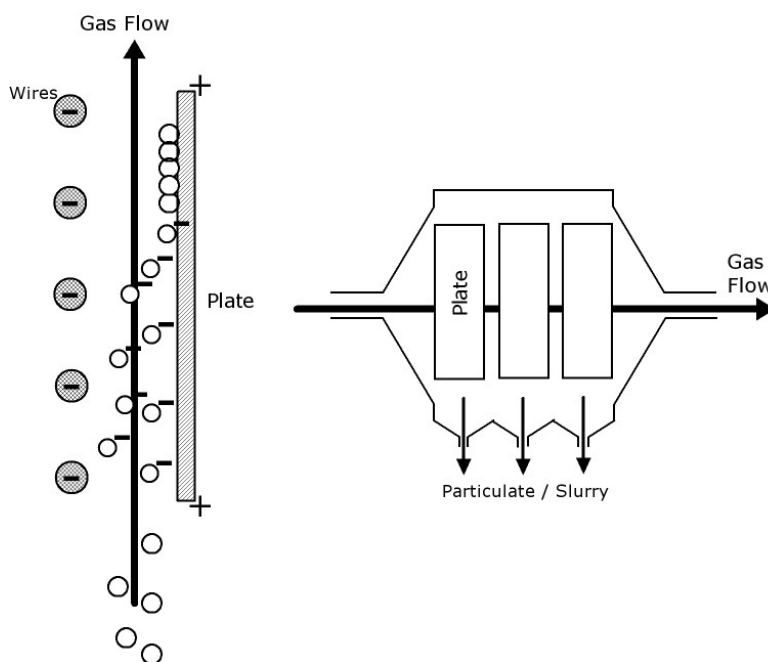


Figure 3-5. Basic Schematic of an Electrostatic Precipitator.

3.5 Impact of Mercury Speciation on Co-Benefit Removal by Existing APCDs

As discussed in previous sections it is reasonable to expect that mercury will be present in biosolids incinerator flue gas in three major forms: particulate mercury (Hg^p), elemental mercury (Hg^0) and oxidized mercury (Hg^{II}). The physical properties of each of these mercury forms, or species, will determine the co-benefit removal potential of an APCD. The information presented in previous sections allow a speculative assessment of which species is expected to be removed by what APCD.

Control of particulate bound mercury has been demonstrated in a number of industries by particulate removal systems such as ESP or fabric filters. Oxidized mercury is very water soluble and easily interned in any type of wet scrubbing mechanism. However, elemental mercury is not effectively captured by either of the previously mentioned techniques and is considered the Achilles heel in any mercury control strategy (Figure 3-6).

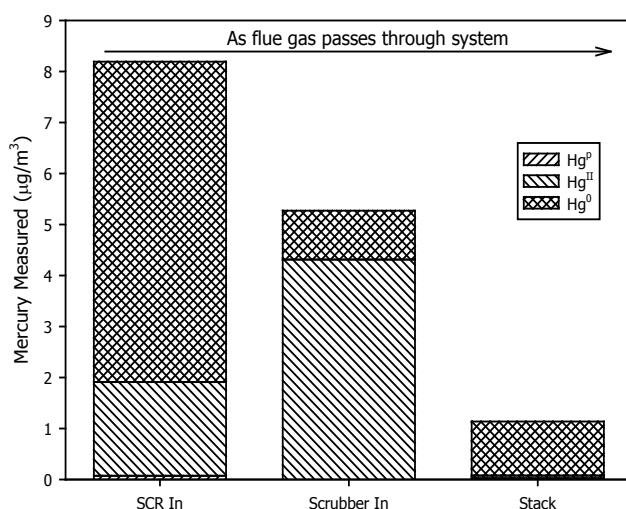


Figure 3-6. Effect of Mercury Species on Co-Benefit Mercury Removal through Flue Gas Treatment Units.

Table 3-3 presents the co-benefit removal of APCDs in the coal fire utility industry.⁵⁸ It is seen that the removal efficiencies have a huge range independent of the APCD. This is simply the impact of the mercury species on the removal efficiency (Table 3-4) and as previously discussed, the proportion of each mercury species present is dependent on the chemical and physical composition of the feed stock and the operational conditions.

⁵⁸ U.S. EPA. (1997b)

Table 3-3. Co-Benefit Removal of APCDs in the Coal Fire Utility Industry.

APCD	Hg Removal %	Mean Hg Removal %	Relative Standard Deviation %
Flue gas desulfurization	0.00 – 61.67	30.85	73.16
Spray dryer adsorption	0.00 – 54.50	25.59	111.53
Fabric filter	0.00 – 73.36	28.47	125.08
Cold-side ESP	0.00 – 82.35	23.98	107.88
Hot-side ESP	0.00 – 83.00	31.17	127.51

Table 3-4. Speculated Mercury Species Co-Benefit Removal of the APCDs Discussed.

APCD	Operation	Hg ^P	Hg ^{II}	Hg ⁰
Venturi scrubber	Wet	X	X	
Impinger tray	Wet	X	X	
Combined system	Wet	X	X	
Wet ESP	Wet	X	X	
Dry ESP	Dry	X		
Baghouse	Dry	X		

With regards to the APCDs reported in the project survey, the co-benefit mercury removal of a wet scrubber system, Venturi or impinger, directly depends on the amount of water soluble Hg^{II} and Hg^P in the flue gas entering the APCD.

Fabric filters typically have a good co-benefit for mercury control and this is reflected in the results of the 1999 U.S. EPA ICR with mercury removal efficiencies up to 98%. This is primarily because of the relatively greater gas-solid contact time with the ash filter cake that builds up on the surface of the bag, acting similar to a sorbent bed, resulting in greater oxidation and capture efficiency compared to other APCD types.⁵⁹ However, it appears that the amount of chlorine in the fuel and/or unburned carbon in the flyash is critical for high capture rates.⁶⁰

It has been shown that ESPs are rarely effective at capturing mercury in coal flue gas because nominally all of the mercury is in the gas phase, this is also expected in the biosolids industry. In some instances, high mercury capture efficiencies for ESPs are possible for feed stocks that are high in chlorine content and unburned carbon in the flyash.⁶¹ However, if a mercury control technology is placed that increases particulate bound mercury, discussed in the next section, there would be an increase in effectiveness of the ESP for co-benefit mercury removal.

It should therefore be understood that any speculation as to the actual ability of existing technologies to add co-benefit mercury removal needs to begin with a thought process, similar to that described in Chapter 6.0, and illustrated in Figure 3-7. This thought process will also be the

⁵⁹ Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A. (2003)

⁶⁰ Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A. (2003)

⁶¹ Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A. (2003)

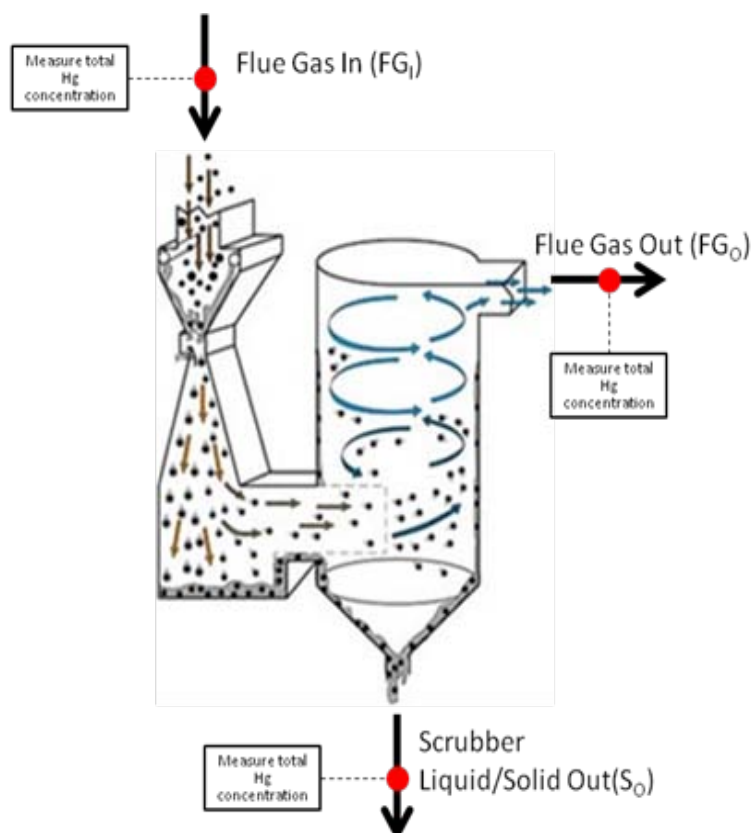


Figure 3-7. Determining the Co-Benefit of Mercury Removal of a Unit.

starting point for understanding if the mercury capture co-benefit can be optimized without disrupting the system or if dedicated strategies for mercury emission need to be investigated.

Figure 3-7 shows that the total concentrations for mercury entering the unit (FGD) whether it is a dry or wet scrubber, is partitioned into the solid/liquid phase (S_O) and the flue gas leaving the unit (FG_O). If FG_O total mercury values are not available, it is possible to equate the co-benefit of mercury removal to the total mercury in S_O. However, because of operational characteristics of the APCDs, it is often more accurate to determine co-benefit mercury removal by equation (3.5-1). Factors that inhibit accurate assessment of the S_O sample are poor sample homogeneity and loss of mercury during collection. There may also be other sources of mercury contributing to the scrubber, such as recycled scrubber water, which bias the co-benefit value.

$$\text{Co-benefit Hg removal} = \text{Total Hg in FG}_I - \text{Total Hg in FG}_O \quad (3.5-1)$$

The other consideration that needs to be understood when understanding co-benefit mercury removal is mercury re-emission. What this means is that with a mercury-saturated wet scrubber, potentially brought about by the recycling of scrubber water, certain chemistries exist that can re-emit the stored mercury. This should not be an issue in the biosolids incinerator APCD, but deserves a comment for awareness as an example of situations that can unexpectedly

affect total mercury assessments in operating units. In recent investigations,⁶² testing, and data evaluation suggested that sulfur complexes are major drivers for the chemical reduction of Hg^{II} to Hg^0 , and that this could result in re-emission of mercury from the wet scrubber. It was observed that the re-emission of Hg^0 resulted from the impact of high SO_3^{2-} concentration (4000 ppm, mg/kg) in recirculating slurry when a trace amount of a sulfide-donating reagent was added. Therefore, it is possible to see more mercury coming out of the unit than is entering a unit. However, the chemistry determined to be necessary, during these investigations was very specific to FGD scrubbers, placed at a coal-fired utility.

⁶² Nolan, P.S., Redinger, K.E, Amrhein, G.T., Kudlac, G.A.(2002)
Minimizing Mercury Emissions in Biosolids Incinerators

CHAPTER 4.0

CURRENT PRACTICES FOR REDUCTION OF MERCURY EMISSIONS BEYOND APCD CO-BENEFIT

4.1 Mercury Control in Coal-Fired Electric Generating Units

The U.S. Department of Energy, the Electric Power Research Institute, the U.S. Department of Environmental Protection (U.S. EPA), and electric generating utility (EGU) companies have been very active in supporting the development of mercury control technology in coal-fired power plants (CFPP) in anticipation of the recently passed regulations on mercury emissions for this industry. The status of the government-sponsored CFPP mercury control technology programs have been nicely summarized and should be referred to for more details.^{63,64,65,66,67,68,69} In particular, the Department of Energy sponsored a Mercury Control Conference in 2006 that provides the most up-to-date information about mercury control in CFPPs. Several novel research-based concepts for mercury control have been investigated, such as in-line noble metal sorbents that can be regenerated *in situ*. However, because of existing fiscal, technological, and regulatory constraints such as the requirement to control other non-mercury emissions, the EGU development has been overwhelmingly focused on a couple of select options for mercury control: 1) improving existing FGD systems for mercury capture and 2) using existing particulate capture technology such as ESPs and fabric filters in combination with mercury adsorption on particulate matter such as flyash or ACI. Because it is well known that Hg^{II} is captured more efficiently in existing pollution control devices in comparison to Hg⁰, there have been several efforts to enhance the fraction of Hg^{II} in flue gas. A general schematic of a coal-fired EGU, the typical pollution control devices and the options to increase the oxidized fraction of mercury is shown in Figure 4-1.

As discussed in the previous chapter, co-benefit mercury removal occurs in most APCDs even though alternate air pollution control is the primary driver for installation. Table 4-1 summarizes average percentage mercury capture as a function of coal type and APCD combination. It was also explained in the previous chapter that the variance in the average capture of the mercury is likely based on the species of mercury present in the flue gas. In

⁶³ U.S. EPA. (2005a)

⁶⁴ Feeley, T.J., Murphy, J., Hoffmann, J., Renninger, S.A. (2003)

⁶⁵ Feeley, T.J. (2005)

⁶⁶ U.S. DOE (2006)

⁶⁷ U.S. DOE (2007)

⁶⁸ Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A. (2003)

⁶⁹ Jones, A.P., Hoffmann, J.W., Smith, D.N., Feeley, T.J., Murphy, J.T. (2007)

Minimizing Mercury Emissions in Biosolids Incinerators

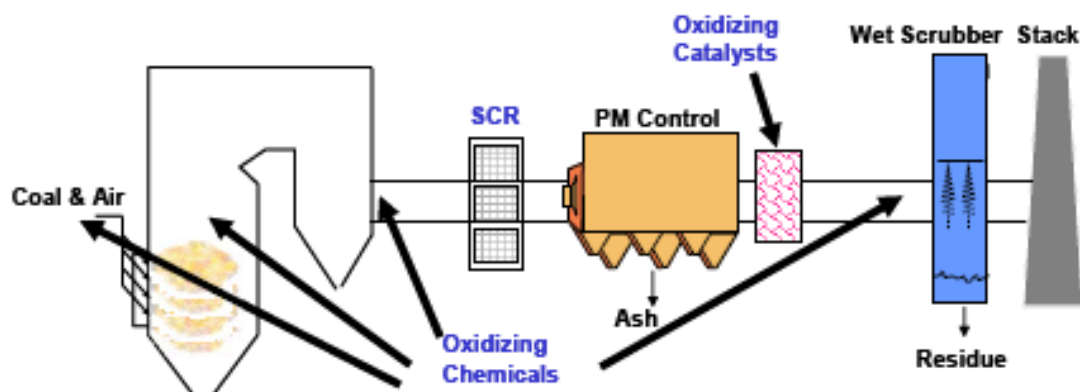


Figure 4-1. Schematic of Existing Pollution Control Devices in Coal-Fired EGUs Used to Capture Mercury and Options for Enhancement by Increasing the Oxidized Mercury Fraction. Selective catalytic reduction (SCR) is used for nitrogen oxide control and the particulate matter control is usually an ESP or fabric filter.

Table 4-1. Shown is a Summary of the Average Percentage Mercury Capture by Coal Rank and APCD Configuration as Reported by the U.S. EPA 1999 ICR for Coal-Fired EGUs.

The range of capture for a particular APCD is not shown, but can be very large.

APCD Configuration	Average Percentage Mercury Capture by Coal Type		
	Bituminous	Sub-bituminous	Lignite
Cold-side ESP	36	3	- 4
Hot-side ESP	9	6	NA
Fabric filter	90	72	NA
Particulate scrubber	NA	9	NA
Spray dryer adsorber + ESP	NA	35	NA
Spray dryer adsorber + fabric filter	98	24	0
Spray dryer adsorber + fabric filter + selective catalytic reduction	98	NA	NA
Particulate scrubber + wet flue gas desulphurization	12	- 8	33
Cold-side ESP + wet flue gas desulphurization	74	29	44
Hot-side + wet flue gas desulphurization	50	29	NA
Fabric filter + wet flue gas desulphurization	98	NA	NA

previous chapters, dependence of the mercury species was presented as a function of combustion conditions and matrix components, such as sulfur and chlorine. All of these contributions are used in concert to manipulate chemistries and create mercury capture systems.

4.1.1 Enhancing Wet Scrubbers for Mercury Capture

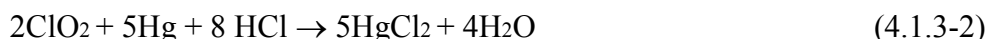
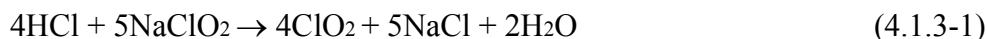
A number of large studies have been completed in the last five years aimed at enhancing the fraction of Hg^{II} in coal flue gas to improve capture by wet scrubbers, predominantly FGDs. The primary study areas for increasing the fraction of Hg^{II} in coal flue gas are:

- ◆ Fuel blending – typically adding small amounts of high sulfur and chlorine bituminous coal to the primary low chlorine and sulfur coal fuel supply.
- ◆ Adding oxidizing chemical additives to the coal fuel before combustion – the additives are often proprietary, but are usually chlorine or other halide salts (e.g., CaCl_2).
- ◆ Combustion modification to increase unburned carbon.⁷⁰
- ◆ Optimizing selective catalytic reduction units designed for NO_x abatement to provide the co-benefit of Hg^0 to Hg^{II} conversion.
- ◆ Using mercury-specific catalysts installed between the ESP/fabric filter and the FGD such as iridium, palladium, gold, activated carbon, and flyash.⁷¹

4.1.2 Methods to Capture Hg^0 and/or Sequester Captured Hg^{II} in Wet Scrubbers

Very few efforts, in the United States have been directed at capture of Hg^0 in wet scrubbers. However, one method has recently been granted a U.S. EPA Phase II Small Business Innovative Research Grant.⁷² This method uses a proprietary chelating agent, which is simply added in a liquid form to the existing wet scrubber liquor to sequester and then co-precipitate the captured Hg^0 . To partition the Hg^0 from the flue gas to the wet scrubber liquor, the gas contact must be optimized. Standard Venturi scrubbers do not have the mass transfer required for this form of mercury capture. However, jet bubble reactors and multiple stage scrubbers, currently entering the commercial market, do have the mass transport required and pilot testing is underway to determine the efficacy.

In Europe, oxidizing scrubbers are being employed. This process is based on the injection of sodium chlorite in the flue gas, which reacts with dissolved hydrogen chloride forming chlorine dioxide, Equation (4.1.3-1). This then passes over the phase interface and oxidizes the mercury according, Equation (4.1.3-2).



As discussed in previous sections, re-emission of captured Hg^{II} can be problematic. In other words, more Hg^0 is observed at the outlet of the wet scrubber than at the inlet because of chemical reactions. At least three chemical additives have been tried to reduce re-emission of captured Hg^{II} in wFGDs. The first is sodium hydrosulfide (NaHS), which not only reduced the re-emission of Hg^{II} , but also captured some of the Hg^0 for a total Hg removal rate of 78%.⁷³ Another method uses a proprietary chemical additive called TMT-15 (Evonik's – previously Degussa) in alkaline wet scrubbers. The chemical reduction of ionic mercury to elementary

⁷⁰ U.S. EPA. (2005a)

⁷¹ Presto, A.A., Granite, E.J. (2006)

⁷² U.S. EPA. (2007)

⁷³ U.S. EPA. (2005a)

mercury by SO₂ is suppressed by chelating the ionic mercury in the scrubber water with TMT-15.⁷⁴ Finally, a thiosorbic compound was tried and mixed results were observed in two short tests.⁷⁵

4.1.3 Mercury Capture by Spray-Dryer Adsorbers and Fabric Filters

Hot, untreated flue gas, when introduced into a spray dryer absorption chamber contacts a fine spray of reagent slurry. A significant part of the acidic components in the flue gas are rapidly absorbed into the alkaline droplets as the water evaporates simultaneously. Control of gas distribution, slurry flow rate and droplet size ensure that the droplets are dried to a fine powder before they touch the chamber walls of the spray dryer absorber.

The use of spray dryer absorbers followed by fabric filters can be a very effective mercury control method if the flue gas is mostly oxidized mercury and/or if high levels of active chlorine species remain past the spray dryer absorber to help oxidize and capture elemental mercury on the flyash filter cake.⁷⁶ This phenomenon was most evident in a full-scale test where sub-bituminous coal had poor mercury capture with a spray dryer absorber-fabric filter until the coal was blended with a higher chlorine bituminous coal to achieve 80% mercury capture.⁷⁷ The use of a spray dryer absorber-fabric filter system in the coal industry is not very common and is largely applied to western, low-chlorine sub-bituminous coals. Thus, much of the recent research for spray dryer absorber-fabric filter systems has been focused on ACI, discussed below.

4.1.4 Halide Addition

One method that has been extensively studied in the coal-fired industry is halide addition to promote oxidized mercury, improving mercury capture in wet scrubbers.⁷⁸ As the biosolids industry has low chlorides this may be a viable approach to improving mercury capture. It has also been shown that bromide addition improves mercury capture two-fold more than mercury capture after chloride addition. Coincidentally, recent concern regarding the corrosive effects of chloride addition have been addressed by the substitution of chloride with bromide. However, some leaching of bromine from the resulting ash was observed, although the environmental impact of this is currently unknown.

4.1.5 Mercury Capture by Activated Carbon Injection in Coal-Fired Utilities

The use of ACI for mercury control is a rapidly emerging area of research and full-scale application in coal-fired flue gas. For more details on ACI, see the proceedings of the 2006 Department of Energy Mercury Control Conference.⁷⁹ In the principle of ACI is based on the physi-sorption or chemi-sorption of gas phase mercury compounds on pneumatically injected submicron activated carbon in the ductwork upstream of a particulate control APCD such as a baghouse or ESP. The activated carbon products currently available are numerous, with some being chemically treated with halogens for improved performance.⁸⁰

⁷⁴ Miller, C.E., Feeley, T.J., Aljoe, W.W., Lani, B.W., Schroeder, K.T., Kairies, C., McNemar, A.T., Jones, A.P., Murphy, J.T. (2006)

⁷⁵ Miller, C.E., Feeley, T.J., Aljoe, W.W., Lani, B.W., Schroeder, K.T., Kairies, C., McNemar, A.T., Jones, A.P., Murphy, J.T. (2006)

⁷⁶ U.S. EPA. (2005a)

⁷⁷ Feeley, T.J. (2005)

⁷⁸ Brickett, L. (2007)

⁷⁹ Brickett, L. (2007)

⁸⁰ Sjostrom, S., Dillion, M., Donnelly, B., Bustard, J. (2007)

As described by the U.S. EPA, the variables affecting ACI performance are:

- ◆ Injection rate of the activated carbon, typically given in lb/MMacf (pounds per million actual cubic feet of gas). In coal-fired utilities, ACI rates used are typically 0.5-15 lb/MMacf.
- ◆ Flue gas chemical and physical properties, such as temperature and presence or absence of other reactive compounds such as SO₃, HCl, and flyash
- ◆ The APCD type and configuration, such as a hot-side or cold-side ESP
- ◆ The physical and chemical characteristics of the sorbent, especially particle size and addition of halogens
- ◆ Injection engineering technique, because capture is often mass-transfer limited

A common theme for CFPPs and mercury control using ACI is the wide ranging results because of unique difference between facilities. In other words, only general trends have been established and thus the optimization of mercury control required for a given location has required actual testing and optimization. However, the ACI demonstrations at coal-fired utilities to date have determined the following general trends:^{81,82,83,84,85,86,87}

- ◆ Standard activated carbon material can achieve high mercury capture efficiency nominally greater than 80% at CFPP with cold-side ESPs burning high rank bituminous coals
- ◆ Standard activated carbon is usually inefficient at mercury capture in CFPP burning low rank western sub-bituminous coals with cold-side ESPs. Capture efficiencies can be below 50%.
- ◆ Use of halogen-treated activated carbon improves mercury capture and can result in 70-80% mercury capture efficiency for CFPP burning western sub-bituminous coal and either an ESP or fabric filter.
- ◆ Lower flue gas temperatures result in greater mercury capture using standard ACI. Thus, the control of mercury in a hot-side ESP is still problematic.
- ◆ The use of ACI in front of a fabric filter is nominally better than an ESP because of the better gas contact time with the sorbent material. ESPs suffer from mass transfer limitations that are being solved by improved injection engineering techniques.
- ◆ The halogen-treated ACI greatly improves mercury capture in CFPP burning western sub-bituminous coals with spray dryer absorber-fabric filter configurations.
- ◆ The presence of SO₃ in coal flue gas can dramatically reduce ACI mercury capture efficiency⁸⁸ whereas SO₂ content has no effect on mercury capture efficiency.⁸⁹
- ◆ The economic cost of using ACI in a coal-fired power plant has been estimated to be from \$4,000 per pound of mercury to \$180,000 per pound of mercury removed.⁹⁰ However, the upper level values include the negative economic consequences because of the coal-fired

⁸¹ Sjostrom, S., Dillion, M., Donnelly, B., Bustard, J. (2007)

⁸² Brickett, L. (2007)

⁸³ U.S. DOE. (2006)

⁸⁴ U.S. EPA. (2005a)

⁸⁵ Feeley, T.J. (2005)

⁸⁶ Jones, A.P., Hoffmann, J.W., Smith, D.N., Feeley, T.J., Murphy, J.T. (2007)

⁸⁷ Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath, K.C., Laudal, D.L., Benson, S.A. (2003)

⁸⁸ Sjostrom, S., Dillion, M., Donnelly, B., Bustard, J. (2007)

⁸⁹ Presto, A., Granite, E. (2007)

⁹⁰ Jones, A.P., Hoffmann, J.W., Smith, D.N., Feeley, T.J., Murphy, J.T. (2007)

utility's inability to sell flyash by-products to the cement industry. This problem has been addressed by applying the Toxecon™ and Toxecon™ II engineering strategies where ACI is injected after the ESP into a small fabric filter or at the last section of the ESP, respectively. In this way, the ESP flyash by-product can be sold because it will not include added activated carbon. (It should be noted that there is a trend in the coal-fired industry to discuss the economic cost as relative – low, medium, high – because of the range of values presented by different authors).

- ◆ Using ACI can have negative consequences on the APCDs. For example, increased arcing in the ESP, more frequent cleaning of the fabric filters, and exceeding opacity limits.

4.1.6 Mercury Capture by Activated Carbon in Biosolids Incinerators

Two POTWs recently installed a total of four biosolids incinerators that were voluntarily equipped with mercury removal APCD systems that use activated carbon. Current reported data for these two POTWs are discussed below.

Ypsilanti, Michigan – An incinerator exhaust gas activated carbon polishing system was installed in 2005 at the Ypsilanti wastewater treatment plant to remove mercury, at a cost of approximately \$3 million. Mercury removal was, calculated from measured stack gas emissions of total mercury and total mercury in coming biosolids, observed to be >99% efficient (Table 4-2). However, it should be noted that following the incinerator were two condensation units, a caustic Venturi scrubber, a wet ESP, and then the sorbent bed activated carbon unit. No data were reported across the individual APCDs and no mercury speciation data were collected. It is therefore unrealistic to attribute the >99% mercury removal to the activated carbon polishing component.

Table 4-2. Mercury Removal Calculated from Data Reported from the Ypsilanti, Michigan, Biosolids Incinerator.
Removal was achieved using APCDs and a polishing activated carbon sorbent bed.

Run	Biosolids Hg (mg/hr)	Emission Rate Outlet (mg/hr)	Removal Efficiency (%)
1	2243	2.2	99.9
2	2243	3.6	99.8
3	2994	5.8	99.8
Average	2493	3.9	99.8
% Relative standard difference	17.4	46.9	0.0

St. Paul, Minnesota – In 2004, three new fluidized bed incinerators were placed into service at the Metropolitan wastewater treatment plant in St. Paul, Minnesota. To minimize mercury emissions, an ACI system – followed by a baghouse – was installed in each of the three air pollution control trains. Following the incinerator were condensation units, the ACI system, a baghouse and a wet ESP. In this instance, the mercury was measured separately across the ACI/baghouse system and the wet ESP. The mercury removal across the baghouse was found to be 94% with an extra 4% removal across the wet ESP. It is suggested in the reported data that the wet ESP was just acting as a polishing step after the bulk of mercury was removed by the ACI/baghouse system. Individual performance of the wet ESP was not reported. Examining the data further (Figure 4-2), and ignoring the one assumed outlier at 12 lb/hr of carbon injected, it can be seen that there is some upward trend in mercury capture with an increase in ACI. However, the statistical relevance of the range of ACI versus mercury capture is negligible,

2.4×10^{-5} lb Hg/hr \pm 89%. In fact, at some test points, zero ACI returns an equal or better mercury capture rate than 7, 12, or 14 lb AC/hr injected. It is not obvious whether this may be a function of the mass balance used to determine the mercury removal efficiency (temporal differences in measurements) or that particulate capture by the baghouse is the dominant mercury removal mechanism.

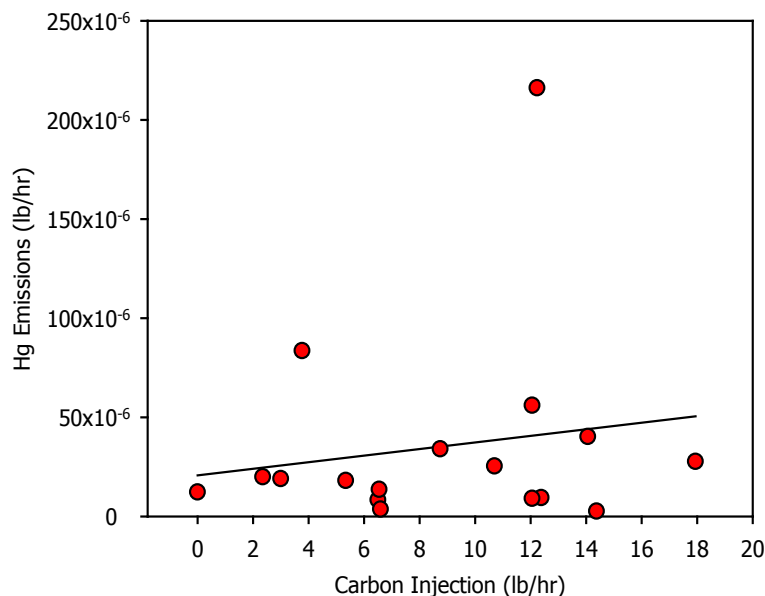


Figure 4-2. Mercury Emissions Calculated as a Function of Activated Carbon Injected at the St. Paul, Minnesota, Biosolids Incinerator.

4.1.7 Mercury Capture in Coal-Fired Utilities by Novel Methods

There are several novel methods of mercury capture that have been tried at coal-fired utilities. Although they have not been widely adapted as feasible approaches, they show some promise and may be worth considering in the biosolids incinerator arena.

In a couple of cases potential unburned carbon was captured or enhanced. The unburned carbon was then expected to act as an in-situ for mercury capture. O'Dowd and colleagues describe the "Thief Process" where a lance is inserted just downstream of the combustion zone to capture unburned carbon particles.⁹¹ The particles are then re-injected into the process in a similar manner to that explained for ACI, for capture with an APCD. Others modified boiler conditions to enhance mercury removal.^{92,93} The modifications described were directed at increasing the amount of unburned carbon in the flyash to improve mercury capture without adversely affecting particulate or NO_x emissions. The potential of both these approaches are low, as most biosolids incinerators desire to operate in a fashion that minimizes unburned carbon.

In bench-scale experiments iron oxide-based sorbents were used to remove mercury and study reaction mechanisms.⁹⁴ It was determined that only in the presence of added H₂S was the

⁹¹ O'Dowd, W.J., Pennline, H.W., Freeman, M.C., Granite, E.J., Hargis, R.A., Lacher, C.L., Harash, A. (2006)

⁹² Romero, C.E., Li, Y., Bilirgen, H., Sarunac, N., Levy, E.K. (2006)

⁹³ Lissianski, V. (2006)

⁹⁴ Wu, S., Uddin, M.A., Sasaoka, E. (2006)

capture of mercury successful because of the formation of reactive elemental sulfur on the iron-oxide sorbent surface. This was unfortunate for the coal-fired utilities, but may indicate a co-use potential for H₂S evolved in the biosolids industry. However, the process is still at a bench-scale level.

The electro-catalytic oxidation process for multi-pollutant control technology,⁹⁵ is a non-thermal, plasma-based process. The process includes dielectric barrier discharge reactor to oxidize SO₂, NO_x, and mercury for subsequent removal in an ammonia-based reagent wet scrubber system. However, this technique has not been economically studied and has the potential to involve large capital expenditure.

In the coal-fired industry small amounts of coal blending is a way to add beneficial sulfur and chloride compounds to flue gas to enhance mercury capture on existing APCDs.⁹⁶ It was reported that mercury capture across a spray dryer absorber-fabric filter system could improve from 25% to nearly 80% by blending small amounts of western bituminous coal with the western sub-bituminous coal. Fuel blending in a coal-fired utility is easy and inexpensive, but may be difficult to translate to the biosolids incinerators.

It should also be mentioned that in the coal-fired utility industry, much research has been done on the conversion of mercury species in selective catalytic reactors (SCRs). As many coal-fired utilities have existing wet FGDs or will be installing them to conform to SO₂ emission regulations, there will continue to be focused research on improving mercury capture by enhancing the fraction of Hg^{II} in flue gas using SCRs.

Although these methods have improved capture in many instances, the impacts on the combustion system and the overall cost-benefits leave the practicality of continuous use open to interpretation based on site-specific information. Some areas for consideration before deciding on a particular mercury capture technology are shown in Table 4-3.

4.1.8 Other Incineration or Combustion Processes

The 1997 Mercury Study Report to Congress defines an inventory of mercury emissions in the United States and describes the control technologies in place in each of the major incinerator industries.^{97,98} However, before examining any technologies in other industries, the differences between plant configurations and fuel stock components must be considered. For example, APCD performance in municipal waste combustors (MWCs) may not directly translate into similar performance in biosolids incinerators, because of differences in plant throughput, duct sizes, mercury concentrations in fuel, and the presence of flue gas components affecting mercury oxidation.⁹⁹ It is imperative that the similarities and differences between the biosolids incineration industry and each of the industries discussed be evaluated before any statements suggesting cross platform application of APCDs.

⁹⁵ Feeley, T.J., Murphy, J., Hoffmann, J., Renninger, S.A. (2003)

⁹⁶ Durham, M.D., Sjoström, S., Starns, T., Wilson, C. (2006)

⁹⁷ U.S. EPA. (1997c)

⁹⁸ U.S. EPA. (1997d)

⁹⁹ U.S. EPA. (2005a)

Table 4-3. Capital and Operating Expense Considerations for Adopting Mercury Removal Technology.

Capital Expense	Area to Consider	Additional Information
	What mercury species dominates the process and what mercury species are being targeted? Equipment costs	Hg ^P needs particulate control, Hg ^{II} needs a wet scrubber of some form Including required redundancies
	Modifications of, or integration into, existing equipment Pilot studies	
	Supplemental monitoring equipment	As equipment becomes more technologically complex, increased monitoring and control infrastructures are required
Operating Expense	Area to Consider	Additional Information
	How robust and proven is the system?	What is the downtime of the new equipment? What is the affect on existing equipment? For example, increased chlorides can increase corrosion
	Increased personnel	
	Raw materials	Cost to purchase Cost to store Variable cost as demand increases
	Material disposal	Is mercury capture causing previously benign byproducts to become hazardous waste? What is the cost of byproduct treatment?
	Loss of byproduct revenue offsets	

4.2 Municipal Waste Combustors

Like biosolids incinerators, MWCs have variable mercury concentrations in the feedstock,^{100,101} but with an average varying around 2-4 mg/kg. Mercury concentrations in the MWC flue gas are reported from < 200 to >1,000 µg/dscm. The majority (85%) of MWCs in the United States have an APCD in place, but mostly to target acid gases and particulate matter with mercury being captured as a co-benefit.^{102,103} Mercury removal rates and costs for some APCD technologies are shown in Table 4-4.

Wet scrubbers in MWCs are typically one of several designs, depending on the primary target pollutant. Single-stage scrubbers are primarily for acid gases and normally are found in-line after other APCDs as a polishing step. Two-stage scrubbers can be installed independently of other APCDs, targeting acid gases and metals. The two-stage scrubbers typically include sections for halogen acid control (HCl, HF, HBr), and a caustic scrubber that targets SO_x.¹⁰⁴ Three-stage scrubbers are actually a two-stage scrubber plus a high-efficiency wet particulate control system that removes fine particulates, metals, dioxins, and furans.

¹⁰⁰ Kilgroe, J.D. (1996)

¹⁰¹ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

¹⁰² U.S. EPA. (1997c)

¹⁰³ Kilgroe, J.D. (1996)

¹⁰⁴ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

Table 4-4. Reported Mercury Removal Rates and Costs for Several APCD Technologies in MWCs.

APCD Type	Hg Removal Rate	Cost
Activated carbon injection	85-99%	\$211-\$870/lb Hg removed, or \$0.7-\$3.5/ton MSW
Carbon filter beds	n/a	513-1083\$/lb Hg removed, or \$5.44-\$9.39/ton MSW
Polishing wet scrubber	85%	\$1600-\$3320/lb Hg removed, or \$5.3-\$13.5/ton MSW

Wet scrubbers are capable of removing 90-95% of the soluble mercury species in a gas stream.¹⁰⁵ However, Hg⁰ capture rates in wet scrubbers is typically <10%, so total mercury removal rates depend on the speciation of the gas and how much of the mercury present is in the elemental form (Table 4-5).

The United States, MWCs often include dry lime injection systems and spray dryers for acid gas control. The spray absorbers using lime have shown removal rates of 50-60% for HgCl₂ and 30% for Hg⁰.¹⁰⁶ The rates can be improved, up to 80-90%, by adding an active carbon sorbent to the spray slurry and combined with a fabric filter as the downstream particulate matter control the overall mercury removal to increases to 90-95%.

Table 4-5. Mercury Removal Efficiencies by APCDs in Municipal Waste Incinerators.

Equipment	Temperature (°F)	HgCl ₂	Hg ⁰	Overall
ESPs	356	0-10%	0-4%	0-8%
Wet scrubbers	149-158	70-80%	0-10%	55-65%
Wet scrubbers with conditioning agent		90-95%	20-30%	76-82%
Spray absorbers + fabric filter (limestone)	266	50-60%	30-35%	44-52%
Spray absorbers + fabric filter (special absorbents added)		90-95%	80-90%	87-94%
Entrained flow absorbers + fabric filter (special absorbents added)	266	90-95%	80-90%	87-94%
Circulating fluidized bed + fabric filter (special absorbents added)	266	90-99%	80-95%	87-98%

In Taiwan, a cyclone/dry lime scrubbing system with fabric filter is being used. A second facility has a series of ESPs and wet scrubbers.¹⁰⁷ In both APCD configurations, ionic mercury is the dominant species, 88% and 77%, respectively. The first APCD configuration returned a 30% total removal rate. The second APCD configuration showed a higher total mercury removal, 45%, as expected primarily because of the increased Hg^{II} removal by the wet scrubber. This example demonstrates the impact of selecting the wrong system for the type of mercury species being targeted. It is very likely that the mercury species were not determined, or correctly determined, before the equipment selection.

¹⁰⁵ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

¹⁰⁶ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

¹⁰⁷ Chang, M.B., Hsiung, C., Hsiu, J., Wu, T., Yi, H. (2003)

ESPs are the most common APCD in MWCs for particulate matter control. However, as previously discussed mercury removal from ESPs is limited (typically <10%) by removing only the mercury that is sorbed onto flyash particles.¹⁰⁸

Newer configurations being introduced into MWC designs add ACI or injection of Na₂S to the other pollution control technologies. It has been observed that mercury emissions are reduced because of the carbon present in the feedstock and the removal was improved by ACI. As previously discussed, tests have shown >90% mercury removal by ACI in coal-fired utilities, but application to other industries is dependent on relative mercury concentration and other characteristics of the gas stream (i.e., coal typically has lower mercury concentrations in flue gas, has competitive species present, different residence times, and mass transfer limitations in comparison to other industries) and is not simple transference.¹⁰⁹

4.3 Medical Waste Incinerators

Mercury emissions from American medical waste incinerators are regulated both nationally and at the state level. Most mercury from medical waste incinerators is observed to emit as HgCl₂, speculated to be caused by the high volume of chlorinated plastics in the waste.¹¹⁰ Studies have shown that the APCD systems used have limited mercury removal.¹¹¹

4.4 Hazardous Waste Combustors

Hazardous waste combustors include aggregate kilns, and cement kilns that have permits to burn hazardous waste as well, but not including Portland cement manufacturing.¹¹²

Types of hazardous waste combustors include rotary kilns, liquid injection incinerators, fluidized beds, and fixed hearths, the last two being similar types as used in the biosolids industry. Hazardous waste combustors are primarily concerned with APCDs for acid gas and particulate matter control, with common technologies being packed towers, spray dryers, wet and dry scrubbers, wet or dry ESPs, or fabric filters. The most popular configuration is the wet APCD. However, at this moment mercury control rates have not been fully uncovered for these facilities. It is expected, because of the APCDs employed, that Hg^P and Hg^{II} will be captured with reasonable efficiency.

4.5 Commercial, Industrial, and Residential Boilers

Businesses and industrial boilers burn natural gas (48%), coal (12%), and oil (39%), with mercury contamination typically coming from the fuel source.¹¹³ Mercury emissions are typically not controlled by this industry, or at least no mercury control is assumed when making emissions estimates. All coal-fired boilers have ash handling systems. From a legal standpoint,

¹⁰⁸ Velson, D.V., Lagenkamp, H., Herb, G. (2002)

¹⁰⁹ Brown, T.D., Smith, D.N., Hargis, R.A. Jr., O'Dowd, W.J. (1999)

¹¹⁰ U.S. EPA. (1997c)

¹¹¹ U.S. EPA. (1997d)

¹¹² U.S. EPA. (1997c)

¹¹³ U.S. EPA. (1997c)

residential boilers are very similar to industrial boilers, and as of 1997 it is assumed that there was no mercury emissions control in residential boilers.

4.6 Crematories

The main source of mercury in crematory emissions is from the volatilization of dental amalgam fillings. Volatility studies for mercury in dental amalgams have shown that complete material decomposition and full mercury release was seen at 1292°F.¹¹⁴ Studies have been performed in Swedish crematories using an addition of selenium to the combustion chamber to reduce mercury emissions.¹¹⁵ An ampoule containing selenium is added to the cremation furnace, allowing the release of selenium soon after the volatilization of mercury (the study showed mercury volatilization from dental amalgams at 1202°F with selenium release following at 1216°F). The selenium and mercury react to form HgSe, a compound that is stable under flue gas and ash release conditions; this reaction showed a reduction in mercury emissions of 80-85%.

4.7 Enersludge™ Process

The Enersludge™ process, also known as Oil From Sludge technology, thermally and chemically treats dried biosolids for energy recovery by converting the biosolids to oil and gas (and several byproducts).¹¹⁶ The biosolids are subjected to high temperatures that would make mercury emission a concern. The process does include a fluidized bed incinerator, which burns biosolids, to generate hot gases used for biosolids drying elsewhere in the process. A plant is in use in Australia, and possible use in Europe is under consideration. The process literature claims to control the metals present in biosolids, including mercury, although limited data are given (mercury emissions levels are reported at 0.008 ng/m³, but input levels are not reported). The Australian-based plant has a Venturi scrubber and packed caustic tower in place for particulate matter and SO₂ control, respectively. There is comment in the literature that the plant maintains the bed temperature at less than 750°C, to minimize heavy metal volatilization as well as other things, but that is unlikely low enough to prevent mercury volatilization.

¹¹⁴ Mills, A. (1990)

¹¹⁵ Hogland, W.K.H. (1994)

¹¹⁶ Bridle, T. (2000)

CHAPTER 5.0

MERCURY TEST METHODS APPLICABLE TO BIOSOLIDS INCINERATORS

5.1 Analytical Methods for the Determination of Mercury in a Biosolids Incinerator Mass Balance

Determining the ideal testing method includes coupling the most relevant sample preparation procedure with an appropriate analytical technique. Methods can be used to determine concentrations of total mercury, various mercury species (e.g., elemental mercury, methyl mercury), or a behavioral chemistry scheme such as leachability or bioavailability. Although the speciation of mercury is significant for understanding the fate of mercury within the mass balance envelope (e.g., mercury speciation in flue gas is important in determining the most efficient technology for reducing mercury emissions; the leachability of mercury from incinerator ash or other waste products can dictate how they are reused or disposed of), it is typical for mercury to be regulated as the total mercury emitted. Chapter 2.0 outlines the relationship between mercury speciation and biosolids incineration.

This study examines the test methods that could be used for a biosolids incinerator mass-balance study. The waste streams most likely to be of interest are categorized into solid, liquid, and gaseous matrices. Particular focus was paid to promulgated methods; brief discussion will be made of non-promulgated and upcoming methods. Of particular interest are the U.S. EPA methods for preparation and analysis of mercury in solids, some of which specifically target biosolids. A number of method variations can also be found in the literature and through public and private sector analytical laboratories.

5.1.1 Sample Collection (Clean Technique)

Because of the extreme sensitivity of current analytical procedures and the prevalence of mercury in an analytical laboratory environment, care must be taken to avoid extraneous sample contamination (Figure 5-1). Sampling equipment and sample containers should be pre-cleaned and determined to be free of mercury.

Following clean sampling techniques, such as an equivalent to U.S. EPA Method 1669, is recommended for sample collection. Method 1669, also known as “Clean Hands/Dirty Hands,” delineates sample collection methods to avoid or minimize sources of contamination for various aqueous sample matrices and source point types. Method 1669 also includes quality control (QC) recommendations to ensure minimal or no sample contamination occurred. This method is intended for use with U.S. EPA 1600-series analytical techniques, and includes preservation recommendations for various metals of interest. For the determination of mercury, recommended preservation methods are 0.5% HCl (for methyl mercury and total mercury) or 0.5% BrCl (for total mercury only) to pH<2, followed by analysis by U.S. EPA Method 1631 for total mercury. Although it is not currently expected for the biosolids incinerators to adopt a complete Method 1669 regime, the method offers an excellent set of guidelines that can be simplified for day-to-

day use with consideration to the expected mercury concentrations to be determined, Appendix C describes a possible adaptation of the Method 1669, for biosolids incinerators.

The U.S. EPA has also compiled the Resource Conservation and Recovery Act Waste Sampling Draft Technical Guidance document (U.S. EPA, 2002), offering suggestions for solid waste sampling schemes including planning, implementation, and data assessment. This document is an update on information gathered since publication of SW-846 Chapter Nine “Sampling Plan” (U.S. EPA SW-846, 1986).

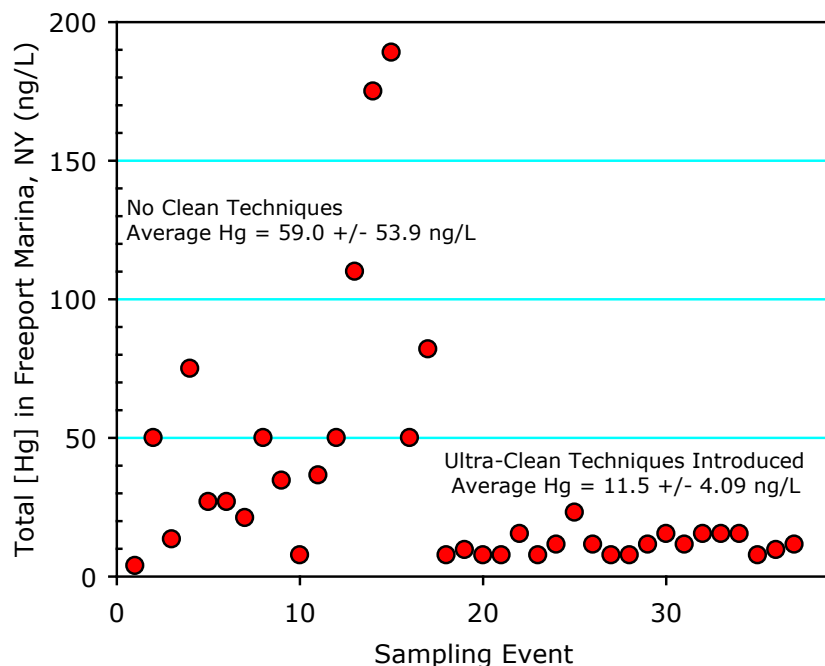


Figure 5-1. Effect of Clean Techniques on Mercury Determinations in the Freeport Marina, New York.

5.1.2 Sample Processing

Sample contamination must also be avoided during sample processing procedures. The preparation and analytical laboratory space must be clean enough to prevent exposure of the sample to airborne mercury vapor or mercury associated with particulate dust. Laboratory materials must be free of mercury, and reagents used in sample preservation or preparation must be pre-tested to assure low mercury content.

Maintaining clean laboratory spaces is addressed in the above-mentioned U.S. EPA methods. Federal Standard 209E (FED-STD-209E, 1992) describes requirements to maintain a laboratory clean room at a specific class designation, based on airborne particulate matter concentrations and regulation of temperature and humidity. Class-100 clean rooms (those that contain less than 100 particles of greater than 0.5 micron diameter per cubic foot of air) are considered standard for clean analytical laboratories. However, the goal of the sampling and analysis regime must be understood. Class-100 clean rooms may be a greater level of contamination control than is necessary to achieve accurate results for regulatory-based sampling.

5.2 Method Detection Limit versus Reporting Limit, Quantitation Limit, or Practical Quantitation Limit

Method Detection Limit (MDL) The minimum level of analyte that can be detected with 99% confidence that the analytical response is greater than zero. This is a statistical assessment, rather than an actual measurement of detection. There are several protocols for determining the MDL, the currently most common is the U.S. EPA's 40 CFR 136 App. B, where the MDL is assessed by analyzing at least seven replicates of reagent water that have been spiked at low levels with the analyte(s) of interest, then processed through the entire analytical method. The MDL value is calculated to be three times the standard deviation of the seven replicates. Considerations must be taken into account with the MDL from a practical point of view: 1) concentrations detected at the MDL should be considered estimates only, as this concentration level is generally outside of the operational quantitative range defined by instrument calibration; and 2) the MDL is calculated using reagent water, which typically does not present any matrix influences to the instrument.

Method Quantitation Limit The lowest non-zero point included in the initial calibration, and establishes the lowest level at which a concentration can be reported without qualification. Again, it should be realized that most calibration standards are produced in reagent water, which typically does not present any matrix influences to the instrument

Practical Quantitation Limit (PQL) The level of analyte that can be routinely detected and quantified in a real matrix. Currently, the PQL can be a multiple of the standard deviation obtained from the MDL study. Frequently used multipliers are 5, 7, 10, and 12. However, as the U.S. EPA moves towards performance-based methods the PQL should be determined from continuous operation i.e. it is a statistical function of the continuous calibration standards used during typical quality assurance (QA) and QC protocols for the method of interest. This results in a PQL that may change over time, but it is a more realistic assessment of the laboratory's capability.

Reporting Limit A level at which a laboratory routinely reports analytical results. The reporting limit is determined by the laboratory based on factors such as the analyte's MDL, PQL, lowest calibration standard, and any applicable regulatory limits. If using a reporting limit to compare methods, the reporting limit equation should be requested as they may differ between laboratories.

5.3 Analysis of Liquids

There are numerous analytical methods for the determination of total mercury in aqueous liquids published and recognized by a range of government organizations (Table 5-1).

Data collected during the survey indicates that most facilities are using one of these recognized methods to test influent and effluent water on a regular basis (Table 5-2). The currently most popular total mercury analysis techniques of liquids typically involve the oxidation of a sample, followed by analysis by CVAAS or CVAFS.

Table 5-1. Published Methods for the Determination of Mercury in Aqueous Liquids.

Number	Source	Method Descriptive	Matrix	Detection Level	Technique	Relative Cost
245.1	EPA-NERL	Mercury by CVAA	Aqueous	0.2 µg/L (200 ng/L)	CVAA	\$\$
245.2	EPA-NERL	Mercury by CVAA (Automated)	Aqueous	0.2 µg/L (200 ng/L)	CVAA	\$\$
7470A	EPA-OSW	Mercury by Manual Cold-Vapor Technique	Aqueous	0.2 µg/L (200 ng/L)	CVAA	\$\$
I-1462	USGS-NWQL	Mercury, dissolved, CVFAA	Aqueous	0.5 µg/L (500 ng/L)	CVAA	\$\$
I-2462	USGS-NWQL	Mercury, dissolved, CVFAA	Aqueous	0.1 µg/L (100 ng/L)	CVAA	\$\$
245.7	EPA-NERL	Mercury by CVAFS	Aqueous	0.002 µg/L (2 ng/L)	CVAFS	\$\$
1631	EPA-EAD	Mercury in Water Using CVAFS	Aqueous	0.0002 µg/L (0.2 ng/L)	CVAFS	\$\$
I-2464-01	USGS-NWQL	Organic plus Inorganic Mercury in Filtered Natural Water by Cold-Vapor AFS	Aqueous	0.005 µg/L (5 ng/L)	CVAFS	\$
I-4464-01	USGS-NWQL	Organic plus Inorganic Mercury in Unfiltered Natural Water by Cold-Vapor AFS	Aqueous	0.005 µg/L (5 ng/L)	CVAFS	\$
200.7	EPA-NERL	Metals in Water by ICP-AES	Aqueous	7 µg/L (7000 ng/L)	ICP-AES	\$\$\$
6010 C	EPA-OSW	Trace elements in solution by ICP AES	Aqueous	17 µg/L (17000 ng/L)	ICP-AES	\$\$\$
200.8	EPA-NERL	Metals in Waters by ICP/MS	Aqueous	0.2 µg/L (200 ng/L)	ICP-MS	\$\$\$

Table 5-2. Methods Reported by the Surveyed POTWs for Analyzing Mercury in Influent and Effluent.
31 POTWs Responded to Survey.

	Influent	Effluent
EPA Method 245.1 or 245.2	22	21
EPA Method 1631	6	8
Other:	2	3
EPA Method 245.7 or variation	1	2
Clean metals	1	1

Where mercury speciation is concerned, there are a number of techniques available for quantification. Most speciation techniques are research-based and there are not promulgated methods available. A noted exception is the monomethyl mercury (MMHg) procedure that has been published as U.S. EPA 1630. Of additional note is that some methods are species-specific [dimethyl mercury (DMHg), MMHg], although others are operationally defined in nature (Hg^0 , Hg^{II}) and require separate aliquots to determine each species. Brief descriptions of each mercury species are listed below.

Particulate Mercury (Hg^{P}) Un-preserved samples are vacuum filtered through acid-cleaned cellulose nitrate membrane filters. The choice of pore size may vary depending of the low range of particle size desired, but in general, a 0.45-µm filter is used for the filtration of ambient and wastewater samples. The filter is rinsed to remove residual filtrate and then subjected to a hot-acid digestion. Results are reported in Hg/volume filtered or in ng/g by direct weighing the mass

of particulate captured by the filter. A more common technique is to analyze the unfiltered sample and the filtrate. The Hg^{P} is calculated by subtracting the filtered concentration from the unfiltered concentration.

Monomethyl Mercury (MMHg) Water samples are preserved with HCl, then distilled to remove potential interferents. The distillate is buffered at pH 5.0 with an acetate buffer and reacted with sodium tetraethyl borate. The volatile $\text{CH}_3\text{CH}_2\text{HgCH}_3$ formed is purged from the aqueous matrix onto suitable trapping media (e.g. CarbotrapTM or Tenax). The trap is then thermally desorbed into an isothermal GC column for species separation and quantified by CVAFS after pyrolytic cracking.¹¹⁷

Dimethyl Mercury (DMHg) DMHg in water is determined by direct purge and trap onto suitable trapping media (e.g., CarbotrapTM or Tenax). In the same manner as MMHg, the trap is thermally desorbed into an isothermal GC column for species separation and quantified by CVAFS after pyrolytic cracking.

Oxidized (Ionic) Mercury (Hg^{II}) Hg^{II} is an operationally defined procedure in that it doesn't specifically identify a species of mercury. In water samples, this species is sometimes referred to as "reducible mercury" or "labile mercury." Analysis is performed by reducing an un-acidified and un-oxidized sample directly with SnCl_2 followed by purge-and-trap pre-concentration of the released Hg^0 onto gold coated sand trap. The trap is then thermally desorbed into the analytical system, and quantified by CVAFS detection. Weakly associated mercury species present in a sample may also be detected by this method, resulting in an overestimate of the true Hg^{II} concentration. It is important to use a purging vessel that is free of oxidizing acids (e.g., purging vessel used for total mercury) because of the potential for transformation of mercury species.

Elemental Mercury (Hg^0) Hg^0 is determined by acidifying samples to pH 1.8 immediately before purging and trapping onto gold-coated sand traps. The trap is then thermally desorbed into the analytical system, and quantified by CVAFS detection. This procedure is another operationally defined method that is sometimes referred to as "volatile mercury" and is not specific for Hg^0 . Other volatile species of mercury present in a sample may also be detected by this method, resulting in an overestimate of the true Hg^0 concentration. It is important to use a purging vessel that is free of possible oxidizing acids or SnCl_2 (e.g., purging vessel used for THg or Hg^{II}) because of the potential for transformation of mercury species.

5.3.1 Cold Vapor Atomic Absorption Spectroscopy (CVAAS) for Determination of Mercury in Aqueous Matrix

All of the CVAAS published methods from Table 5-1 are chemically similar. The difference typically lies with operation being manual or automated; U.S. EPA Method 7470A is equivalent to U.S. EPA Method 245.1, but promulgated for liquid wastes. In brief, aliquots of the working mercury solution are added to a series of sparging bottles. To these bottles concentrated sulfuric acid and concentrated nitric acid are added. The acidic mixture digests the sample. This is followed by the addition of a combination of potassium permanganate solution and potassium persulfate to each bottle and heat is applied. This is intended to complete the sample digestion and oxidize all forms of mercury to Hg^{II} . After sample digestion, sodium chloride-hydroxylamine sulfate solution is added to reduce the excess permanganate. This allows the addition of stannous sulfate solution, which reduces the Hg^{II} to Hg^0 . Immediately, the bottle is

¹¹⁷ Horvat, M., Liang, L., Bloom, N. (1993)
Minimizing Mercury Emissions in Biosolids Incinerators

sparged with argon. The Hg^0 -laden argon passes through a desiccant to remove water vapor and into an absorption cell for mercury measurement at 253.7 nm. The reported method detection limit (MDL) for all three U.S. EPA methods is 0.2 $\mu\text{g/L}$ (200 ng/L) Hg, the U.S. Geological Survey (USGS) equivalents are 0.5 $\mu\text{g/L}$ (500 ng/L) Hg and 0.1 $\mu\text{g/L}$ (100 ng/L) Hg, where the automated method I-2462 has the lower MDL.

Considerations for Mercury Analysis in Water by CVAAS Free chlorine, which also absorbs radiation of 253.7 nm, is created during oxidation. In addition, it is possible that volatile organic materials absorbing at this wavelength may also cause interference. Benzene and toluene have been observed to interfere at a maximum tolerance of 500 $\mu\text{g/L}$.

Organic components in a sample can exhaust the oxidizer. If organics are expected to be present, a higher concentration of reagent and/or adding heat may be needed to ensure complete oxidation of the mercury.

5.3.2 Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) for Determination of Mercury in Aqueous Matrix

All of the CVAFS published methods from Table 4-1 are chemically similar. The difference fundamentally lies with the mercury pre-concentration step used in U.S. EPA Method 1631, but not in U.S. EPA Method 245.7 or the USGS methods, and the filtration step performed in the USGS method I-2464-01 compared to USGS I-4464-01. The filtration step in U.S. EPA Method 1631 is optional depending on the desired analytical target. In brief, a sample is collected using clean-technique (see previous discussion). If dissolved mercury is the desired target, the sample is filtered through a 0.45- μm capsule filter. The sample is preserved by 12N HCl or BrCl solution. It should be noted that concentrated HCl is generally regarded as less hazardous than BrCl solution. A sample aliquot is placed in a purge vessel, and BrCl solution (1631) or KBrO_3/KBr solution (245.7) is added to oxidize all mercury compounds to Hg^{II} . After sample oxidation, sodium chloride-hydroxylamine sulfate solution is added to remove the any remaining free halogens, which allows the addition of stannous chloride solution, which reduces the Hg^{II} to Hg^0 . The Hg^0 is separated from solution by purging with nitrogen. If using U.S. EPA Method 1631, the mercury-laden nitrogen is passed through a gold-coated sand mercury trap. The trapped mercury is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg^0 into the cell of a cold-vapor atomic fluorescence spectrometer for detection at 253.7 nm. If using either of the USGS methods the mercury-laden nitrogen is passed directly into the cell of a CVAFS for detection at 253.7 nm. The reported method detection limit (MDL) for U.S. EPA Method 1631 is 0.2 ng/L Hg, the USGS methods are 5 ng/L Hg because of the lack of pre-concentration on a gold mercury trap.

Considerations for Mercury Analysis in Water by CVAFS Because of the low detection limits for this method, sample and equipment contamination should be regarded as a major concern. Clean technique must be followed from sample collection to final analysis.

At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, mercury recovery will be reduced from 100% to 0%. The destruction of the gold traps may occur if free halogens are purged onto them (gold-halides are volatile), or if they are overheated ($>500^\circ\text{C}$). Failure of the desiccant, between the purge bottle and the gold trap, may allow excess water vapor to condense in the fluorescence cell, resulting in a physically induced false peak. In addition, the fluorescent intensity can be “quenched” if molecular species are present in the carrier gas.

High purity argon (99.998%) must be used as the carrier gas. Using nitrogen may reduce the sensitivity 8-fold, whereas the use of air may reduce the sensitivity 30-fold.¹¹⁸

5.3.3 Inductively Coupled Plasma for Determination of Mercury in Aqueous Matrix

Note: Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is the same instrument as ICP optical emission spectroscopy (ICP-OES). ICP-OES is a more correct term as both atom and ion light emissions are monitored, however AES is historically entrenched. To reduce confusion, the term ICP-AES will be used in the discussion.

ICP-based techniques are a very powerful tool for trace (ppb-ppm) and ultra-trace (ppq-ppb) elemental analysis. In fact, ICP mass spectrometry (ICP-MS) is rapidly becoming the technique of choice in many analytical laboratories for the accurate and precise measurements it can deliver.

In ICP, a high-powered RF current is applied to argon gas; the resulting gas plasma consists of highly excited argon ions, electrons and neutral particles. Prepared liquid samples are then sprayed into the argon plasma, where the sample components are atomized and ionized. In the case of ICP-AES an optical train captures the light emitted from the emission of atoms or ions of target species, such as mercury (typically at the 184-nm wavelength). The intensity of an emission is proportional to the amount of that species in the original sample. In the case of ICP-MS the resulting ions are passed through a series of apertures (cones) into a high vacuum mass analyzer. In the mass analyzer the isotopes of the elements are identified, with the intensity of an isotope being proportional to the amount of that isotope (element) in the original sample.

The U.S. EPA 200 series methods are a complete, fixed method from sample preparation to instrument configuration, and are designed to present a single set of protocols that are consistent across any laboratory. They are typically required for anyone sampling under the Clean Water Act. In brief, the U.S. EPA 200 series methods require the sample to be digested in a hot-block using a nitric acid and hydrochloric acid combination. A hot-block is a digestion system that can simultaneously digest >50 samples in polymer disposable digestion tubes designed to withstand the temperatures required for U.S. EPA-fixed protocol digestions. A major advantage of a hot-block system is the ability to uniformly heat the samples, addressing consistency in sample preparation. The samples are then aspirated directly into the plasma or diluted and then aspirated directly into the plasma. U.S. EPA Method 200.8 using the ICP-MS (EPA Method 200.7 uses the ICP-AES) does not allow the use of a collision cell/dynamic reaction cell, to aid in the reduction of isobaric and molecular interferences, as cell designs differ by instrument manufacturer.

The EPA 6000 series methods are design to give flexibility in processing the analytical sample, assuming that sampling is being done outside of the CWA. The U.S. EPA 6000 series allows the use of any of the U.S. EPA 3000 series methods, including, for example, digestion of the sample by addition of just nitric acid and heating on a hot plate.

¹¹⁸ U.S. EPA. (1996)

Considerations for Inductively Coupled Plasma (ICP) for Determination of Mercury in Aqueous Matrix ICP-AES and ICP-MS is not the favored method for analysis because mercury can deposit in the sample introduction system and be released during subsequent analyses. Preserving the sample with gold chloride appears to help this issue and subsequently the technique is becoming more popular for mercury.

In ICP instruments the sample introduction system does not have 100% sample transport to the detection system, thus the presence of reducing agents in the solution may reduce mercury to volatile Hg^0 causing false high results because of more mercury entering the instrument than calibrated. It should be noted that the sample transport percentage is operationally defined and consistent under fixed conditions.

The ICP-AES methods and ICP-MS methods should be considered on the basis of the reporting limit or PQL and not the MDL (explained previously). The ICP-MS uses the direct impact of ions to monitor the signal, whereas ICP-AES monitors "clean" photons. This means that the ICP-MS has a physically limited tolerance for the total quantity of ions (target ions and ancillary ions) entering the mass analyzer. As a result, in most cases, samples need to be diluted before analysis to bring the total dissolved solids concentration into instrument specifications. The higher the amount of total dissolved solids concentration the more the sample needs to be diluted. Therefore,

$$ML_{\text{actual}} \propto MDL \times N_{\text{dilutions}} \quad (5.3.3.1-1)$$

Where :

ML_{actual} = The actual method detection limit

MDL = Method detection limit

$N_{\text{dilutions}}$ = Number of dilutions

The reported MD) for U.S. EPA Method 200.7 is 7 $\mu\text{g/L}$ (7000 ng/L) Hg, EPA Method 200.8 is 0.2 (200 ng/L) $\mu\text{g/L}$ and EPA Method 6010C is 17 $\mu\text{g/L}$ (17000 ng/L).

5.3.4 Future Methods to Consider for Mercury Determination in Liquids

Although U.S. EPA Method 200.8 does allow for mercury determination by ICP-MS, U.S. EPA Method 6020 does not recommend ICP-MS for mercury analysis. However, mercury analysis by ICP-MS is becoming more popular with several modifications on the protocols to aid in mercury determination in complex matrices. Two of those modifications are described below:

- ◆ Isotope dilution in ICP-MS for mercury determination was originally reported in 1993.¹¹⁹ Isotope dilution essentially uses the enrichment of a specific metal low abundance isotope as an internal standard to improve precision and accuracy by reducing the problems with calibration and sample preparation matrix effects. U.S. EPA Method 6800 claims that detection limits for mercury are sub- $\mu\text{g/L}$, although no values are reported. Because of the more complicated nature of the technique, it should be expected to be significantly more costly than those reported on Table 5-1.

¹¹⁹ Smith, R. (1993)

- ◆ Electrothermal vaporization ICP-MS is currently being used for determination of mercury in matrix complex samples, such as blood or urine.¹²⁰ The MDL reported for mercury, was 0.02 µg/L (20 ng/L).

5.4 Analysis of Solids

Analysis of mercury in solids focuses on the digestion techniques. The methods used by the project survey responders are discussed here. After digestion, the analytical methods used are similar to those described in the analysis of liquids section. Treatments are typically oxidative in nature, although on occasion heating with a reducing agent can be effective. Oxidative procedures divide into two categories: 1) wet-ashing using liquid oxidizing agents, normally acids and 2) dry ashing by ignition of the organic compound in air or oxygen. The analysis of the digestate after wet ashing commonly uses a method or equivalent method from the “Analysis of Liquids” section. It therefore recommended that the liquids section be read before this discussion as will focus on the digestion techniques and alternative methods of solids analysis.

Before selecting a digestion method, the desired goal of the analysis should be fully understood. The procedure selected will depend on the speed and convenience and the desirability to avoid introduction of interferences. For example, a potent, hot hydrochloric/nitric acid (HCl/HNO₃) digest will make available all but mercury bound to silica-based mineral lattices. Concentrated nitric acid (HNO₃) is an oxidizing acid that finds wide use in metal digestion, although it will not digest the platinum group metals. Although HNO₃ will liberate mercury from all mercury salts and dissolve elemental mercury. A combination of HNO₃ and HCl is required to dissolve mercury sulfide. To assure complete recovery of total mercury, a hydrofluoric acid (HF) digestion component is necessary. Certain methods only aim to recover leachable metals, as is the case with total threshold limit concentration (TTLC) determination for metals on biosolids ash. This method only requires a cold HNO₃ digestion and specifies classification of solids as hazardous if the analyte concentrations exceed the TTLC limit issued by the authorities.

The solid matrices include biosolids feedstock, incinerator ash, and APCD byproducts such as spent dry injection materials or wet scrubber solids. As mentioned, solids can be prepared for total mercury analysis by digestion with one or a combination of acid reagents with the addition of heat. Acids used include nitric, hydrochloric, hydrofluoric, boric, and sulfuric acids. If KMnO₄ is used as a digestion reagent, there is a likelihood of elevated method detection limits because of high background mercury in the reagent.

Typical digestion heat sources are ovens, hotplates, or microwaves. Some species of mercury are volatile and when heating a potential loss of sample is important to consider. Heated digests that include the use of HF are also appropriate for the digestion of incinerator ash and many APCD sorbent materials. For trace mercury analysis, it is also necessary to consider the amounts and types of reagents used in digestion. Solid preparation and analysis methods were compiled from the 31 POTW survey responders (Tables 5-3 and 5-4). Other published methods

¹²⁰ Lee, K.H., Jiang, K.H., Liu, H.W. (1998)

Table 5-3. Preparation Reagents for Mercury in Solids in 31 POTWs Survey Responders.

Solids Preparation Method	Biosolids	Ash
HNO ₃	5	2
HNO ₃ /HCl (Aqua Regia)	15	6
HNO ₃ /HCl/HF	0	1
HNO ₃ /H ₂ SO ₄ / KMnO ₄ /K ₂ S ₂ O ₈	2	2
Microwave-assisted HNO ₃ /HCl or HNO ₃	2	2

Table 5-4. Preparation Methods for Mercury in Solids in 31 POTWs Survey Responders.

Solids Analysis Method	Biosolids	Ash
245.1 or 245.2 or 245.5	14	7
1631	2	2
7471A or 7470A	14	10
6020	1	0
105	1	0
1311	0	1

for biosolids digestion use HNO₃ and HF,¹²¹ sometimes in conjunction with H₃BO₃¹²² or HCl. These methods are performed either in an oven or microwave.¹²³

Compared to traditional hot plate or oven methods, microwave digestion has proven to be significantly faster. Digestions process in Teflon polytetrafluoroethylene-sealed vessels. Little or no acid is lost during the digestion and mercury losses through volatilization are minimized. If HNO₃ is the digestion acid, vessel pressure can rise suddenly at temperatures above 140-160°C if the sample matrix has a high organic content. If the pressure surpasses the pressure limit, the vessel will vent and mercury will be lost. Inorganic solids and most soils and sediments tend not to generate large amounts of gaseous by-products.¹²⁴

An alternative testing technique is mercury by thermal decomposition. This combustion/trap technique can have significant advantages over wet ashing techniques. The combustion/trap technique does not require sample preparation, therefore positive or/and negative bias generated during sample preparation can be eliminated. A manual, cheap to build, relatively accurate method is reported in the literature,¹²⁵ of more interest to the operator is the U.S. EPA Method 7473 that uses an automated thermal decomposition analyzer, such as the Milestone DMA 80 or the LECO AMA254.¹²⁶ These techniques have limitations because of small sample size and the need for sample homogenization or a statistically significant number

¹²¹ Yao, H., Naruse, I. (2005)

¹²² Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

¹²³ Gulyurtlu, I., Abelha, P., Cabrita, I., Santos Oliveira, J.F. (2006)

¹²⁴ U.S. EPA. (1998a)

¹²⁵ Liang, L., Lazoff, S., Horvat, M., Swain, E., Gilkeson, J. (2000)

¹²⁶ U.S. EPA. (1998b)

of samples to create bulk sample representativeness. In addition, co-absorbing gases such as free chlorine and certain organics should not interfere with mercury measurement as these interferents decompose and are isolated from the analytical train.

Direct analysis of biosolids slurry is possible with a graphite furnace (GF).¹²⁷ A KMnO_4 and palladium modifier added to the slurry before combustion improves volatilization characteristics. Recoveries for this method ranged between 83.5-96.2% for sewage sludge (Certified Reference Material 007-040 and 144R). The sample preparation and the analysis time of 15 minutes with low risk of contamination. Preparing the slurry in bulk followed by analytical sub-sampling helps alleviate some of the potential homogeneity issues incurred when using a technique that requires small sample aliquots for analysis.

5.5 Mercury in Air and Flue Gas

A summary of mercury methods for flue gas and ambient air is presented and an introduction is given to speciation considerations with these techniques. The methods described capture all collective mercury species (total mercury), or have the ability to capture and detect individual mercury species. The methods are further broken down into flue gas emissions and ambient air – fate and effects. Although the latter is less relevant with regard to biosolids incinerators, it is included for the sake of completeness.

5.5.1 Introduction and Speciation Considerations

Mercury in ambient air or flue gas consists of various levels of elemental mercury (Hg^0), oxidized (ionic) mercury (Hg^{II}), and particulate-bound mercury (Hg^{P}). In ambient air, Hg^{II} is also known as reactive gaseous mercury (RGM). Both Hg^{II} and RGM are catchall categories for gas-phase mercury halides. In certain instances, RGM may also include oxides, sulfur or nitrogen based mercury compounds. Total gaseous mercury (TGM) includes all gas-phase mercury compounds of Hg^0 and Hg^{II} .

Below is a summary of mercury methods for flue gas and ambient air, sorted into descriptive classifications (Table 5-5). The methods capture all collective mercury species, or have the ability to capture and detect individual mercury species. Biases can occur in TGM quantification and mercury speciation measurements with improper method selection. Adherence to sampling procedures and firm understanding of potential matrix effects inherent to the analytical technique assures high-quality data. In addition, good flue gas and air mercury measurements require strict control of potential sources of contamination during sampling, gas transfer, sample handling, digestion and analysis. A rigorous QA program is always beneficial to help identify and minimize errors.

¹²⁷ Baralkiewicz, D., Gramowska, H., Kozka, M., Kanecka, A. (2005)
Minimizing Mercury Emissions in Biosolids Incinerators

Table 5-5. Published Methods and Instruments for the Determination of Mercury in Gases.

Method Number	Source	Method Descriptive	Type	Matrix	Detection Level	Technique	Relative Cost
TGM=Total Gaseous Mercury, Hg ^P =particle-bound mercury, Hg ²⁺ =oxidized gaseous mercury, Hg ⁰ =elemental mercury							
IO-5	EPA	TGM and Hg ^P	Batch, Lab	Air	0.0002 µg/m ³ TGM 5X10 ⁻⁶ µg/m ³ Hg ^{P***}	CVAFS	\$\$
-	Jerome	Hg ⁰	Batch, Real-Time	Air	3 µg/m ³	ECR [^]	\$\$
-	Lumex	Hg ⁰	Continuous Semi-Automated	Air	0.005 µg/m ³	Z-CVAAS	\$\$\$
-	Tekran 2537A	TGM	Continuous Automated	Air	0.0001 µg/m ³	CVAFS	\$\$\$
-	Tekran 2537/1130/1135	TGM, Hg(II) and Hg ^P	Continuous Automated	Air	0.0001 µg/m ³ TGM, 2x10 ⁻⁶ µg/m ³ RGM/Hg ^P	CVAFS	\$\$\$\$
D-6350	ASTM	TGM	Batch, Lab	Natural Gas	0.001 µg/m ³	CVAFS	\$\$
101A	EPA	TGM and Hg ^P in Biosolid Incinerators	Batch, Lab	Source Gas	0.05 - 0.13 µg/m ^{3**}	CVAAS	\$
29	EPA	TGM, Hg ^P & Metals	Batch, Lab	Source Gas	0.56 µg/m ³	CVAAS	\$\$
FGS-069	FGS	Sorbent Trap TGM	Batch, Lab	Source Gas	0.003 µg/m ^{3*}	CVAFS	\$
FGS-FAMS	EPA-PBMS DOE/NETL	Hg ⁰ , Hg ²⁺ and Hg ^P	Batch, Lab	Source Gas	0.08 µg/m ³	CVAFS	\$\$
Draft-30B	EPA	TGM Reference Method	Batch, Onsite Lab	Source Gas	0.01 µg/m ³	CVAFS Z-CVAAS	\$
EPA-CAMR Appendix K	EPA	Sorbent Trap TGM Continuous Emission Monitor	Batch, Lab	Source Gas	0.003 µg/m ^{3*}	CVAFS, CVAAS, Z-CVAAS	\$\$
D-6784	ASTM	Hg ⁰ , Hg ²⁺ and Hg ^P	Batch, Lab	Source Gas	0.5 µg/m ³	CVAAS	\$\$\$
436	CARB	TGM, Hg ^P & Metals	Batch, Lab	Source Gas	0.004 - 0.04 µg/m ^{3*}	CVAAS	\$\$
-	Opsis AR602	Hg ⁰ only Cont. Emission Monitor	Continuous Automated	Source Gas	~1.0 µg/m ³	DOAS	\$\$\$\$
EPA-CAMR	Various [#]	Hg ⁰ and Hg ²⁺ Cont. Emission Monitor	Continuous Automated	Source Gas	0.05 to 1.0 µg/m ³	CVAAS, CVAFS	\$\$\$\$

*Assumes collection volume of 1.5 m³

**Range depends on instrument configuration

***Based on FGS IDL of 0.02 ng/trap and collection volume of 1.5 m³

[#]Tekran, Thermo Electron, Durag, Horiba, GE, Lumex

[^]ECR - Electro-Chemical Resistance

5.5.2 Sorbent Trap Collection

The sorbent trap collection technique is an accurate and simplified method for measuring TGM, which represents the sum of vapor phase elemental and oxidized forms of mercury. These methods have gained favor with the U.S. EPA as an alternative for impinger-based techniques for monitoring mercury in the flue gas sector. A gas-sampling console pumps a metered quantity of gas through the sorbent trap. Mercury species present in the gas stream are chemically bound to the sorbent while other gas constituents pass through the trap. By employing U.S. EPA Clean Air Mercury Rule Appendix K, total mercury in gas can be determined from 10 minutes to 10 days. As Appendix K is approved for emissions compliance monitoring, the method is subject to yearly relative accuracy test audits. To address the need for relative accuracy test audit testing, the U.S. EPA developed Draft Method 30B. Both Appendix K and Method 30B use analytical techniques developed at Frontier Geosciences as Sorbent Total Mercury method FGS-069. Mercury concentrations are determined on a mass basis (µg/trap) and then combined with gas data from the sampling console to determine the overall mercury concentration in the source gas (µg/m³). For a more developed description of sorbent trap sampling, refer to Appendix B.

5.6 Flue Gas Emissions

Understanding the changes in mercury speciation along the biosolids incineration process is a key component in the development of a sound emission-control strategy for mercury. Frontier Geosciences developed the FAMSTTM sorbent speciation trap to provide a simplified technique that relies on sequential selective capture to separate and quantify three mercury species. The specific mercury species measured are particulate (Hg^{P}), gaseous oxidized (Hg^{II}), and gaseous elemental (Hg^0). For this technique, sampling is conducted at a flow rate of 0.5 L/min and the FAMSTTM sorbent train is heated to $95 \pm 5^\circ\text{C}$. This temperature prevents water condensation in the trap and assures quantitative capture. The FAMSTTM method has recently undergone rigorous validation in coal flue gas against the American Society for Testing and Materials-promulgated Ontario-Hydro Method.^{128,129,130} The use of dry sorbent traps greatly improves ease of field sampling in that the use wet chemicals and specialized glassware in the field is completely eliminated. This simplicity reduces the chance of accidental contamination, facilitates a higher degree of accuracy, and improves overall safety.

5.6.1 Sorbent Trap Analysis

When collected, sorbent trap analysis typically occurs at an off-site laboratory. The sorbent material is removed from the trap and is subjected to a strong acid leaching digestion to recover the mercury. Once digested, analysis occurs by a variety of techniques, with the most typical methods being CVAAS or CVAFS. Of the two techniques, CVAFS is most sensitive and allows for the widest range of range of detection. CVAFS analysis is capable of determining gaseous mercury concentrations of $0.01 \mu\text{g}/\text{m}^3$ - $100 \mu\text{g}/\text{m}^3$ for controlled and uncontrolled emission sources.

In development of the Clean Air Mercury Rule Appendix K method, the U.S. EPA has prepared a full set of QA protocols for the sorbent trap. The method requires paired sampling of three-bed sorbent traps for every collection. The two results must agree within 10% relative difference (difference/sum) to prove method precision during the integrated sampling period. During collection the sampling flow rate must remain proportional ($\pm 25\%$) to the stack flow rate, assuring that overcollection/undercollection does not occur if stack gas flow or concentration fluctuates during collection. Each trap has breakthrough section that must have less than 5% of the mass captured by the primary trap section. Each trap is required to have a mercury spike prepared on the tertiary trap bed that is $\pm 50\%$ of the expected trap loading. This spike must recover within $\pm 25\%$ of the true value to validate the sample. The trap spike is the best overall assessment of method efficacy as it evaluated every aspect of process including trap preparation, transport, sample collection, digestion, and analysis. The method also outlines typical analytical QC protocols such as calibration criteria and certified reference material recovery verification.

In addition to chemical digestion, the dry sorbent traps also allow for direct analysis using a combustion analyzer. The sorbent material is removed from the traps and is heated in a furnace up to the point of combustion. The absorbed mercury is thus freed from the sorbent and is carried into the detection cell of the analyzer. A combustion module can be purchased for the Lumex analyzer to configure the detector in this manner. Of definite advantage is the ability to

¹²⁸ U.S. Department of Energy, National Energy Technology Laboratory (2001)

¹²⁹ Nott, B. (1995)

¹³⁰ Laudal, D., Nott, B., Brown, T., Roberson, R. (1997)

determine dry sorbent trap concentrations shortly after collection if the combustion analyzer has been set up in the field. The combustion method is a destructive technique, and there is no possibility of re-analysis to verify results. In addition, the combustion method does not allow the same degree of QC checks as afforded by standardized laboratory digestions techniques.

5.6.2 Impinger-Based Collection

The impinger-based collection techniques use aqueous solutions to capture mercury species. To collect the sample, a metered quantity of gas is drawn through a series of glass impingers that contain chemical agents that are selective to the individual mercury species in the gas stream, thus allowing the mercury to be solvated or trapped in the solutions. The gas volume is precisely pumped and metered with a gas sampling console that records flow, temperature, volume, and pressure. Methods that use impinger techniques are U.S. EPA Method 29 and U.S. EPA Method 101A. Method 29 uses a particulate filter to measure particulate-bound mercury followed by a hydrogen peroxide impinger to capture oxidized mercury species and finally a potassium permanganate impinger that oxidizes elemental mercury and facilitates dissolution. Method 101A uses a particulate filter to measure particulate-bound mercury followed by a potassium permanganate impinger that captures all remaining mercury species. For both methods, unique impinger solutions are configured in pairs so that there is a primary impinger that the sample passes through first, and an identical secondary impinger solution directly downstream of the first. This allows measurement of mercury breakthrough from the primary solution. Mercury concentrations are determined on a mass basis ($\mu\text{g}/\text{impinger}$) and then combined with gas data from the sampling console to determine the overall mercury concentration in the source gas ($\mu\text{g}/\text{m}^3$).^{131,132}

Although versatile, impinger-based methods can be difficult to deploy in the field and demand a high level of expertise to perform successfully. Because the method is aqueous based there are a number of solutions that must be accurately prepared, cleanly maintained, and properly deployed in the field. The chemical agents used in the solutions require knowledge of safe handling procedures and proper protective equipment. Impinger methods use a fair amount specialized glassware that has delicate connection points. The numerous connection points must maintain a leak-tight configuration for the duration of sampling. The combination of these factors usually necessitates an outside contractors perform the collection, thereby increasing the overall cost.

5.6.3 Impinger Solution Analysis

Impinger-based capture of mercury results in an aqueous solution. The analytical techniques for impinger solutions closely resemble typical water analysis as described in Section 4.5. Generally, solvated mercury undergoes chemical reduction to an elemental form followed by purging from solution into the analytical system. The mercury is either directly introduced into a CVAAS or CVAFS detector, or else is pre-concentrated using gold traps. Data collected during the survey indicate that biosolids incinerators are predominately using U.S. EPA Method 29 to test gaseous emissions on a regular basis. A summary of the test methods used by survey responders is presented in Table 5-6.

¹³¹ U.S. EPA. (1979)

¹³² U.S. EPA. (2000b)

Table 5-6. Methods Reported by Surveyed POTWs for Mercury in Gas.
31 POTWs Responded to Survey.

TEST METHOD	Gas
Method 29	19
Method 101A	1
Other	3

5.6.4 Continuous Emission Monitors

Continuous emission monitor (CEM) analyzers generally use CVAAS or CVAFS detectors and are specifically designed for use with combustion source gasses. They provide high-resolution near real-time data for monitoring and recording data from combustion sources. These instruments meet measurement requirements outlined in new U.S. EPA regulations to control mercury emissions from the coal-fired utility industry.¹³³

Table 5-7. Gas Emission Concentrations Reported by the Surveyed POTWs.
31 POTWs Responded to Survey.

POTW	Gas Emissions			
	Before 2000	2000-2001	2002 - 2003	2004-2006
	Annual Average $\mu\text{g}/\text{m}^3$	Annual Average $\mu\text{g}/\text{m}^3$	Annual Average $\mu\text{g}/\text{m}^3$	Annual Average $\mu\text{g}/\text{m}^3$
1	-	0.103	-	-
2	-	30.8	46.8	-
4	-	-	46.8	30.8
5	160	-	-	-
7	-	-	-	0.466
9	142	-	-	-
10	-	96.7	-	75.5
17	-	71.3	53.5	-
18	98.5	-	-	-
19	-	-	120	-
20	-	-	-	284
21	-	-	-	74.6
22	-	113	-	-
24	-	72.2	-	-
25	-	66.7	-	-
26	-	-	118	-
27	-	46.8	-	-
28	-	-	-	107
29	40.8	-	82.2	-
31	-	-	-	-

The development of CEM instruments for monitoring of mercury is an emerging market. By installing CEMs, the coal-fired utility industry is helping to improve overall, accuracy, reliability, and long-term performance. Current applications of CEMs on coal flue gas have

¹³³ U.S. EPA. (2005b)
Minimizing Mercury Emissions in Biosolids Incinerators

spanned the range of excellent performance to very questionable performance. The biggest drawback for the CEM is the cost of purchase, setup, and continued operation.

The gaseous matrix of concern in biosolids incineration is chiefly combustion gasses that result from the burning of municipal solid waste. The average biosolid concentration reported by the 31 survey responders from 2002-2005 was 0.8 mg/kg on a dry weight basis. For this period, the annual quantity of biosolids combusted was 12,800 dry metric tons per year. With incineration and the absence of any APCD, it is likely that a significant portion of the mercury present in biosolids will report to the gas phase. This makes direct monitoring of the mercury content of emission gasses an important component in an overall plant mass balance. Below is a summary of responses to the gas emission section of the 2006 survey (Table 5-7). (Note: Only 20 of the 31 responses listed concentrations for gaseous emission.)

5.7 Gas Sampling Techniques

For both flue gas and ambient air, mercury is normally pre-concentrated from a known volume of gas and then analyzed instrumentally in real-time or sent to a qualified laboratory for batch analysis. The pre-concentration trapping media are generally solid sorbents that bind mercury (such as gold- or carbon-based) or else use impingers that solvate mercury in aqueous solutions. When returned to the laboratory, mercury is recovered from the sorbent using acidic digestion, or additional preservative may be added in the case of impinger solutions. However, some methods depend on a direct determination of mercury on the solid sorbent by thermal heating directly into the instrument. This direct-thermal approach works well and helps to minimize matrix interferences from the sample gas. A few instrumental methods do not pre-concentrate mercury on a solid sorbent or solution; instead they depend on spectroscopic techniques to improve sensitivity and avoid interferences.

5.7.1 Electrochemical Resistance for Determination of Elemental Mercury Detection in a Gas Matrix

The Jerome analyzer measures Hg^0 in air and is primarily designed for high-level industrial health monitoring. The instrumental detection is based on electrical resistance across a gold foil. Mercury species in the gas amalgamate to the foil and alter the foil's resistance to an electric current. The change in resistance is directly proportional to the concentration of gaseous mercury in air. The Jerome is subject to matrix interferences, such as ammonia, sulfur, and organic compounds. Thus, the Jerome does not work well in combustion source gas or other complex gas matrices. Additionally, the detection limit of the Jerome is considerably high at $3 \mu\text{g}/\text{m}^3$ because of the limited gas volume and detection method.

5.7.2 Zeeman CVAAS for Determination of Elemental Mercury Detection in a Gas Matrix

The Lumex RA-915+ analyzer can directly determine elemental mercury in air in real-time. The Lumex RA-915+ mercury analyzer is based on atomic absorption spectrometry. Selectivity is achieved primarily by using the Zeeman effect using high-frequency modulation of polarized light at the 253.7-nm wavelength. The instrument provides real-time measurements and is field portable. By interfacing with a computer, the Lumex can electronically capture measurement results. The Lumex analyzer operates in ambient air, but can be adapted to analyze other matrices. Because of the excellent selectivity of the instrument, there are no known spectroscopic interferences. The main cell windows are not accessible and cannot be cleaned without returning the unit to the manufacturer. The side cell of the instrument is field-serviceable.

and can be tasked to monitoring of more complex air or flue gas matrices, such as combustion source gas. Research is currently underway to develop a Lumex-based continuous emission monitor for coal-combustion flue gas.

5.7.3 U.S. EPA Method I-05 for Determination of Vapor Phase and Particulate Mercury in Ambient Air

Method I-05 is for both long-term integrated sampling as well as short-term intensive studies. The technique uses heated sampling lines to capture both particulate-bound mercury onto Teflon filters, and vapor phase mercury onto gold traps. This requires separate sampling trains as the two mercury species are sampled at different rates. Background levels for atmospheric mercury are typically at concentrations around 2 ng/m³ and therefore require a great deal of care during collection and handling to prevent contamination. Clean techniques comparable to those listed in U.S. EPA Method 1669 are required. After collection, gold traps are analyzed directly by CVAFS. The Teflon filters are acid-digested followed by analysis by CVAFS.¹³⁴

5.7.4 Continuous Monitoring of Speciated Mercury in Ambient Air Using Manual and Automated Techniques

Manual and automated annular denuder methodologies provide high-level resolution of ambient elemental mercury, oxidized mercury, and particulate mercury measurements. Sample gas passes first through a quartz annular denuder coated with KCl to absorb oxidized mercury species. Next, the sample gas passes through a quartz filter to capture particulate bound mercury. Finally, a side stream of the sample gas passes through a gold-coated quartz trap to capture elemental mercury. In the manual technique, heating applied manually to the individual sections desorbs captured mercury. The desorption temperature is high enough to thermally decompose the non-elemental species back to elemental mercury for detection at the instrument. A Tekran 2537 analyzer quantifies the signal using CVAFS detection.¹³⁵ The automated analyzer adds two more equipment pieces: the Tekran 1130 and Tekran 1135. The automated technique uses the same general process as the manual method. Adding the 1130 and 1135 allows automated switching valves to control gas flow and automated heating coils to control desorption cycles. This allows continual ambient air speciation measurements on a 5-min Hg⁰ cycle, and RGM and Hg^P on a 2-hr cycle.¹⁻⁷⁷

5.8 Current U.S. EPA-approved Gas Testing Methods for Regulatory Monitoring

The data quality objectives (DQOs) for compliance monitoring are specific in that the main goal is to prove that emission levels are below a specific emission rate. Under current regulations, POTWs are required to demonstrate that per site total mercury biosolids incinerators emission does not exceed the mercury NESHAP limit of 3200 g/24 hr. Regulatory agencies require that methods used for reporting be fully established and promulgated. Current industry gas testing methods such as U.S. EPA Method 29 offer the sensitivity required to prove emissions are below the regulatory limit. The summary of U.S. EPA gas testing methods is listed in Table 5-8.

¹³⁴ U.S. EPA. (1999b)

¹³⁵ Risch, M., Prestbo, E.M., Hawkins, L. (2007)
Minimizing Mercury Emissions in Biosolids Incinerators

Also U.S. EPA approved are solids testing methods that measure concentration of total mercury in biosolids, discussed more fully in Section 5.4, Analysis of Solids. In lieu of U.S. EPA Method Number 29, POTWs may report emissions based on the mercury concentrations detected

Table 5-8. Summary of U.S. EPA Air Testing Methods.

Method Number	Method Descriptive	Detection Level	Technique	Relative Cost
101A	TGM and Hg ^P in Biosolid Incinerators	0.05–0.13 µg/m ³ **	CVAAS	\$
29	TGM, Hg ^P & Metals	0.56 µg/m ³	CVAAS	\$\$
EPA Clean Air Mercury Rule, Appendix K	Sorbent Trap TGM Continuous Emission Monitor	0.003 µg/m ³ *	CVAFS, CVAAS, Z-CVAAS	\$\$

TGM=total gaseous mercury, Hg^P=particle-bound mercury

*Assumes collection volume of 1.5 m³

**Range depends on instrument configuration.

in biosolids samples and a conservative 0% mercury control efficiency assumption for particulate air pollution control systems.

5.9 Future Considerations

With the reduction of mercury entering POTWs because of source control and/or installation of mercury-specific APCDs, mercury levels will continue to decrease in the stack gas. This downward trend in mercury gas concentrations must be considered when selecting an analysis method. There is also the potential that the U.S. EPA will lower emission limits, which will add additional pressure to adopt methods with lower detection limits. U.S. EPA's Clean Air Mercury Rule Appendix K offers excellent method sensitivity and ease of collection, and low relative cost. This has allowed Appendix K to become widely established in the coal-fired power plant industry.

As the U.S. EPA explores regulation of biosolids incinerators for mercury emission, an important unknown factor is the required testing frequency. In the coal-fired power plant industry, the U.S. EPA adopted a continuous monitoring requirement for mercury emission. This necessitated the development of continuous emission monitors and U.S. EPA's Clean Air Mercury Rule Appendix K sorbent trap integrated sampling. If frequent measurements are required for biosolids incinerators, impinger-based sampling may be less desirable because of difficulty in method implementation, and need for outside contractors to conduct the sampling, and potential for sample contamination. CEM instruments would offer real-time measurement capabilities, however they are a relatively new technology that is still undergoing refinements and has not been applied to biosolids incinerators. In absence of a continuous monitoring requirement by the U.S. EPA, the expenditure to install a CEM may not be justified.

Ultimately, the biosolids industry must decide which method meets U.S. EPA reporting requirements and DQOs.

CHAPTER 6.0

RECOMMENDED APPROACH FOR CONDUCTING A MASS BALANCE AROUND A BIOSOLIDS INCINERATOR

6.1 Material Balances – Introduction

Material balances (mass balances) are based on the fundamental “law of conservation of mass.” Completing a ‘mass balance’ should aim to account for what happens to each of the chemicals used in a process; in the case of this study the target chemical is mercury. Ideally, to determine the mass balance for mercury across a biosolids incinerator, all input and output streams (solid, liquid, or gas) should be measured and assessed.

In general a total mass balance equation can be written as:

$$\Sigma_{FS} - \Sigma_{PS} = \Sigma_{Acc} \quad (6.1-1)$$

Where:

Σ_{FS} = Masses entering via feed streams

Σ_{PS} = Masses exiting via product streams

Σ_{Acc} = Masses accumulating

If the process is assumed to be at steady-state,¹³⁶ there is no accumulation of mass within the process. Thus:

$$\Sigma_{FS} = \Sigma_{PS} \quad (6.1-2)$$

This is under the assumption that the mass of mercury in every stream is accounted. The above equation can be applied to continuous processes as:

$$\Sigma_{FSF} = \Sigma_{PSF} \quad (6.1-3)$$

Where:

Σ_{FSF} = Masses entering via feed streams as a function of flow

Σ_{PSF} = Masses exiting via product streams as a function of flow

¹³⁶ It should be recognized that some plant configurations may have internally recycled mercury-laden water resulting in an accumulation component. This is approach likely to increase in as water re-use receives more attention.

If the process involves chemical reactions or transformation of species (e.g., organic bound mercury is thermally driven to elemental mercury), the formation of product chemicals and the consumption of feed chemicals should be accounted. For this case, we must write a mass balance for each species and account its formation and consumption as follows:

$$\Sigma_{FSF} + \text{Mass formed by reaction} = \Sigma_{PSF} + \text{Mass used by reaction} \quad (6.1-4)$$

Luckily, if there is a change in mercury species it can be embedded into the analytical measurements. In other words determining the total mercury in all the defined input and output streams takes into account any species conversion within the system.

It must be recognized that no major input or output mercury source can be assumed. For example, when one stream is missing data, there is a tendency to deductively assume the value of a major input or output stream on the basis of indirect or historical data. If the input mass of mercury is known and there are two potential emissions, but only one is measured, often the input mass is compared to the output mass of the measured emission stream and the unmeasured emission source is assumed to contain the balance of the mercury mass. The error of the assumption is increased when the measured input and measured output are very close in mass and the unmeasured stream is assumed to contain very little mercury. Making such assumptions does not deliver a defensible mass balance.

6.2 Designing a Mass Balance for a Biosolids Incinerator

To successfully execute a mass balance study, QA and QC should be factored into the planning process from the beginning. If they are to be effective, the study's quality systems must be formulated in advance and communicated to all involved parties before the first sample is collected. The goal is to address the concepts of precision, bias, representativeness, completeness, comparability, and sensitivity in all aspects of the study. The steps and activities described below are essential to mercury mass balance studies at biosolids incinerators.

A successful mass balance study depends on the completion of certain QA milestones:

- ◆ Establishment of a project team
- ◆ Creation of DQOs
- ◆ Establishment of measurement quality objectives (MQOs) that meet DQOs
- ◆ Development of a project design plan
- ◆ Development of a quality assurance project plan (QAPP)

Figure 6-1 presents a potential thought process for the development of a mass balance around a biosolids incinerator. The figure should not be regarded as a perfect approach – all facilities have their own nuances and influences – but can be considered a starting point for planning and discussion. No assumptions have been made as to a budget for the process, but it should be recognized that the development of a sound scope and protocol for conducting the mass balance, considering all the impacts and the assumptions, is the single most valuable step in conducting a mass balance that will withstand scrutiny and cynicism.

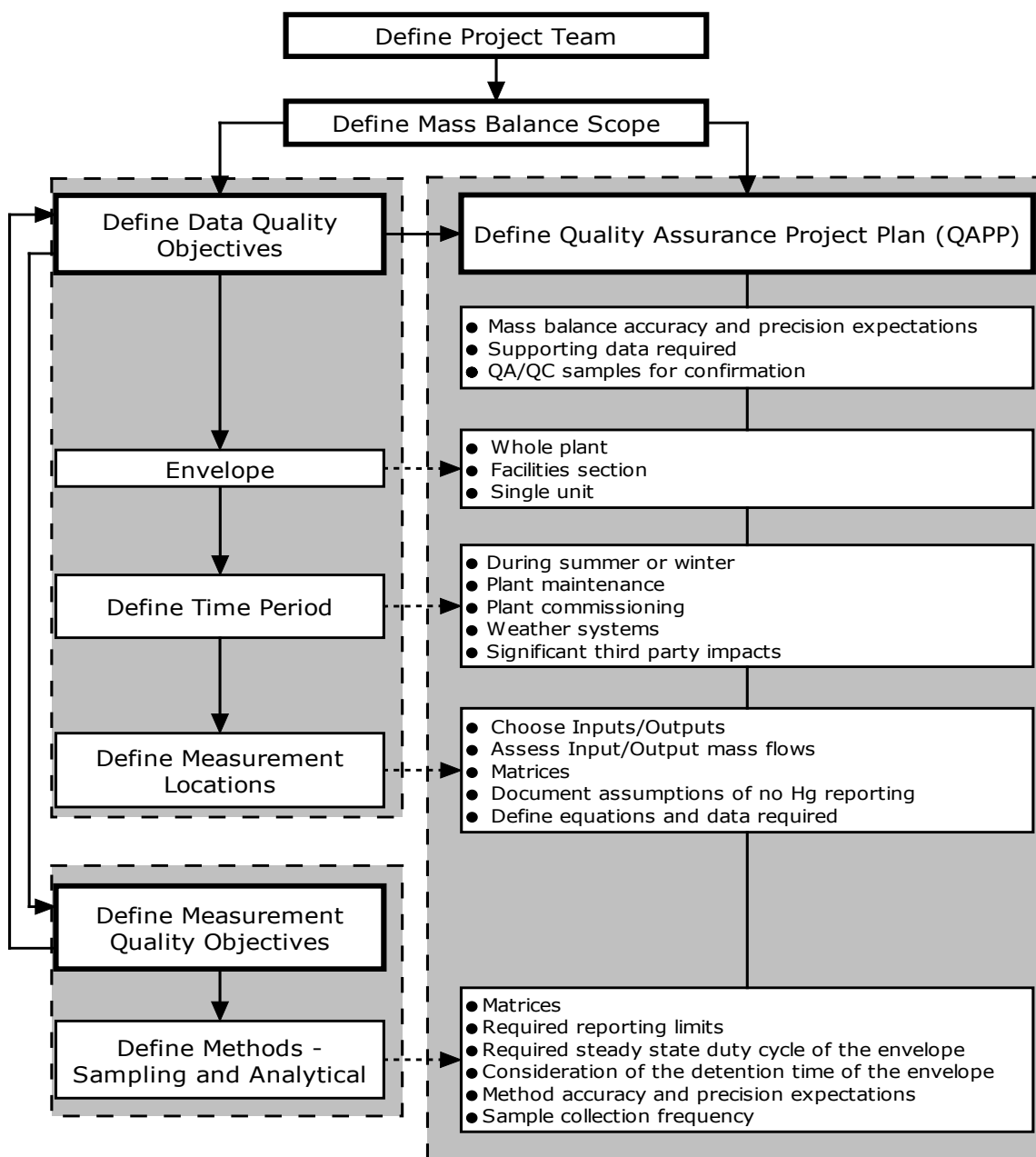


Figure 6-1. Example of a Process Scheme for Developing a Mass Balance.

6.2.1 Project Team

A mass balance typically requires the assembly of some or all of the following participants:

Principal Investigator(s) The principal investigator is the primary scientific researcher of the mass balance study. They take responsibility for completion of a funded project, directing the

research and reporting directly to the funding agency. Although their expertise is used in all aspects of the project, actual data collection may be performed by others.

Laboratory(ies) All laboratories selected to perform the various analyses should have demonstrated proficiency in analysis of the types of samples collected for the study (influent, effluent, emissions samples, biosolids) and be able to meet the MQOs detailed in the study plan.

Field Crew(s) Field crews selected to collect plant samples should have demonstrated proficiency in collection of the types of samples collected for the study (influent, effluent, emissions samples, biosolids) and be able to meet the field QC requirements.

Statistician(s) Often, the statistical analyses associated with project planning and data interpretation are beyond the expertise of other participants, therefore a statistician should be part of the project team.

QA Personnel Because most quality systems are implemented by a third party, mass balance studies should select QA personnel that are independent of data production. If this independence cannot be achieved within the laboratory, an external consultant may be used.

6.2.2 Data Quality Objectives

Once the project team has been assembled, it may begin to establish DQOs, which lay out, in specific language, what type, quantity, and quality of data is needed to meet the specified project goals. A well-executed mass balance study represents a snapshot in time. The mercury that enters the biosolids incinerator is followed from the moment it enters the plant until it leaves.

DQOs are unique to each individual project, developed to answer the specific question posed. As a result, a generic listing of them is not useful to the planning process. U.S. EPA has outlined a process for developing DQOs in its Quality System document QA/G4: Guidance for the Data Quality Objectives Process.¹³⁷ Although this document is useful as a guide, strict adherence to the DQO process is not critical to the success of executing the mass balance study. Certain studies often require project-specific DQOs developed using this process. For studies without this requirement, the project team is free to use only those portions of the process they feel are critical to the success of their study. The critical point is to decide on these objectives at the beginning of the study, and not to try and sort them out after the data have been collected.

With respect to this type of study, the general objective is to generate an accurate assessment of the mass balance of mercury across the biosolids incinerator. The term “accurate” is subjective unless it is grounded in defined numeric and narrative objectives. In addition, it is important to consider the motivation for performing the study in the first place. Is the study intended to be a preliminary look at how mercury distributes itself throughout the biosolids incineration process, or are the study findings intended to be used in future projections (for example, are the results of the mass balance going to be used to project the stack emissions of mercury based on the measured concentrations of the biosolids incinerated). The type and quality of data needed to address this question are very different from that needed to perform the preliminary study.

¹³⁷ U.S. EPA. (2006)

6.2.2.1 Envelope

The mass balance envelope defines the desired limits to the mass balance. Should the mass balance be conducted around the whole facility, a section of the facility or a single/series of processing units? Figure 6-2 shows a simplified schematic of the Metropolitan Sewer District of Greater Cincinnati biosolids incinerator with a mass balance envelope.

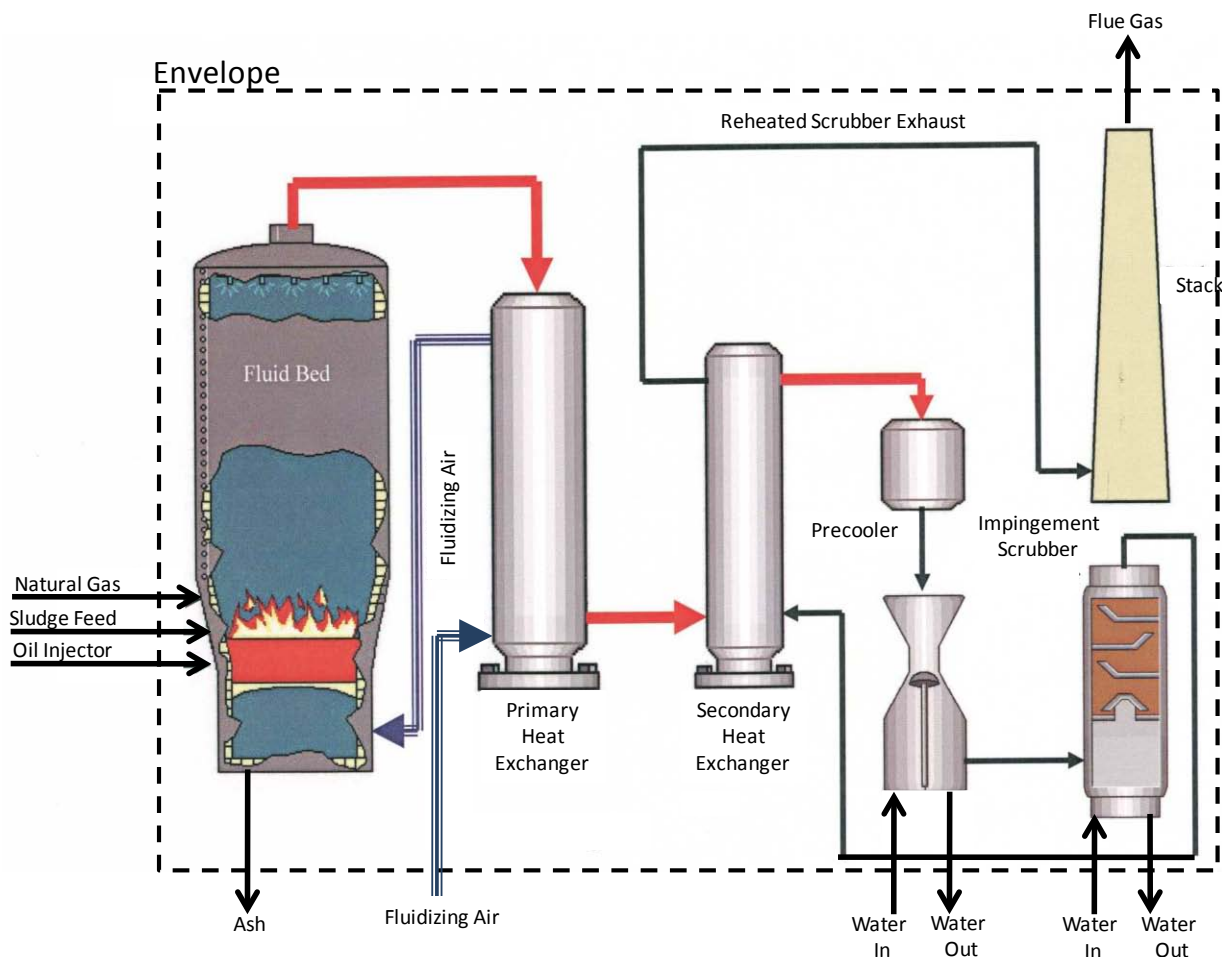


Figure 6-2. A Simplified Schematic of the Metropolitan Sewer District of Greater Cincinnati Biosolids Incinerator and the Potential Mercury-containing Feed and Product Streams.

6.2.2.2 Define Time Period

The period of operation of the biosolids incinerator during the mass balance needs careful consideration. Although ideally the mass balance should always close around 100% no matter what the operating conditions, the recorded may be used in other functions, thus the mass balance should be conducted with the facility as close to steady state operation as possible. In addition, the possibility does exist that a large pulse of mercury into the system can affect the partitioning of the mercury during the incineration process, resulting in a non-typical distribution of mercury to the different outputs being monitored. The overall mercury loading, and potential

speciation, into the biosolids incinerator will be defined by several historically predictable, unrealized and random occurrences. The predictable occurrences are such things as winter or summer operation, weekday or weekend operation and diurnal versus nocturnal operation. Unrealized events would be such things as plant maintenance or cleaning, the commissioning of a new facility unit or operation adjustments not communicated to the mass balance team. Random events are normally uncontrollable such as weather systems driving high storm water run-off into the system, or significant third party impacts. Weather events can be somewhat avoided by conducting the mass balance during more predictable weather periods, but third-party impacts are likely only to be detected once the mass balance data are processed analyzed and reviewed. It is strongly recommended that either the mass balance be conducted during a period that can be aligned with historical data, or the period defined for the mass balance become the period that future analytical diagnostic work occurs. This will allow a greater use of data over the facilities' lifetime. [Editor's note: If the mass balances do not close (typically within 30%), reconsider your assumptions regarding variability within your steady state operations.]

6.2.2.3 Define Measurement Locations

A typical biosolids incinerator system is a continuous process requiring the feed streams and product streams moving chemicals into and out of the process at all times. At every instant, the process is fed and products are produced. To achieve an actual mass balance each feed and product stream in the system would need to be continuously monitored, in real time. This economically undesirable, and currently unfeasible for mercury; therefore the mass balance must be simplified.

If the previous schematic of the Metropolitan Sewer District of Greater Cincinnati biosolids incinerator is considered (Figure 6-2) a further simplification of the schematic can be made (Figure 6-3A).

By making some basic assumptions the schematic can be simplified even further in anticipation of a mass balance:

- ◆ The supplemental fuel sources contribute negligible amounts of mercury compared to the biosolids.
- ◆ The fluidizing air has no mercury present
- ◆ The scrubber inlet water may contain minimal amounts of mercury
- ◆ The “rogue” discharges and emissions are minimal in a well-operated system.

This results in a mass balance that focuses on the most likely avenues of mercury movement in the biosolids incinerator system and is practically and economically achievable (Figure 6-3B). It should be noted that, anecdotally, quantifiable amounts of mercury in natural gas have been reported, although nothing substantive has been published.

Before proceeding with the mass balance, the streams assumed to contain no mercury should be documented. If the mass balance doesn't close correctly and the QA/QC for the analytical techniques is correct, there is a strong possibility that one of these assumptions is incorrect.

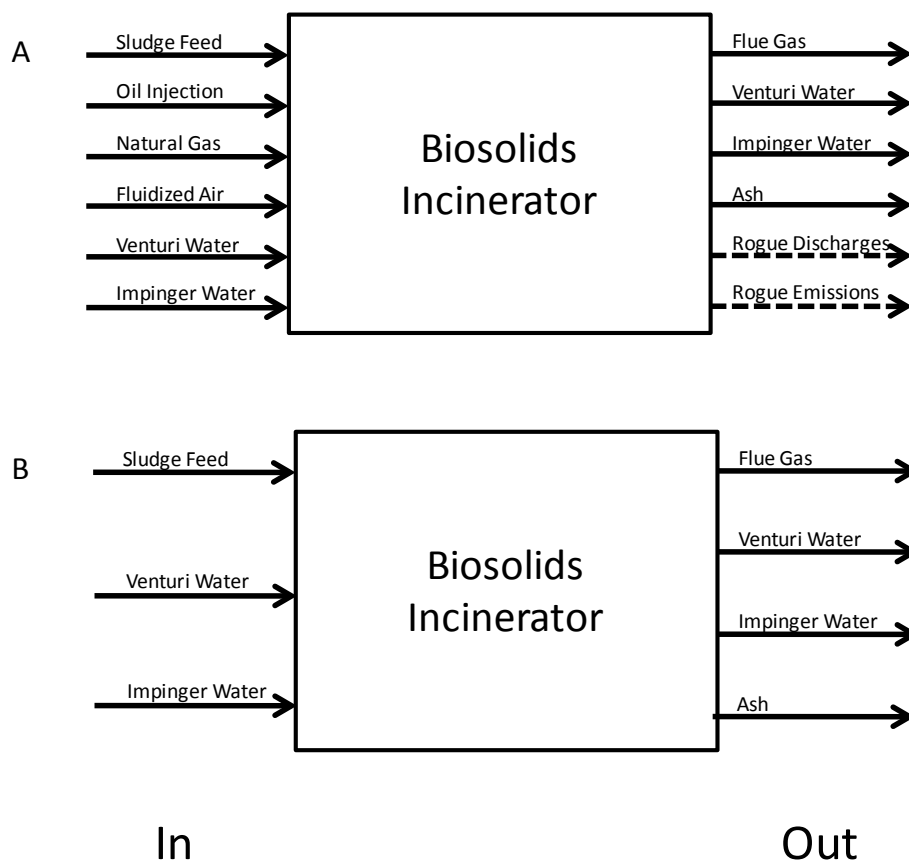


Figure 6-3. A Simplified Schematic for a Mass Balance Study of a Biosolids Incinerator.

For completing a mass balance study on a biosolids incinerator, total mercury analysis of each contributing input/output stream is the most important. However, thought and consideration must be paid towards the speciation of mercury in certain matrices within those mass balance measurements:

Flue Gas Mercury speciation in flue gas is important in determining the most efficient technology for reducing mercury emissions. Speciation of mercury effects capture rates in all APCDs; for example, wet scrubbers are capable of removing water-soluble or ionic forms of mercury and particulate mercury, but have limited Hg^0 capture [although Hg^0 is slightly soluble in water, $60.8 \mu\text{g/kg}$ (ppb) at 25°C (77°F) and 1 atm].¹³⁸ If the dominant species of mercury in the flue gas is particulate, a simple particulate control system would be appropriate. The determination of the mercury species in flue gas allows a facility to determine the optimal pollution control scheme for the mercury species present. Additionally, in coal-fired utilities, speciation of mercury has been shown to be affected by feed product, vapor phase constituents, and firing conditions.¹³⁹

¹³⁸ Clever, H.L., Johnson, S.A., Derrick, M.E. (1985)

¹³⁹ Brown, T.D., Smith, D.N., Hargis, R.A. Jr., O'Dowd, W.J. (1999)
Minimizing Mercury Emissions in Biosolids Incinerators

System Water As mentioned, particulate matter and water soluble mercury can be trapped using wet scrubbers. This water is then discharged, treated and discharged or partially re-used. In some situations, especially if the waste water is recycled within the POTW, biomass or utility water may become saturated with mercury. Once saturated a change in conditions can occur and an unexpected mass of mercury may enter the mass balance. This would obviously close the mass balance at >100%. Although discussion of liquid treatment technologies for mercury removal is outside the scope of this report, operators should be aware that under certain conditions the APCD train discharge water disposal has the potential to impact final effluent, the overall mercury emission control efficiency and the mass balance being conducted.

When completing a mass balance it is critical to understand the matrices of the input/output streams measured. Equally important is the accurate and precise determination of mass flows. With concentration and flow values, it is possible to evaluate the mobility of mercury throughout the process and close the mass balance calculation. The flow values are especially important for gaseous mercury determination. Gaseous concentration is highly dependent on temperature, pressure, and gas content; therefore, measurement of all parameters requires equal attention. The relationship of concentration and flow on detection limit is listed below, in Figure 6-4. Measurements involving solids need no special consideration assuming that the percent solids content is consistent and the mercury concentrations are reported on a dry weight basis. If the biosolids entering the system is homogeneous, or could be blended to be homogeneous on sampling, then the mercury mass can be directly calculated from the incoming biosolids flow, assuming that the correct analytical technique is used.

Figure 6-4 gives a graphical depiction of detection limit changes as a function of gas concentration. Each line represents a steady mercury input rate with changing flow rates. Gas concentration is functionally equivalent to method detection limit. As an example, for the 0.002 lb/hr line at a flow of 30,000 m³/hr, a method capable of 3.0 µg/m³ or lower is necessary to assure detection. Reading the graph vertically, it is demonstrated how reduction in the mercury emission rate (such as related to installation of a mercury-specific APCD) will require a more sensitive method to ensure detection.

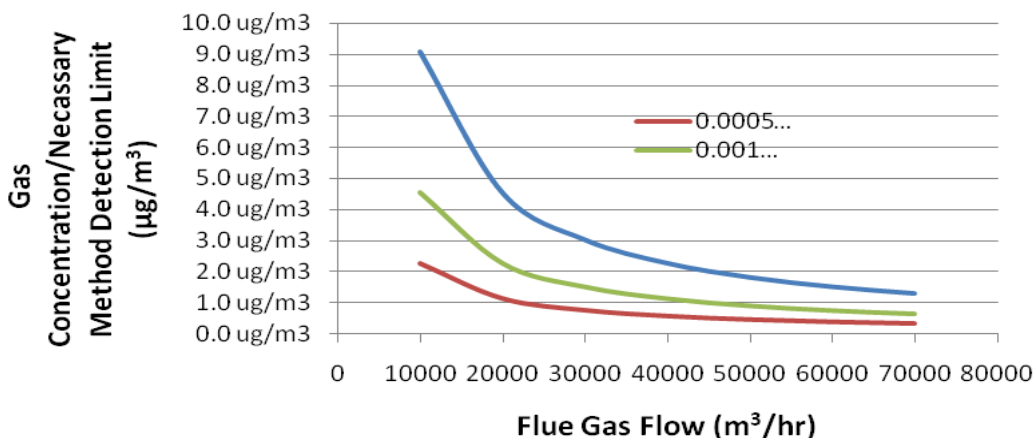


Figure 6-4. Effect of Flue Gas Flow on Mercury Detection Limit.

6.2.2.4 Calculations

Finally, after identifying the input and output streams, before the mass balance being initiated, the actual equations that will be used for the mass balance should be defined. This is regarded as a good check and balance to make sure that all that needs to be collected will be collected. As described previously the basic mercury balance equation (6.2.2.4-1) requires the input and output mercury streams to be equal.

$$(\Sigma_{\text{HgGas}} + \Sigma_{\text{HgLiquid}} + \Sigma_{\text{HgSolid}})_{\text{Input}} = (\Sigma_{\text{HgGas}} + \Sigma_{\text{HgLiquid}} + \Sigma_{\text{HgSolid}})_{\text{Output}} \quad (6.2.2.4-1)$$

The individual loading equations are described below for a gas stream (6.2.2.4-1), liquid stream (6.2.2.4-3) and solid containing stream (6.2.2.4-4). Although these equations may require adaptation depending on the sampling methods used and the data units preferred by the operators, the input and output streams will use the same equation basis.

$$\Sigma_{\text{Hg Gas}} = q_{\text{vg}} \times [\text{Hg}]_{\text{g}} \quad (6.2.2.4-2)$$

$$\Sigma_{\text{Hg Liquid}} = q_{\text{vl}} \times [\text{Hg}]_{\text{l}} \quad (6.2.2.4-3)$$

$$\Sigma_{\text{Hg Solid}} = q_{\text{ms}} \times [\text{Hg}]_{\text{s}} \quad (6.2.2.4-4)$$

Where:

$\Sigma_{\text{Hg Gas}}$ = Mercury loading in the gas phase (kg Hg/day)

$\Sigma_{\text{Hg Liquid}}$ = Mercury loading in the liquid phase (kg Hg/day)

$\Sigma_{\text{Hg Solid}}$ = Mercury loading in the solid phase (kg Hg/day)

q_{vg} = Gas volume flow rate (m^3/day)

q_{vl} = Liquid volume flow rate (L/day)

q_{ms} = Solid flow rate (kg/day)

$[\text{Hg}]_{\text{g}}$ = Concentration of mercury ($\mu\text{g Hg}/\text{m}^3$)

$[\text{Hg}]_{\text{l}}$ = Concentration of mercury ($\mu\text{g Hg}/\text{L}$)

$[\text{Hg}]_{\text{s}}$ = Concentration of mercury (mg Hg/kg)

Some streams, such as the biosolids stream or ash, may require a conversion from volume flowrate to mass flow rate. When historical data are used, this often requires assumption of percent solids, specific gravity, and fluid density. When the mass balance is conducted, it is strongly advised that direct measurement of mercury and solids are taken from the same sample.

i.e. If 1 L of wet biosolids is collected, the sample should be split in two. Five hundred milliliters (500 mL) will be sent for mercury determination and 500 mL will be sent for percent solids determination. This is making the assumption that the mercury in the stream is due only to the solids, with no significant contribution from the aqueous phase. The resulting data will allow the solids containing streams to be directly defined on either a wet ($\mu\text{g Hg}/\text{L}$) or dry ($\mu\text{g Hg}/\text{kg}$) biosolids basis, depending on operator preference.

Conversion factors that may also be of interest include:

1 gallon (gal) [US, liquid] = 3.79 liter (L)

1 cubic foot (ft³) = 0.0283 cubic meter (m³)

1 gram (g) = 0.00220 pounds (lbs)

1 gram (g) = 1x10³ milligram (mg)

1 gram (g) = 1x10⁶ microgram (μg)

1 gram (g) = 1x10⁹ nanogram (ng)

6.2.3 Measurement Quality Objectives

After the type and quality of data is identified (through completion of the DQO process), concrete acceptance criterion for the data can be formulated as MQOs. The U.S. EPA defines MQOs¹⁴⁰ as acceptance criteria for the quality attributes measured by project data quality indicators such as precision, bias, representativeness, completeness, comparability, and sensitivity. Although this definition is useful to a point, it does not help in understanding how the MQOs are practically used in the study.

With respect to the mass balance study, the MQOs are the QC acceptance criterion used to evaluate whether or not the data are acceptable for use in the study (in other words, do the data answer the question posed by the study?). The methods employed to analyze the samples will often times specify general acceptance limits for the required QC samples (matrix spikes, laboratory replicates, reference materials, and blanks). This is a good starting point for establishing the study-specific MQOs, however the project team should then review these against the established study DQOs to ensure that they are stringent enough to meet the study goals, or alternatively to ensure that they are not too strict, resulting in wasted effort (such as reanalysis or exclusion of data that are perfectly suitable to meet the DQOs).

Definitions of the QC samples and how they are calculated, project-specific considerations that should be taken when establishing the MQOs, examples of MQOs that may be applied to the project and examples of corrective actions can be found in Appendix F.

6.2.3.1 Define Methods – Sampling and Analytical

It is important to define the analytical methods to be used for mercury determination before sampling methods are considered. Each mercury technique may require certain collection methods to maintain integrity of the sample before analysis.

Several parameters must be cross referenced to determine which analytical technique should be used; Figure 6-5 presents a potential thought process flow to aid decision of analytical method.

Essentially, any historic data collected should give a reasonable idea of the reporting/detection limits required from the analytical technique. The matrix will dictate the analytical methods needed and will determine the type of sample preparation (homogenization/digestion) required. If historic data are not available or the operator is not confident in the data, it

¹⁴⁰ U.S. EPA. (2002)

is strongly suggested that a pre-test of all the identified input/output streams is conducted. This can be a simple screening test, the goal is to determine the approximate concentration of mercury expected to be seen during the mass balance. Failure to have a strong prediction of the potential mercury concentrations, either by historical data or pre-screening, could result in a significant increase in cost for the mass balance or failure of the analytical methods chosen.

In addition to the number and type of streams that should be monitored for mercury, the time resolution of the monitoring is also important. Simultaneous collection of samples or monitoring of streams does not take into account residence time of the system (e.g., the biosolids feedstock entering the incinerator may take hours to reach the ash sampling point). Therefore, any biosolids and ash sample collected simultaneously will have different original sources and thus potentially different mercury values. For this reason a time-based monitoring scheme should be used during sample collection during a mass balance. The extent of the time-based monitoring scheme will be determined by the intended accuracy of the mass balance, the period of operational interest, the analytical techniques chosen, the ability to extrapolate the results with a meaningful model and the mercury fluctuations in the feed stream.

If a continuous emissions monitoring system is not available, it will be found that the mercury in gas techniques are integrated sampling techniques (i.e., the mercury is captured over a period of time by passing a sub-sample of the flue gas through a liquid or solid sorbent). Integrated sampling is an excellent method for a mass balance as it gives a direct measurement of mercury loading as a function of time, and for the mass balance period no assumptions or extrapolations need to be made. This said, the sample integration period should span the length of the mass balance study. If the integration period is too small to do this, whether by method definition or because the mass balance is being performed over an extended period, then multiple integrated samples should be collected to span the length of the mass balance.

Collection of the other streams (liquid and solid) should occur during the period of sample integration for the gas sampling methods. If budget is of concern, the number of samples to be processed can be reduced through composite sampling. For example, over 24 hr, every hour a sample is taken and stored appropriately. After the collection period, or during, the samples are mixed thoroughly and a sub-sample set of replicates are extracted.

Accuracy and precision of the sample collection should be considered. For definition, accuracy is the degree of conformity of a measured or calculated quantity to its actual (true) value. Accuracy is closely related to precision, which is also called reproducibility or repeatability, the degree to which further measurements or calculations show the same or similar results. Ultimately, although an accurate and precise measurement is ideal, for a mass balance accuracy is more important than precision. As long as the measurement is accurate, the precision of the result can be established over the period of sampling and analysis, assuming that multiple samples were collected. If integrated sampling is used then the sampling scheme should be repeated at least three times. This is also true for composite samples, however, composite sampling can be sub-sampled to achieve the correct statistics, and however, if integrated sampling is being repeated three times then the composite sampling should be repeated three times, during the same periods.

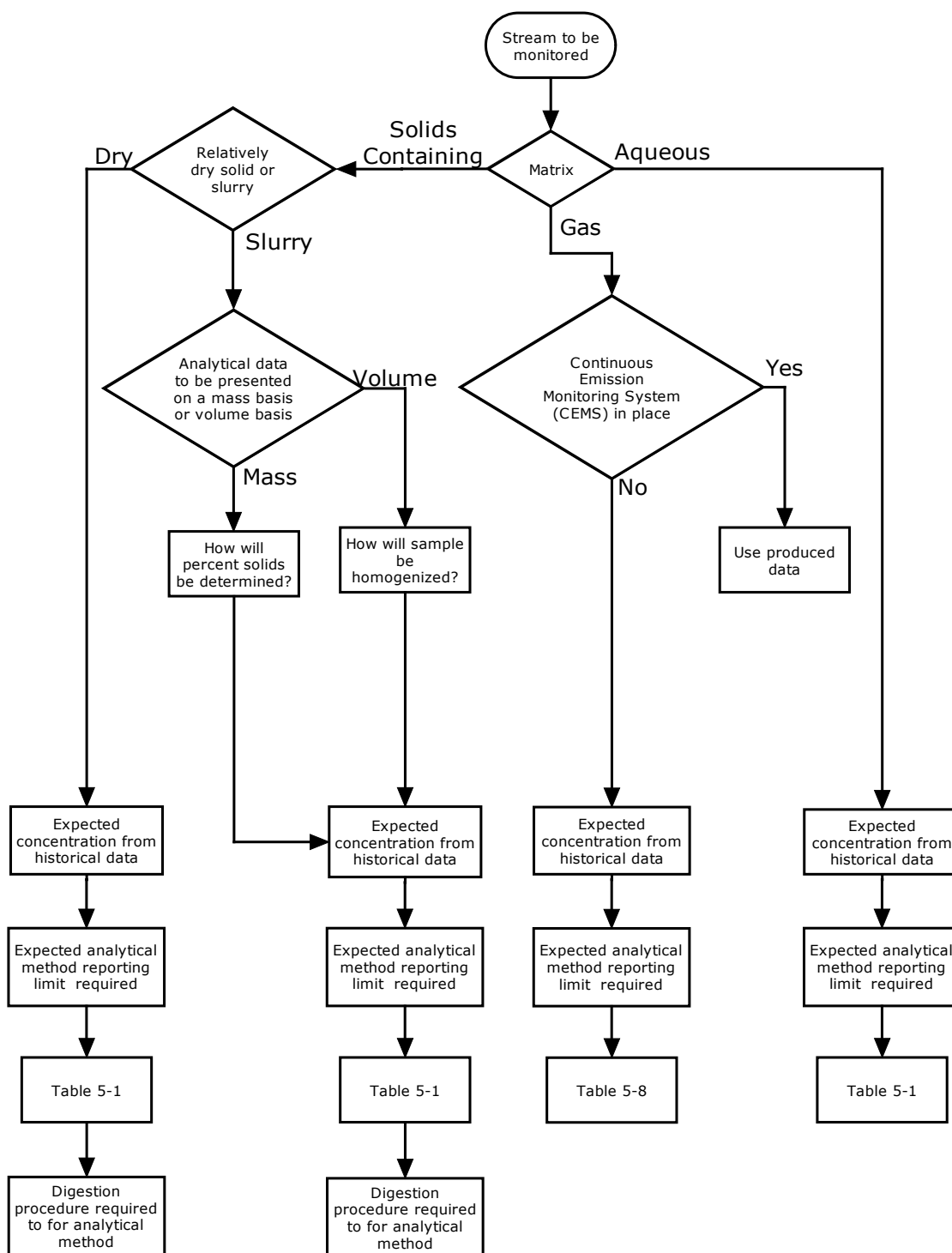


Figure 6-5. Example of a Process Scheme for Choosing the Analytical Methods to be Used in the Mass Balance.

6.2.4 The Quality Assurance Project Plan

A QAPP describes the intended technical activities and project procedures that will be implemented to ensure that the results will satisfy the stated performance or acceptance criteria. Even if the project does not formally require generation of a QAPP, it is critical to the success of the study and should be undertaken even if the study is voluntary. Drafting a QAPP for a mercury mass-balance prompts the people involved in the study to address questions and issues related to QC before the formal start of the investigation. Laying out the objectives of the study also helps clarify how the study goals will be achieved, and can help pinpoint weak portions that prompt changes to the study design. Including this as part of the planning process means that adjustments to the study while minimizing loss of time and effort. A number of the QAPP elements pertain largely to administrative issues that do not directly affect the data quality of the study. Directions for drafting a QAPP can be found in U.S. EPA Quality System Document QA/G-5: Guidance for Quality Assurance Project Plans.”¹⁴¹ If a QAPP is a requirement of the study, directions for completing these elements will be found in U.S. EPA document QA/G-5. If the QAPP is being generated on a voluntary basis, only the element deemed helpful to the overall quality of the study need consideration. Selected QAPP elements are discussed in Appendix F, with a focus on improving the overall quality of the mass balance study.

¹⁴¹ U.S. EPA. (2001)
Minimizing Mercury Emissions in Biosolids Incinerators

APPENDIX A

PROJECT SURVEY 2006

Survey Results – Statistical Summary

Figure A-1. Daily Flow in Millions of Gallons Per Day (MGD) as a Function of POTW ID.

			Count	Average	Lowest	25th Percentile	Median	75th Percentile	Highest
Average Daily Flow (MGD)			31	60	10	25	39	92	225
Average Industrial Loading (% of Average Daily Flow)			29	13	0	5	9	12	83
Municipal flow (MGD)			31	54	5	19	37	80	214
Industrial flow (MGD)			31	6	0	1	3	10	22
Biosolids Incinerated	2002	US Wet Tons (per Year)	28	50516	413	8468	31221	67614.5	224000
		Average % Solids (per Year)	23	28	16.3	22.65	28	29.9	48
	2003	US Wet Tons (per Year)	29	53621	3168	12013	32602	69866	248000
		Average % Solids (per Year)	24	27	17	23.275	26.85	29.7725	47
	2004	US Wet Tons (per Year)	29	53470	3581	12800	32299	65085	255000
		Average % Solids (per Year)	24	28	18.2	22.925	26.6	30.07	47
	2005	US Wet Tons (per Year)	31	52405	3892	13686	32123	60320.5	278000
		Average % Solids (per Year)	31	26	18.4	21.15	24.75	29.15	47
Supplemental Fuel Used (GBTU)	Natural Gas	2002	24	39	0.03	0.88	25.87	56.83	234.95
		2003	24	46	0.04	0.95	18.38	63.69	417.89
		2004	24	43	0.04	1.00	21.43	42.16	462.93
		2005	25	36	0.04	10.79	27.60	57.98	154.93
	Fuel Oil	2002	4	15	0.01	2.32	11.28	23.81	36.85
		2003	11	8	0.11	0.76	2.56	8.93	36.65
		2004	12	14	0.46	1.79	3.89	13.40	71.45
		2005	11	13	0.02	0.46	3.93	6.87	80.62
	Other	2002	5	36	0.29	16.50	18.75	22.25	123.11
		2003	5	34	0.18	10.26	14.71	43.60	103.62
		2004	5	35	0.29	2.95	14.87	39.13	120.24
		2005	5	28	0.21	2.34	10.79	19.40	105.20
Biosolids	2002	Annual Average mg/Kg, Dry	27	0.75	0	0.46	0.57	1.06	3.00
		Highest mg/Kg, Dry	26	1.40	0	0.75	1.00	1.77	5.02
	2003	Annual Average mg/Kg, Dry	27	0.82	0	0.57	0.73	1.13	1.60
		Highest mg/Kg, Dry	26	1.55	0	1.01	1.54	2.18	2.67
	2004	Annual Average mg/Kg, Dry	27	0.79	0	0.47	0.69	1.02	1.96
		Highest mg/Kg, Dry	27	1.53	0	0.84	1.20	1.97	4.99
	2005	Annual Average mg/Kg, Dry	30	0.84	0	0.42	0.72	1.18	2.60
		Highest mg/Kg, Dry	29	1.95	0	0.69	1.70	2.30	8.80
Influent	2002	Annual Average ng/L	22	9086	0.00	58	165	300	196200
		Highest ng/L	22	37595	0.00	201	491	627	810000
	2003	Annual Average ng/L	24	6272	0.00	0	100	265	147100
		Highest ng/L	23	38312	0.00	193	380	653	870000
	2004	Annual Average ng/L	23	9104	0.00	1	130	251	206300
		Highest ng/L	23	70526	0.00	158	420	627	1600000
	2005	Annual Average ng/L	24	12390	0.00	97	103	232	277400
		Highest ng/L	24	55835	0.00	263	397	705	960000
Effluent	2002	Annual Average ng/L	21	58	0.0	0.0	3.0	15	470
		Highest ng/L	20	378	0.0	1.5	7.4	27	6620
		Annual Average ng/L	24	46	0.0	0.6	3.0	11	500
	2003	Highest ng/L	22	475	0.0	2.4	6.5	20	10000
		Annual Average ng/L	25	45	0.0	0.2	2.6	6	500
	2004	Highest ng/L	22	136	0.0	0.9	4.9	17	2240
		Annual Average ng/L	26	36	0.0	1.9	3.4	10	300
	2005	Highest ng/L	24	84	0.0	3.4	5.7	24	1000
Mercury Incinerator Emissions Test	Mercury Emissions mg / dry SCM		24	0.089	0.035	0.049	0.082	0.104	0.284
	Mercury Emissions lbs / hr		27	0.004	0.002	0.002	0.003	0.005	0.006

Survey Results - Graphics

Figure A-2. Daily Flow in Millions of Gallons Per Day (MGD) as a Function of POTW ID.

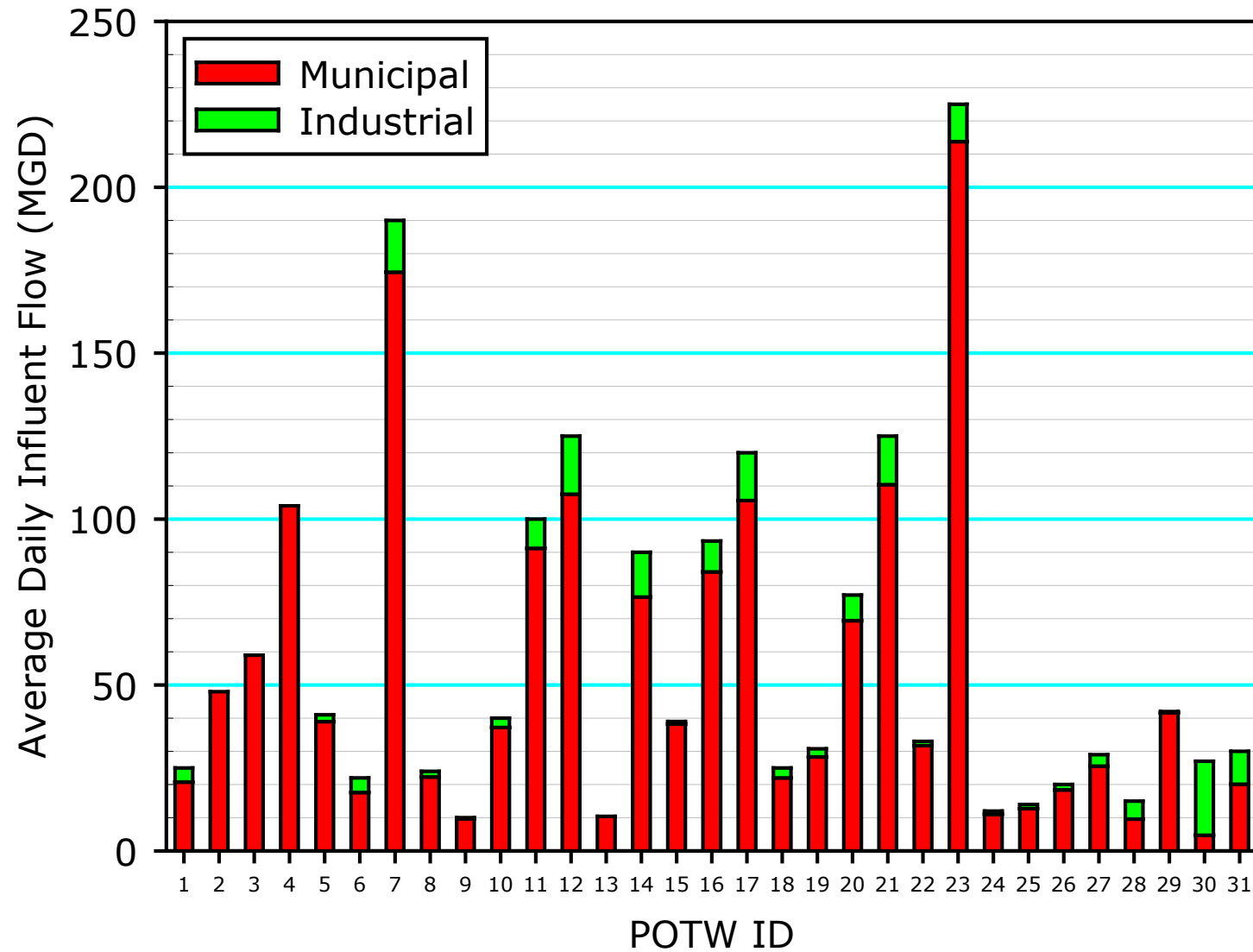


Figure A-3a. Types of and Numbers of Incinerators Used as a Function of Location.

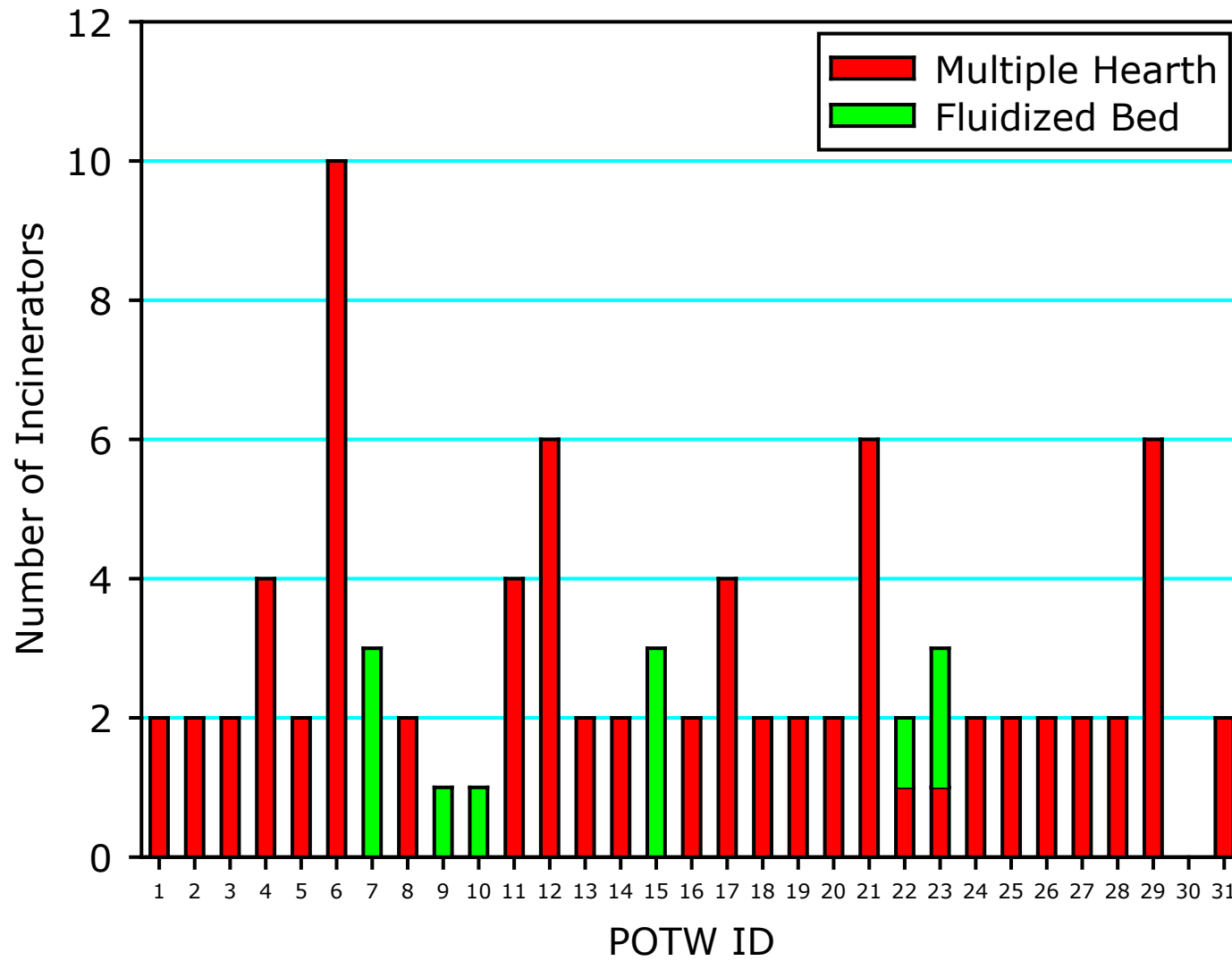


Figure A-3b. The Distribution of Multiple Hearth Incinerators.

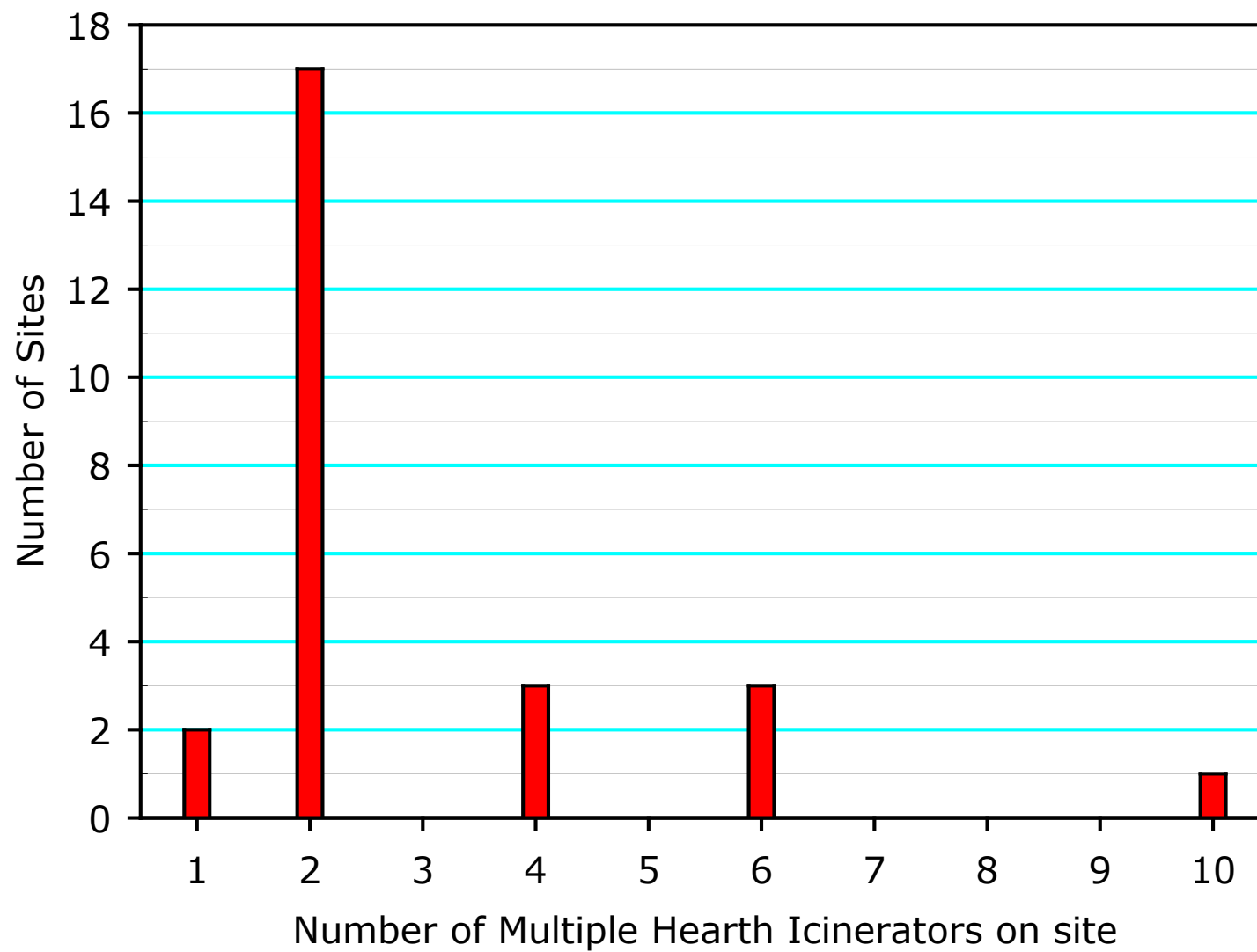


Figure A-3c. The Distribution of Fluidized Bed Incinerators.

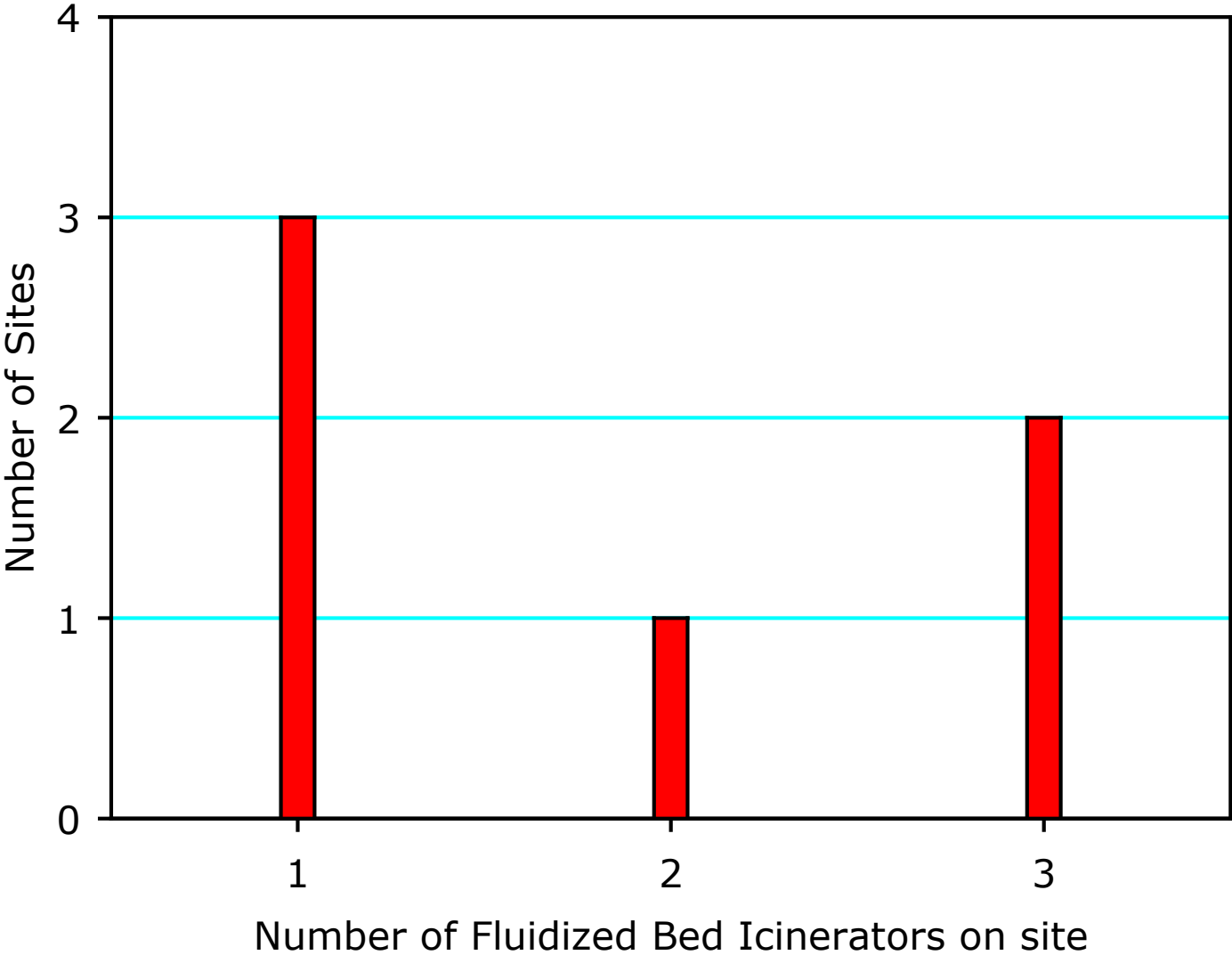


Figure A-3d. Distribution of Fluidized Beds verses Multiple Hearth Incinerators.

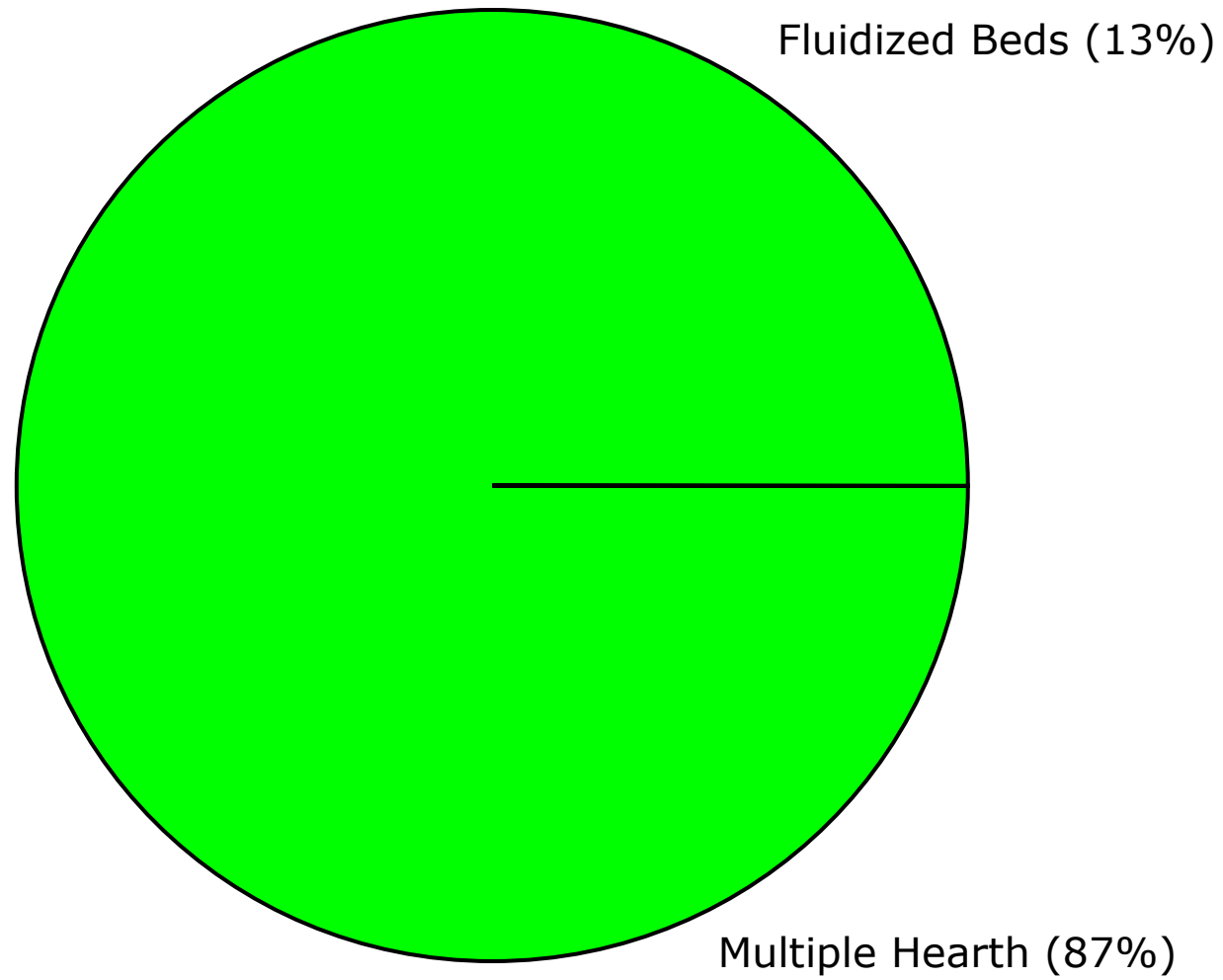


Figure A-4. Conditioning Methods for Biosolids.

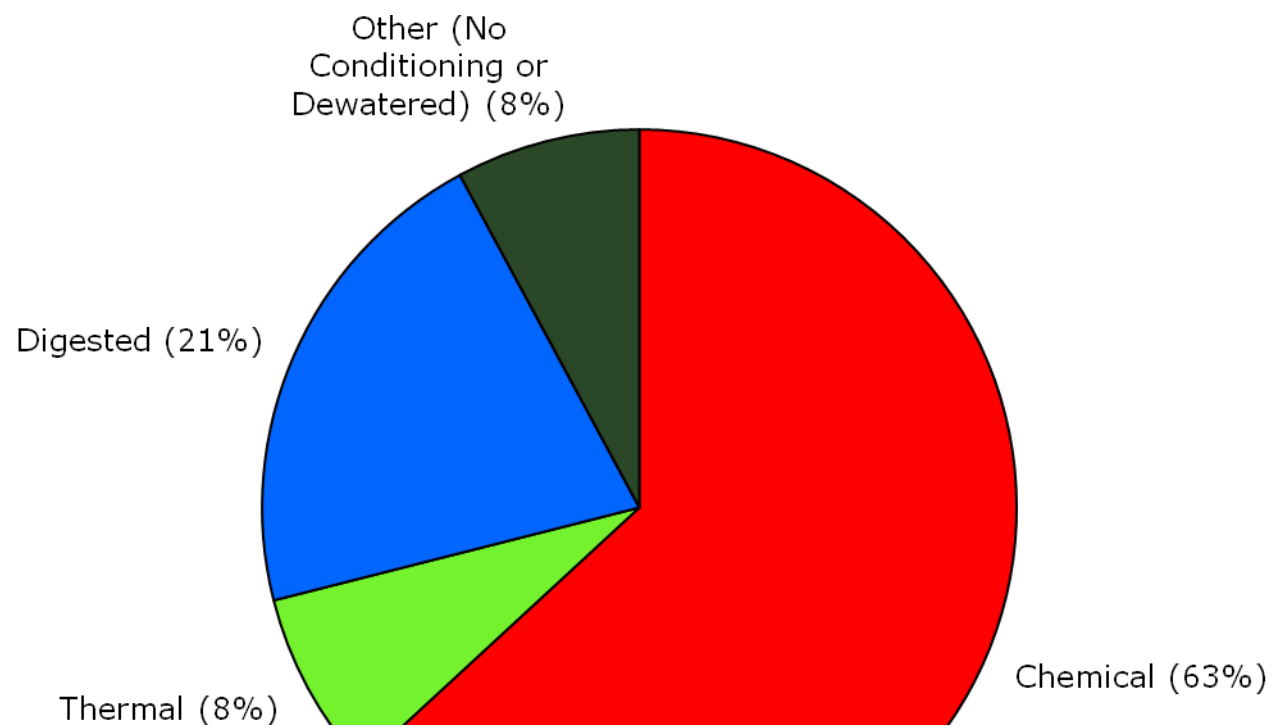


Figure A-5. Dewatering Methods.

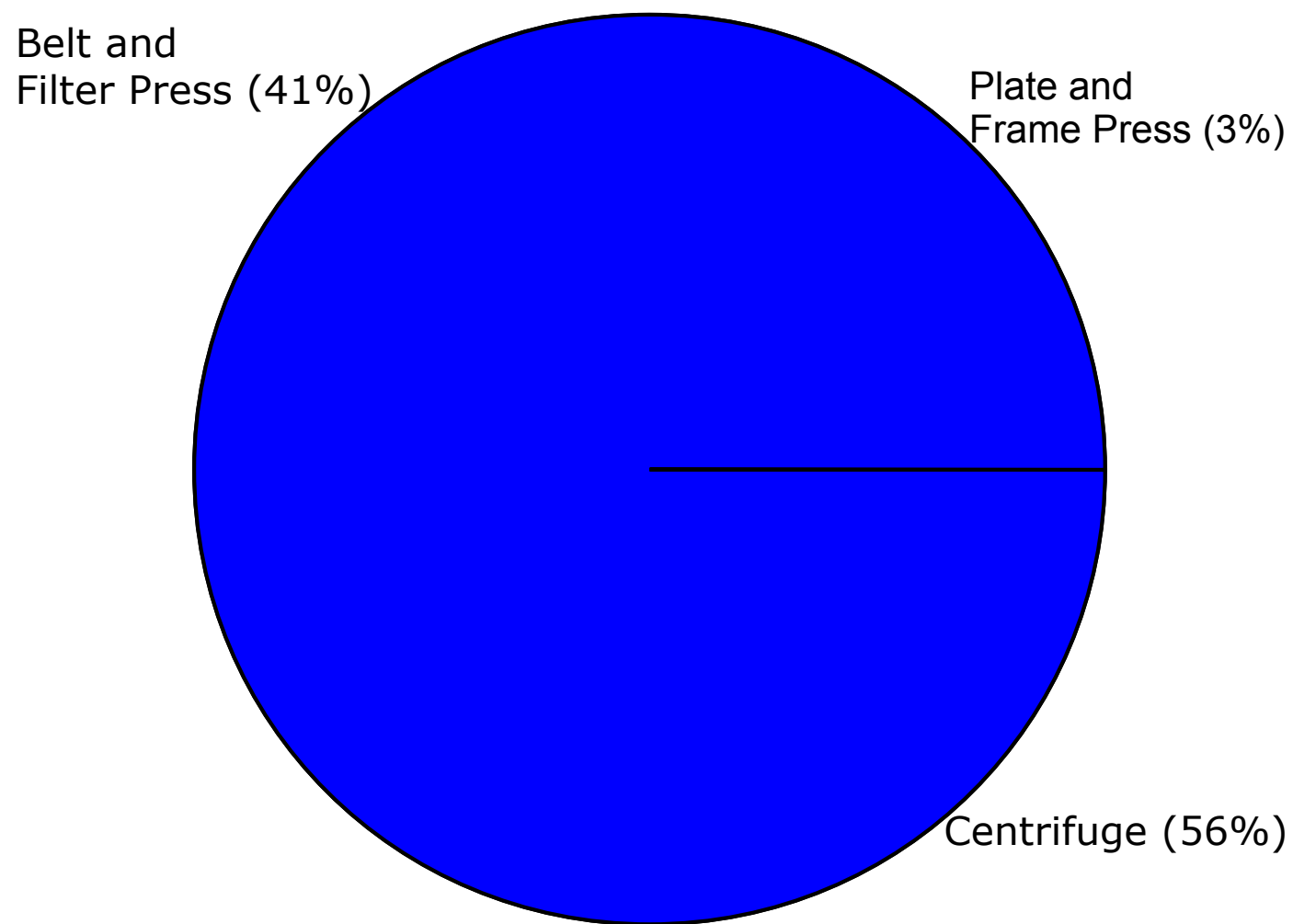


Figure A-6a. Mass of Biosolids Incinerated as a Function of Location and Year.

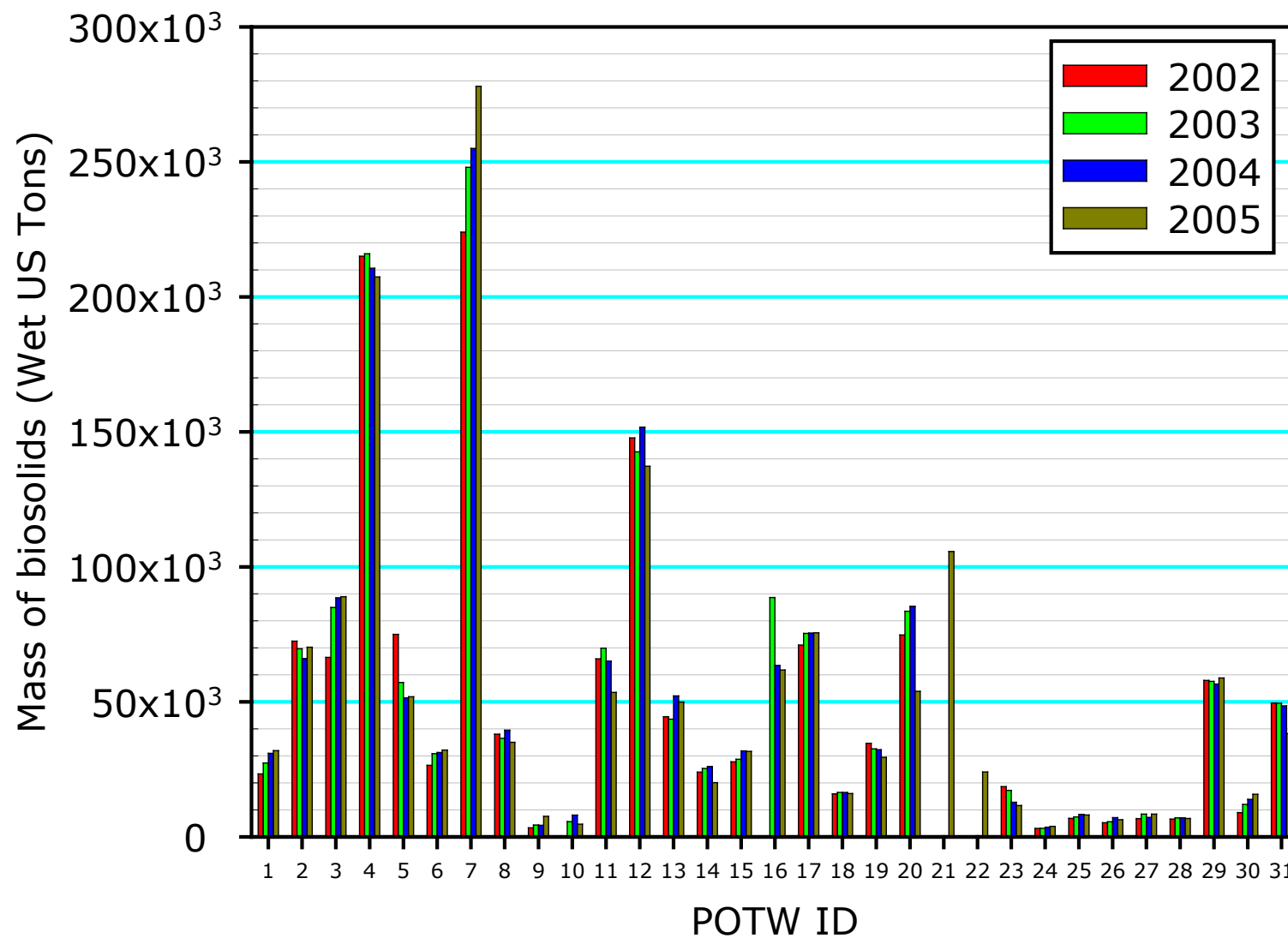


Figure A-6b. Percent Solids of Biosolids Incinerated as a Function of Location and Year.

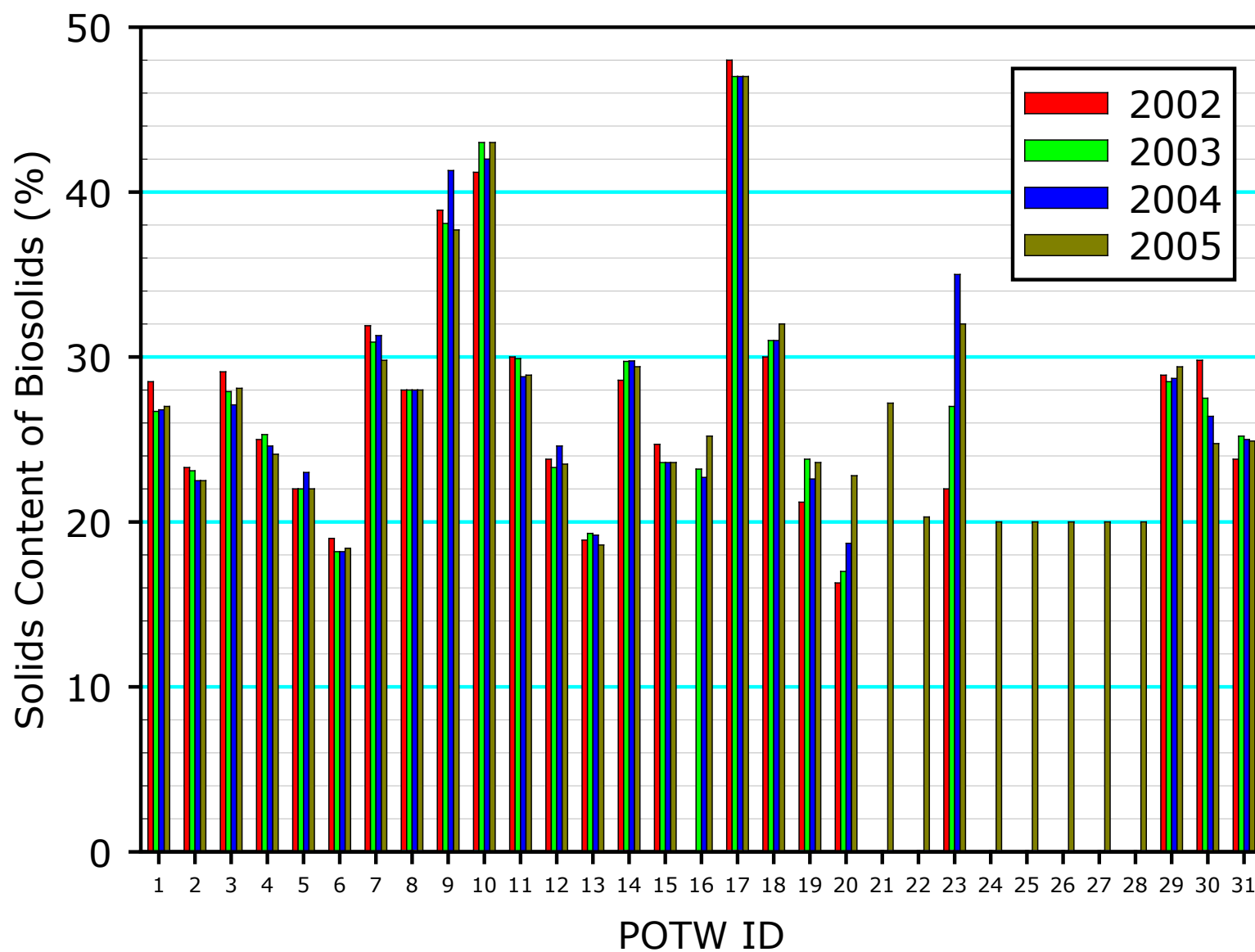


Figure A-7. Burning Zone Temperatures as a Function of Location.

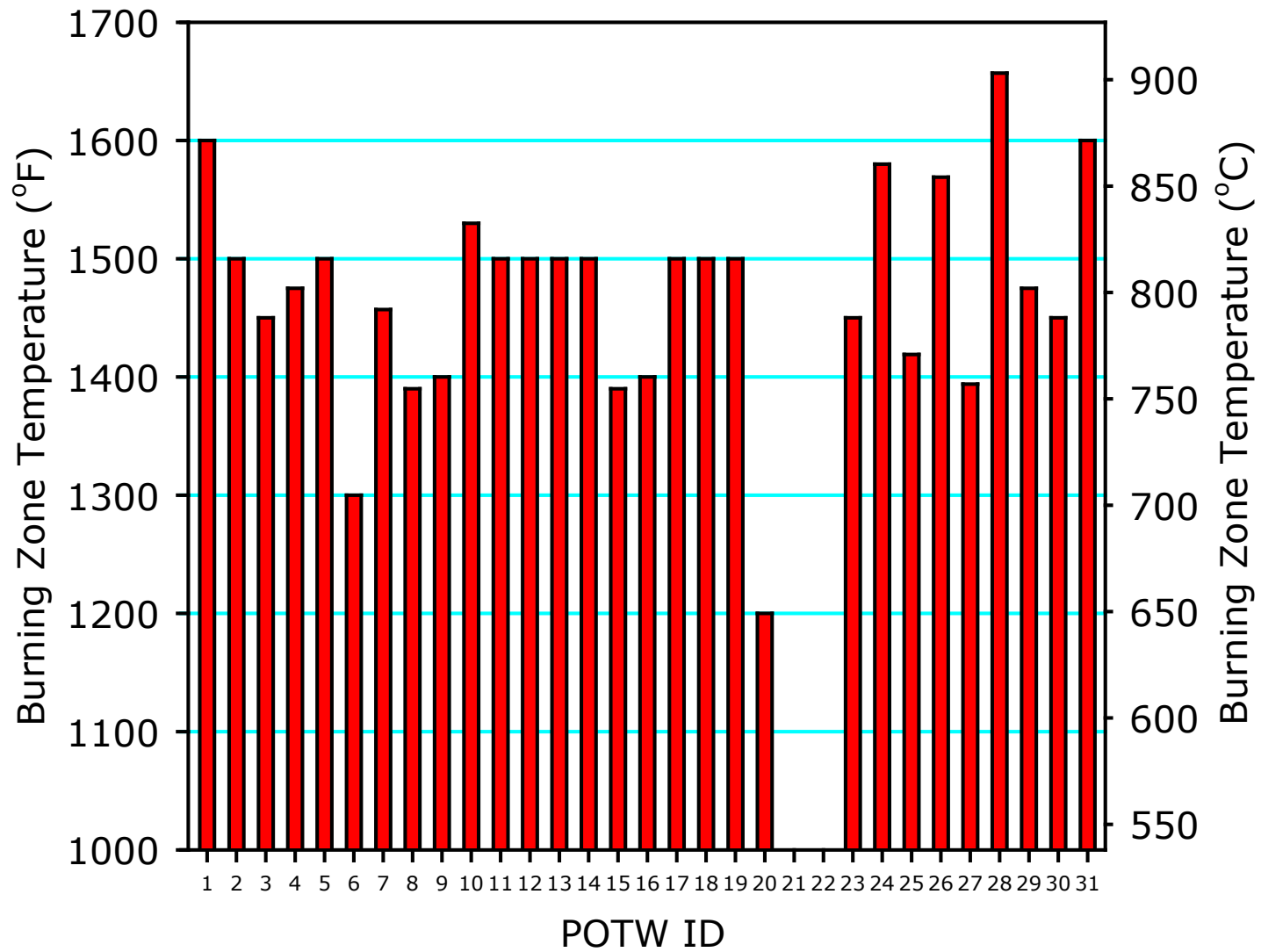


Figure A-8a. Use of Natural Gas as a Supplemental Fuel as a Function of Location.

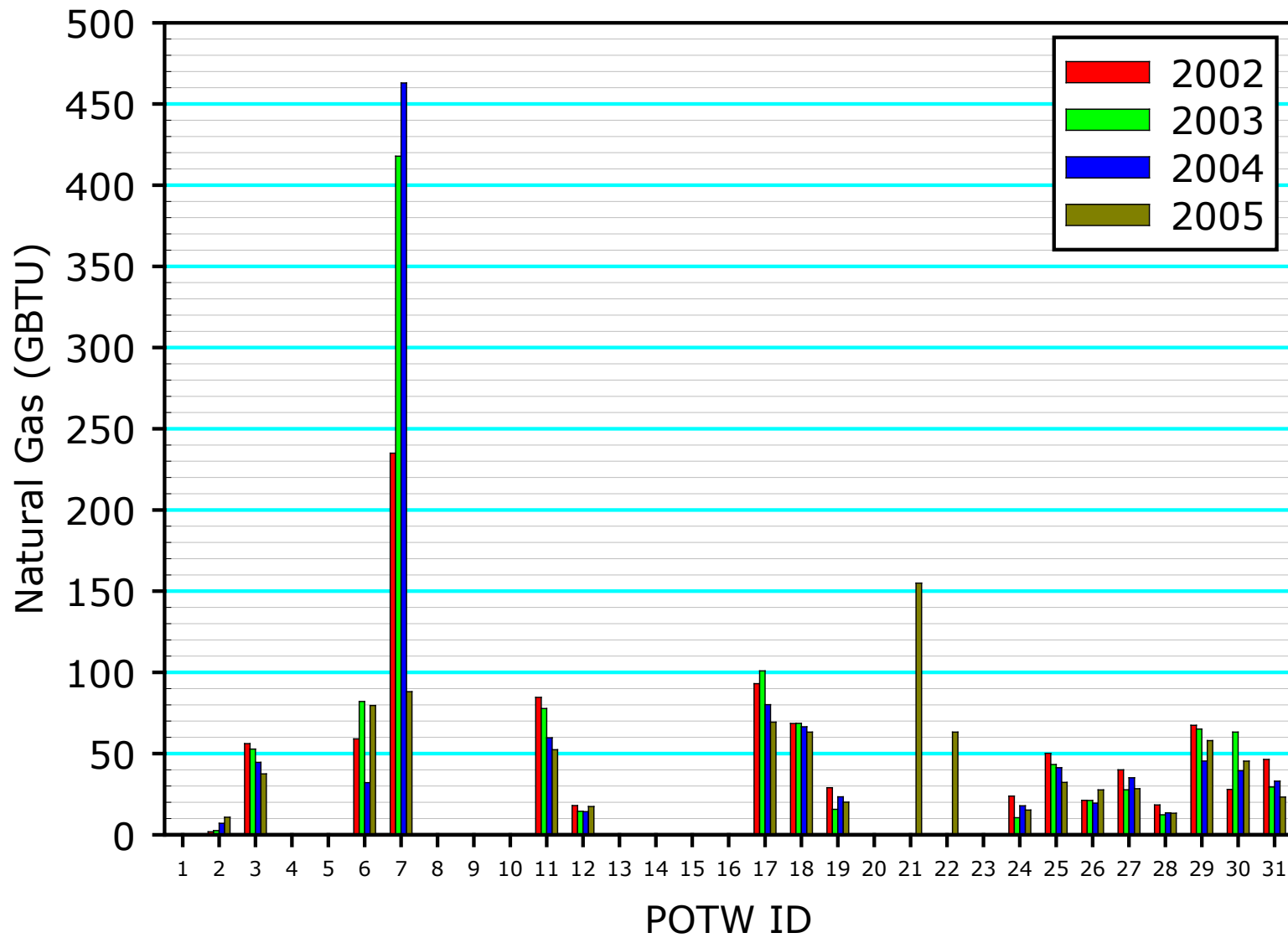


Figure A-8b. Use of #2 Fuel Oil as a Supplemental Fuel as a Function of Location.

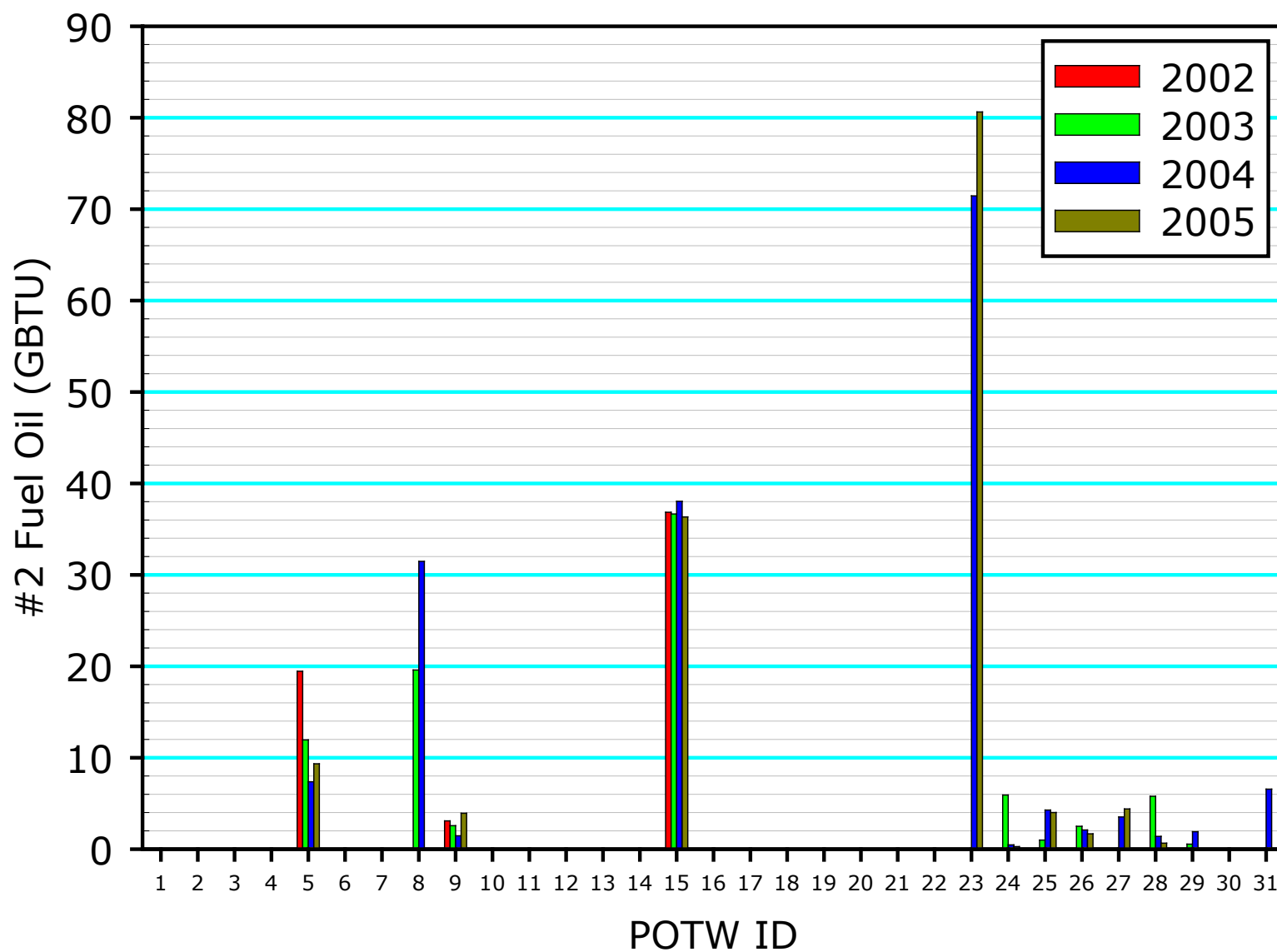


Figure A-8c. Use of Other Fuels as a Supplemental Fuel as a Function of Location.

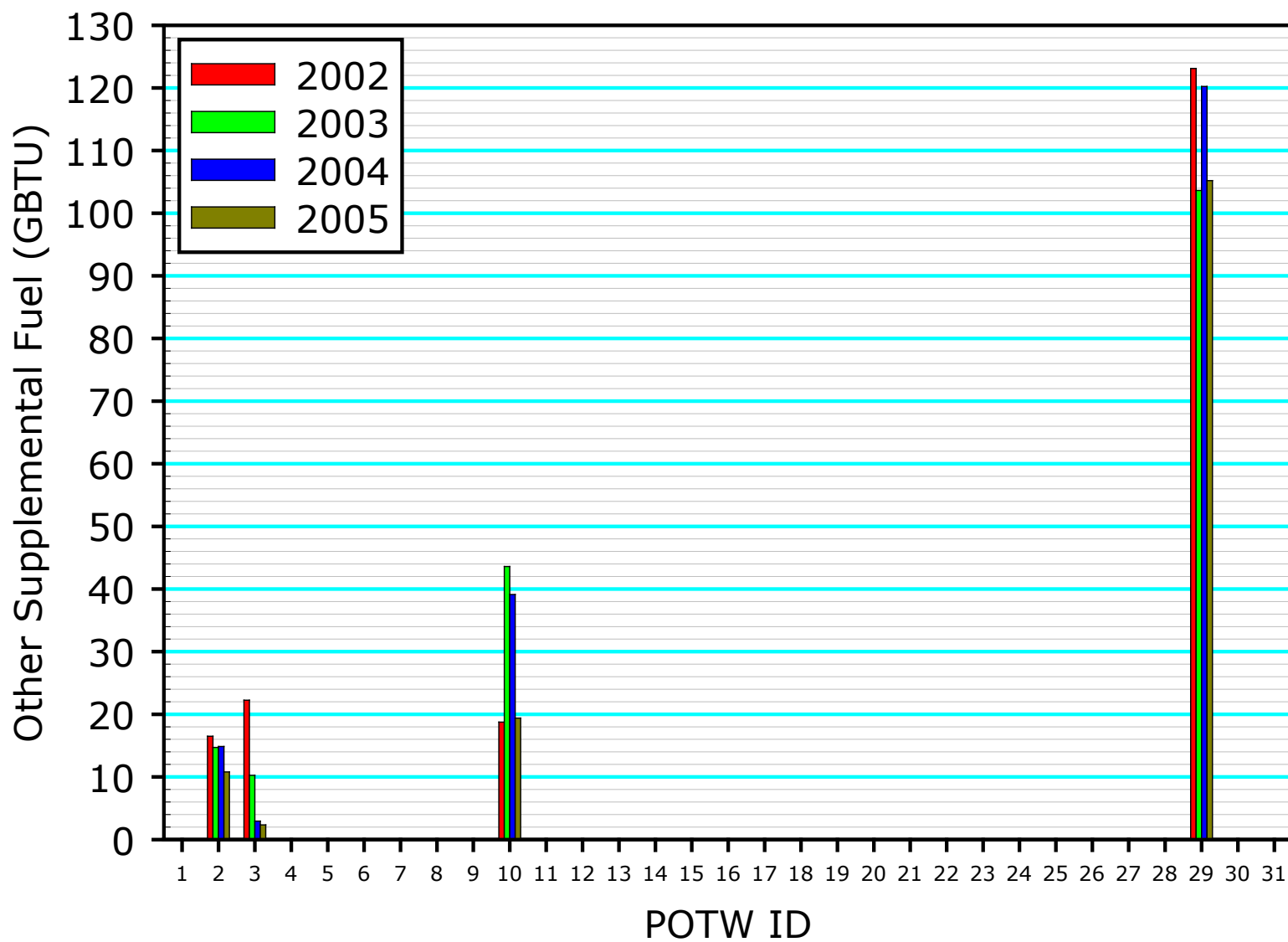


Figure A-8d. Distribution of Supplemental Fuel Oil as a Function of Location.

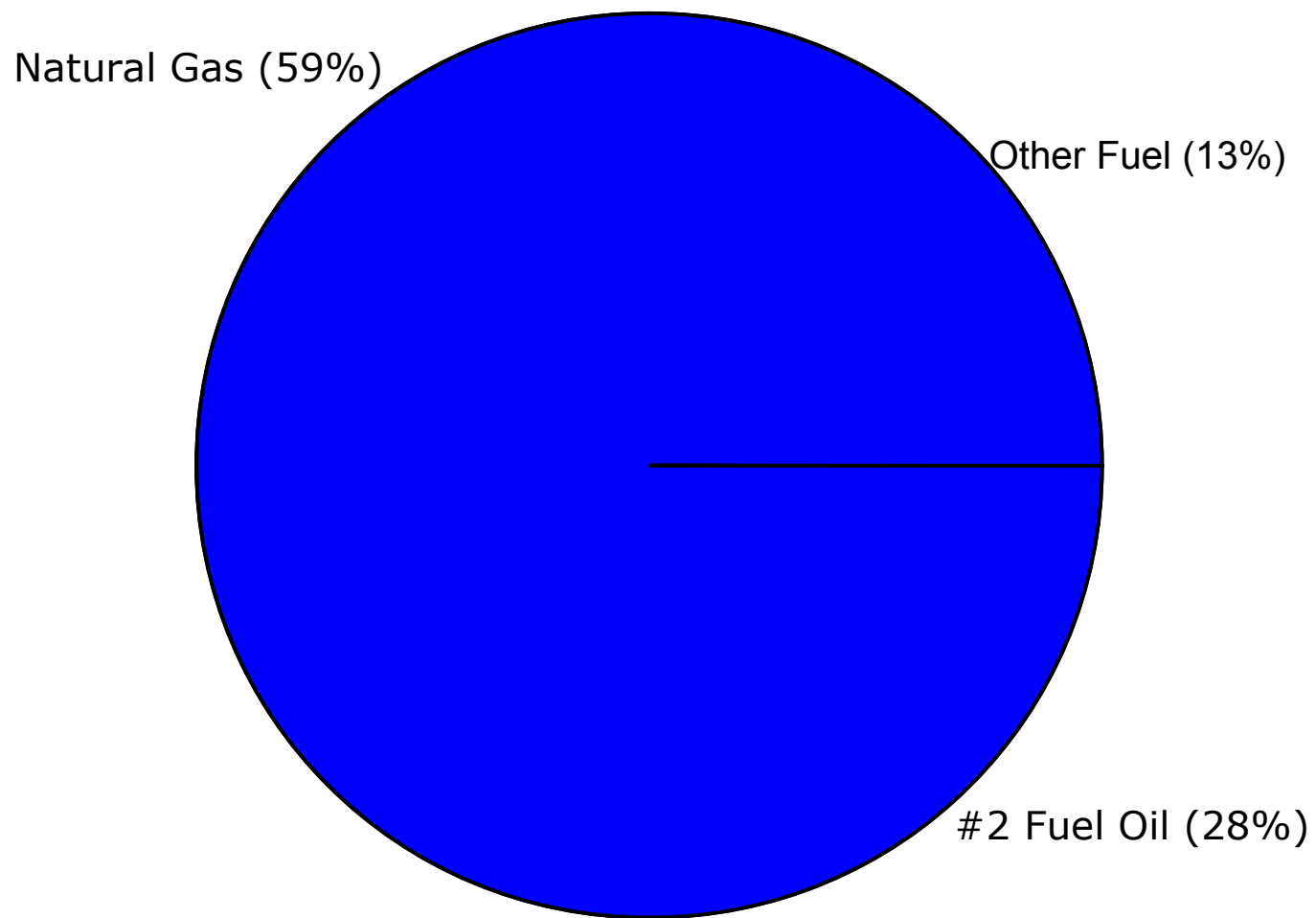


Figure A-8e. Distribution of Supplemental Fuel oil as a Function of Year in BTU. Other Fuel Includes Propane, Landfill Gas, Stoker Coal, and Digester Gas.

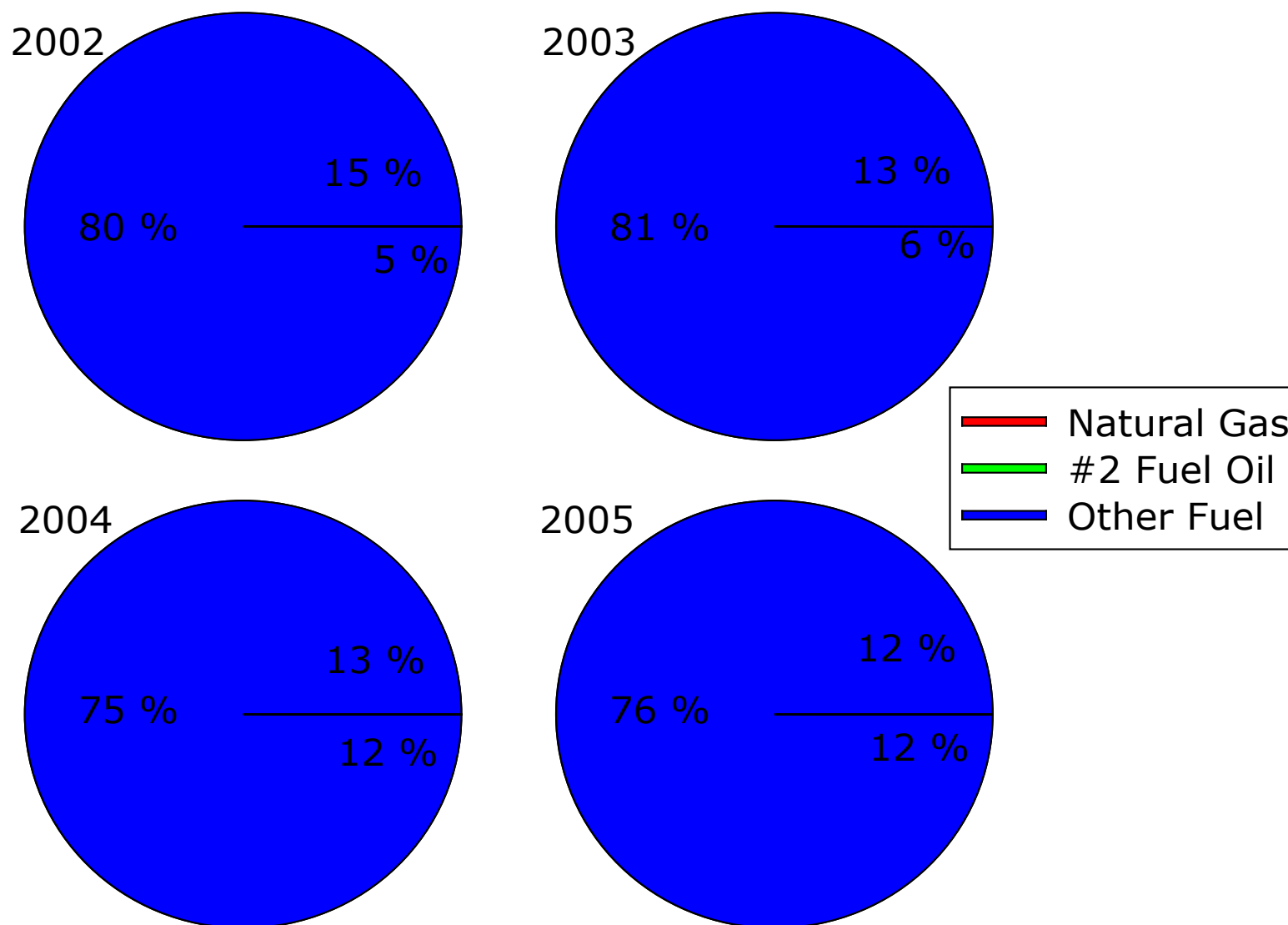


Figure A-9a. Type of Air Pollution Control Device as a Function of Location.

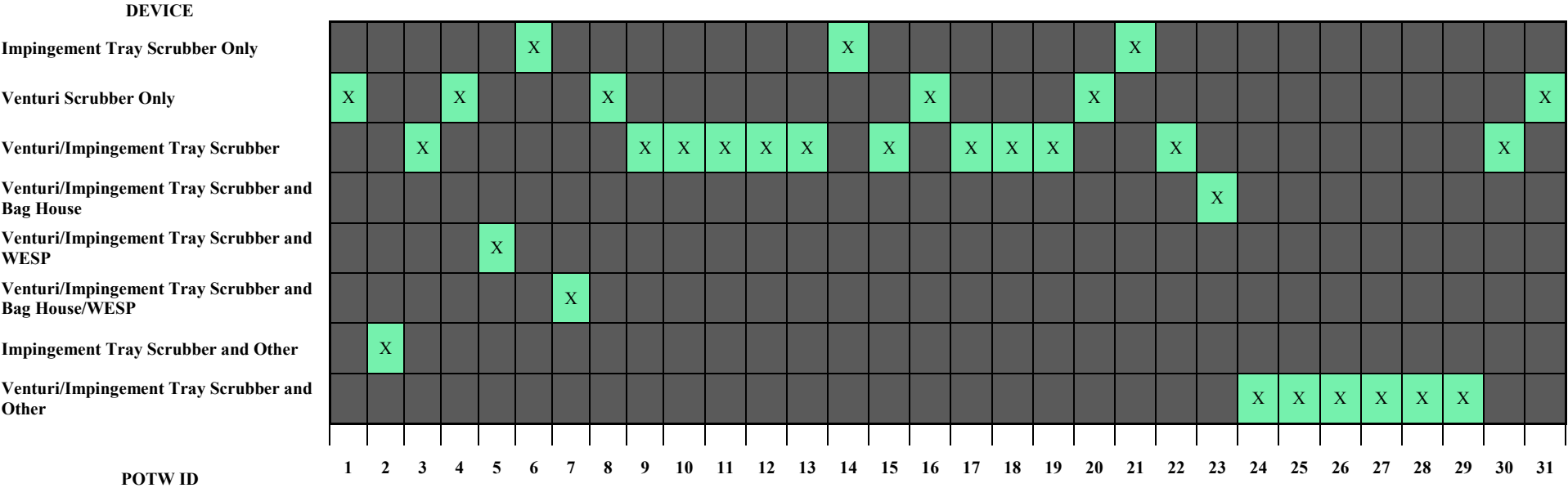


Figure A-9b. Distribution of Air Pollution Control Devices.

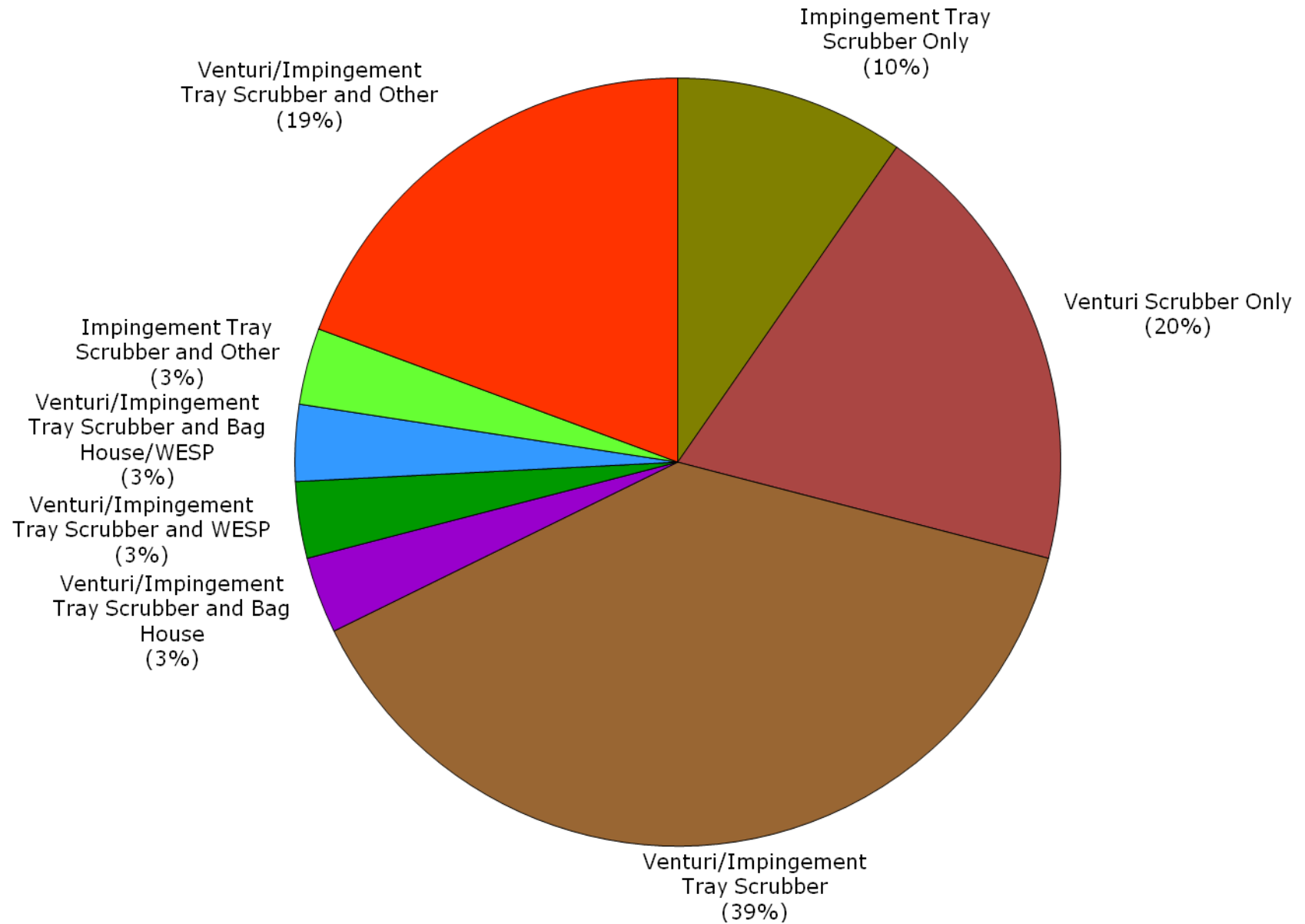


Figure A-9c. Destination of Scrubber Water Effluent.

USAGE																																
	POTW ID	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
		X				X	X	X	X	X	X	X		X	X	X		X	X	X	X			X	X	X	X	X	X	X	X	X
										X			X			X	X	X				X	X									
								X																								
			X									X											X									

Figure A-10. Digestion Methods Used for Biosolids and Ash Prior to Analysis.

Biosolids	
HNO ₃	X
HCl/HNO ₃	X
Other	X

Ash	
HNO ₃	X
HCl/HNO ₃	X
HCl/HNO ₃ /HF	X
Other	X

Figure A-11. Analytical Methods Used for Biosolids, Ash, Influent and Effluent.

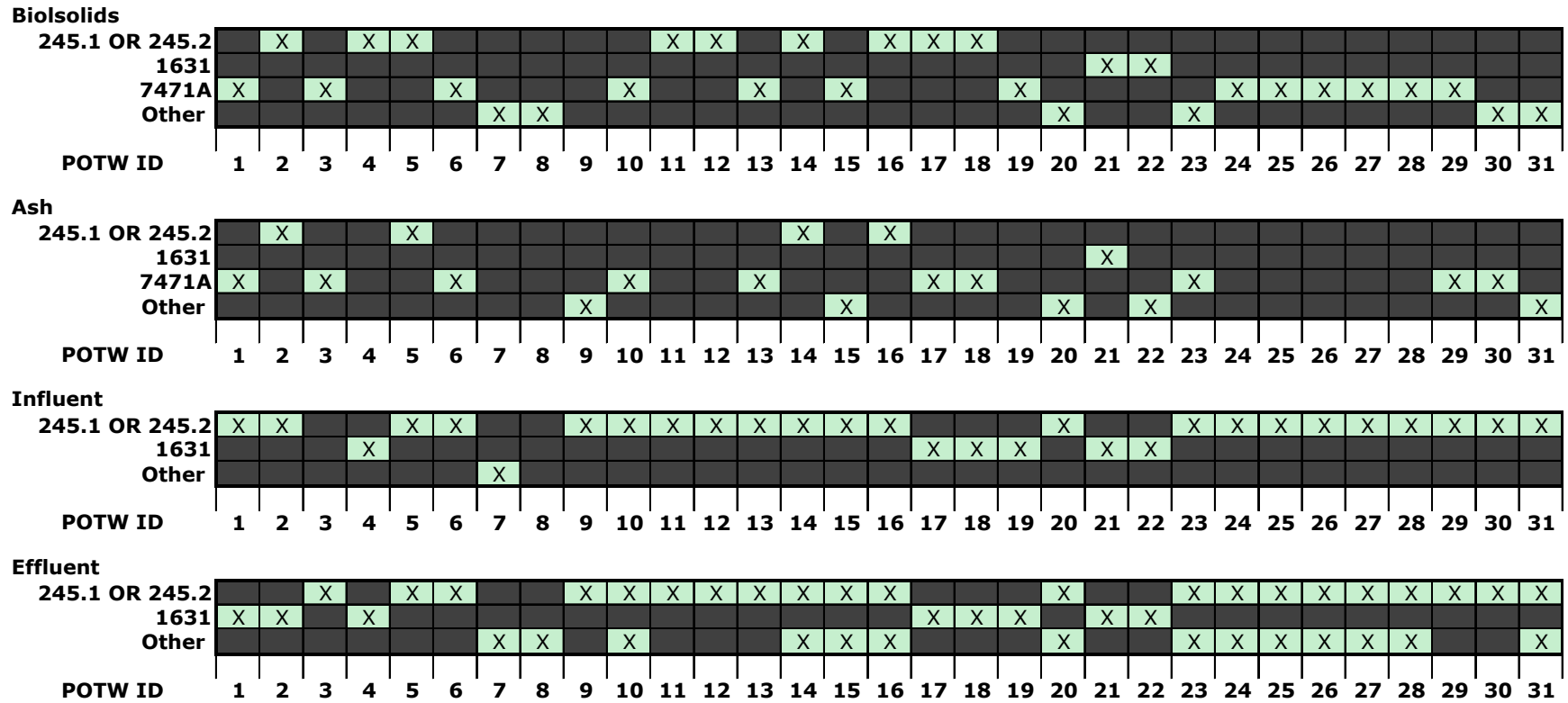


Figure A-12a. Number of Times Per Year that Biosolids are Tested for Hg as a Function of Location.

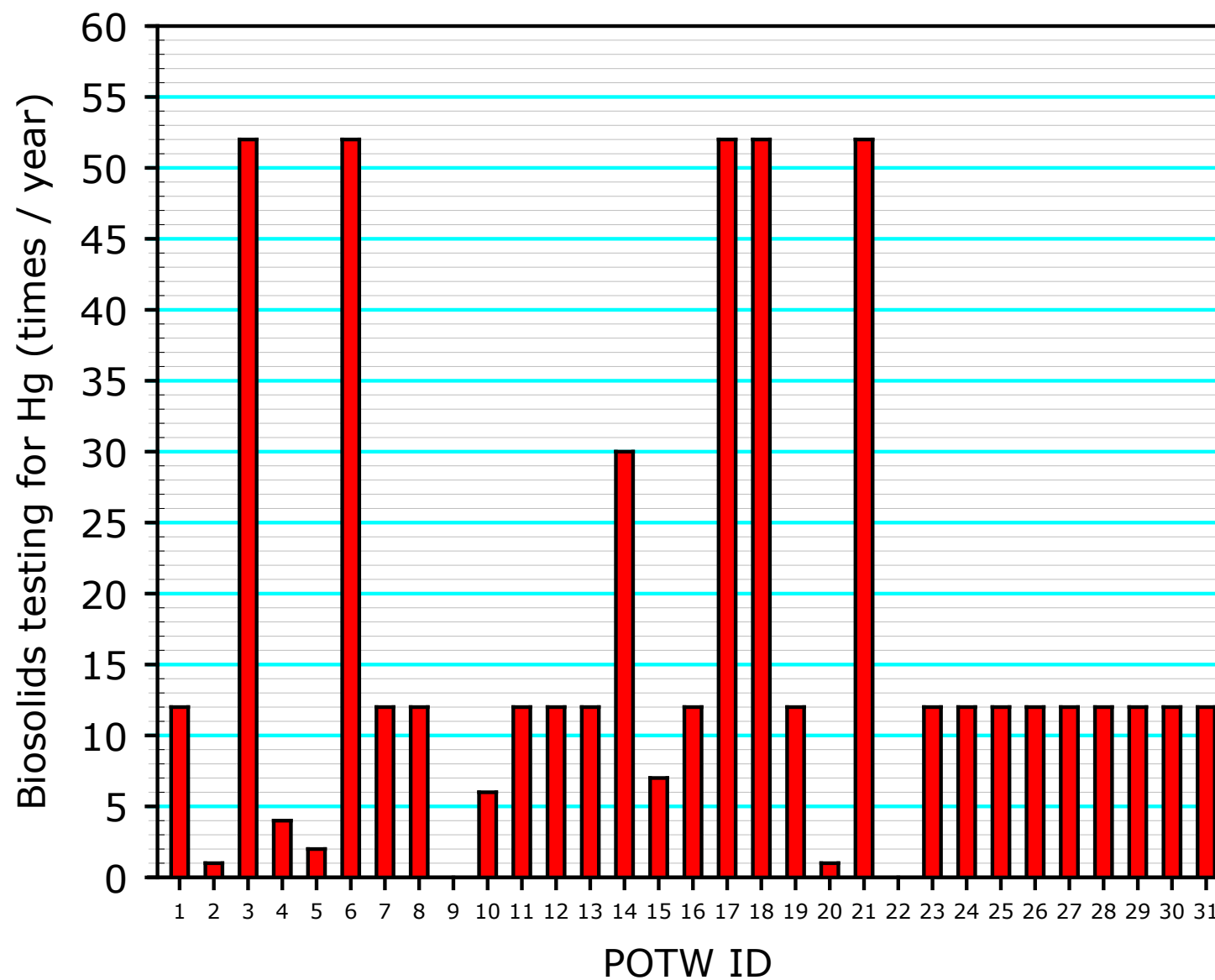


Figure A-12b. Distribution of the Frequency for Testing Biosolids for Hg.

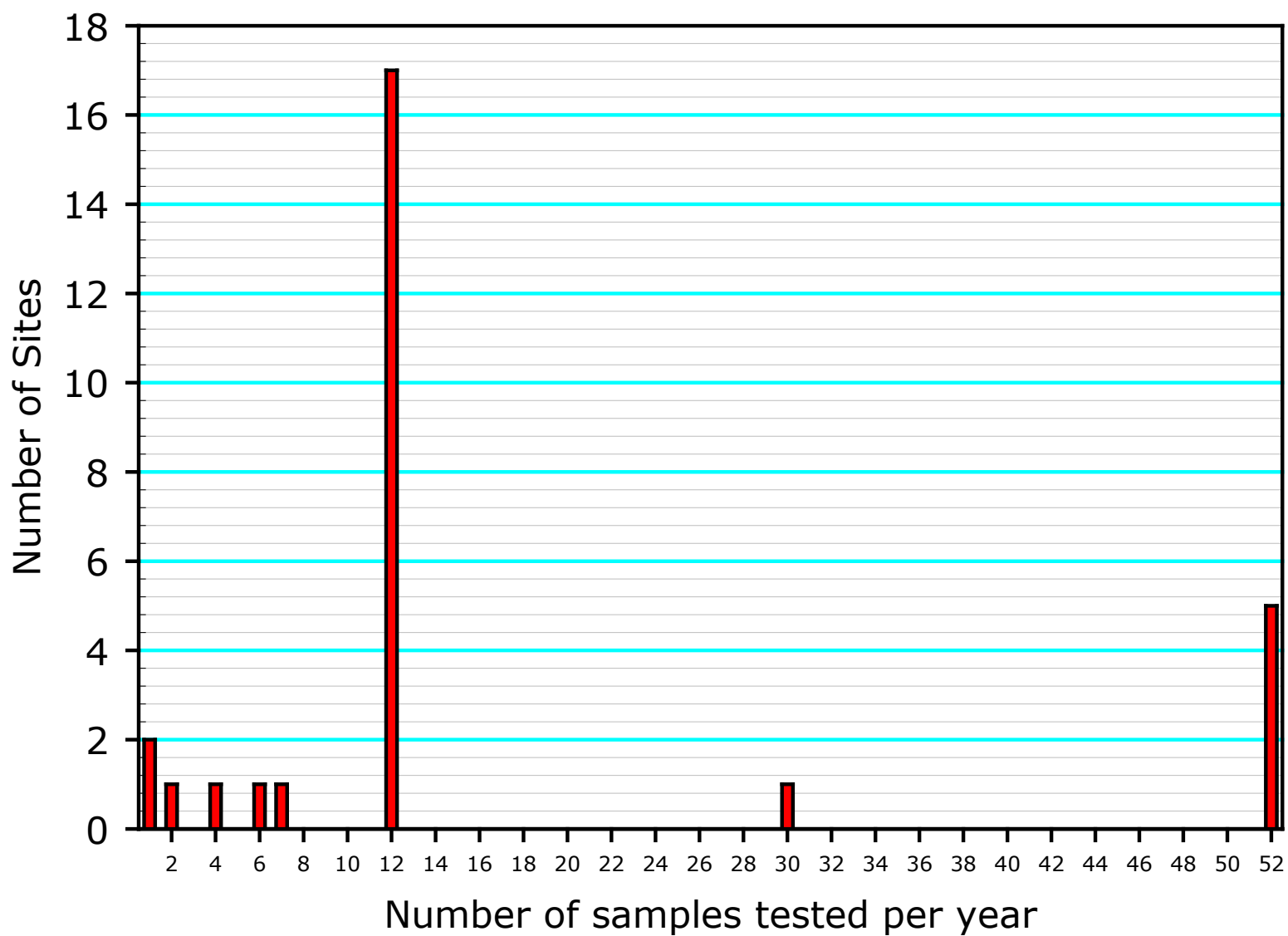


Figure A-12c. Average Concentration of Hg in Biosolids as a Function of POTW and Year.

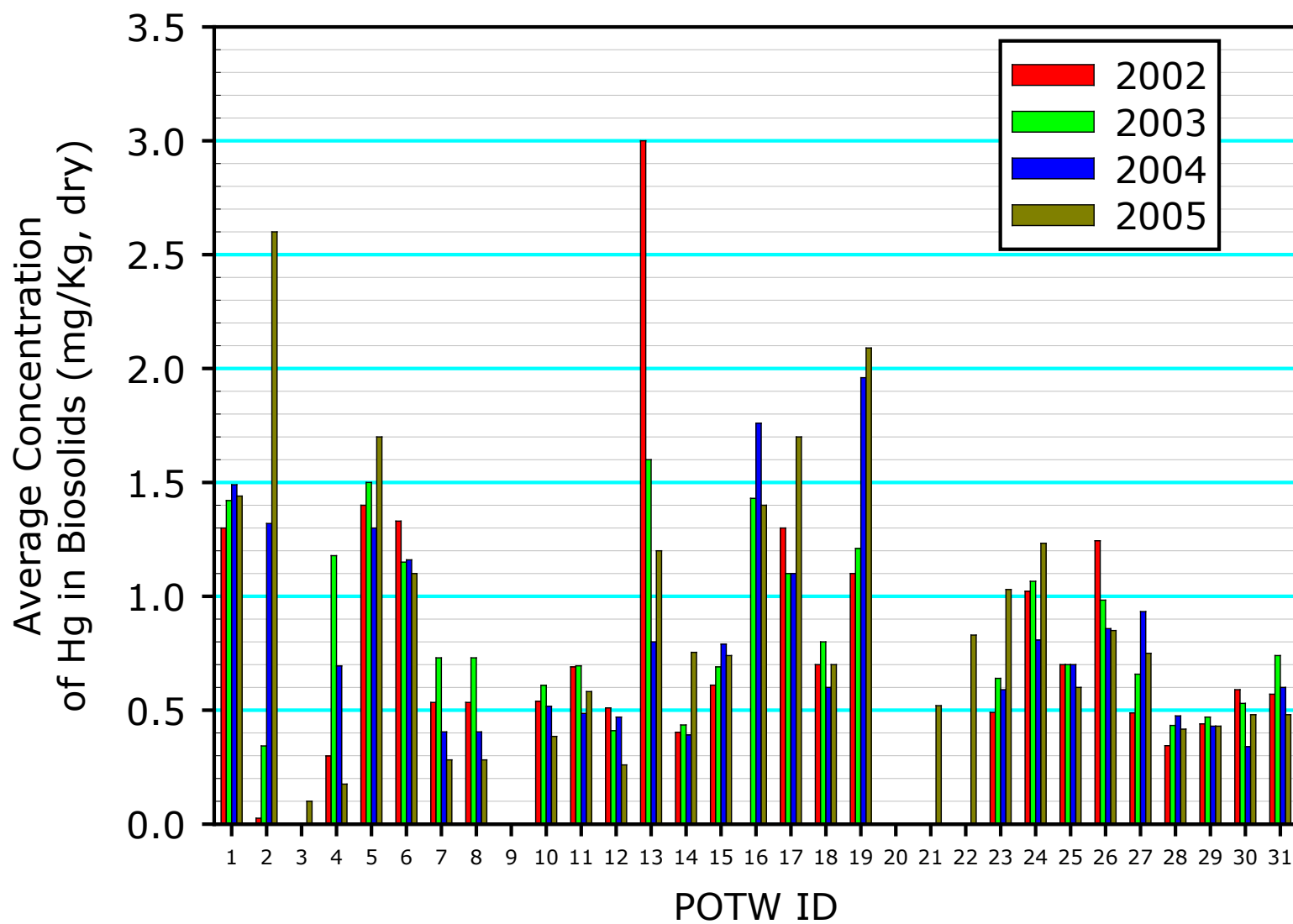


Figure A-12d. Highest Concentration of Hg in Biosolids as a Function of POTW and Year.

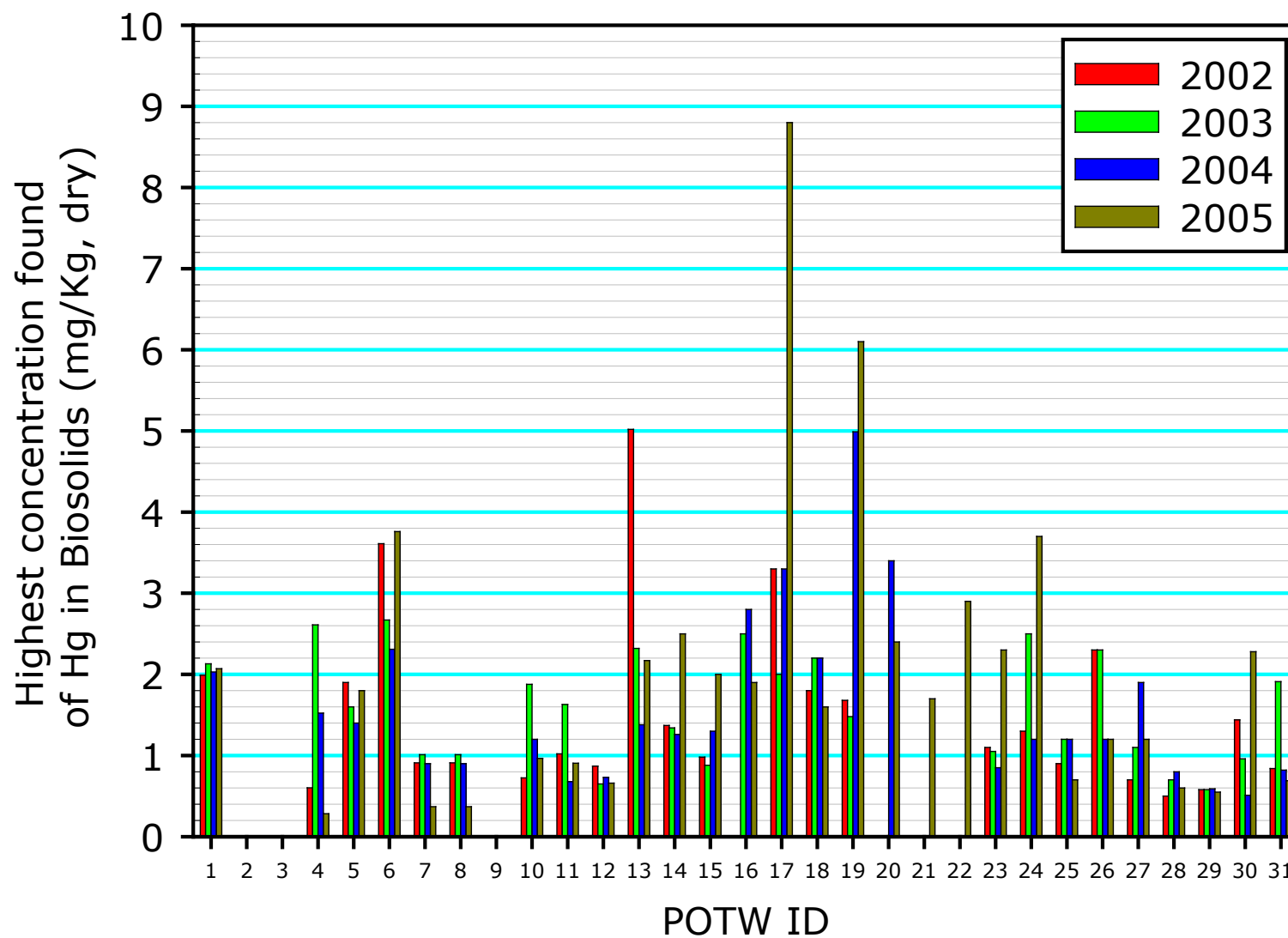


Figure A-13a. Number of Times Per Year That Ash is Tested for Hg as a Function of Location.

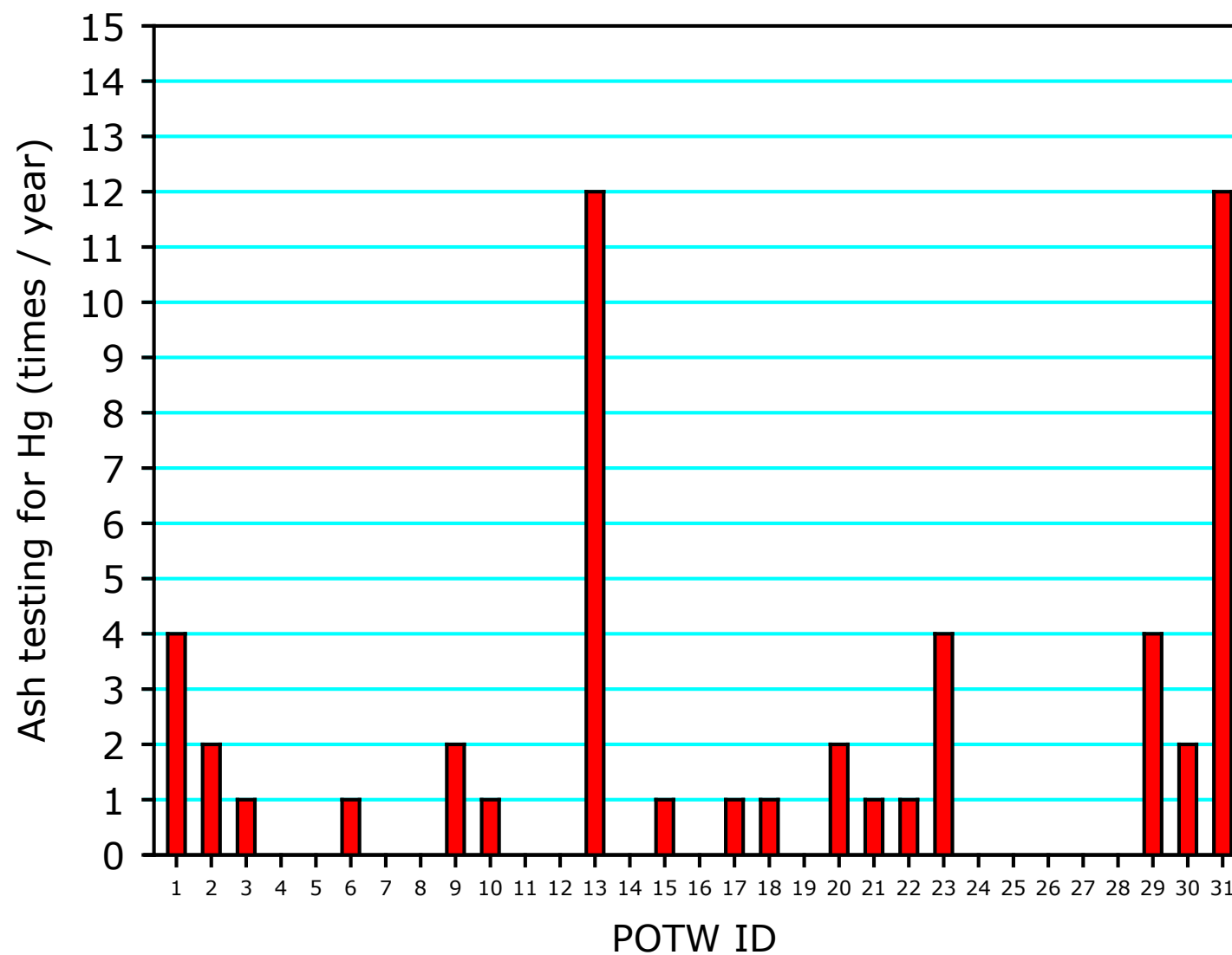


Figure A-13b. Distribution of the Frequency for Testing Ash for Hg.

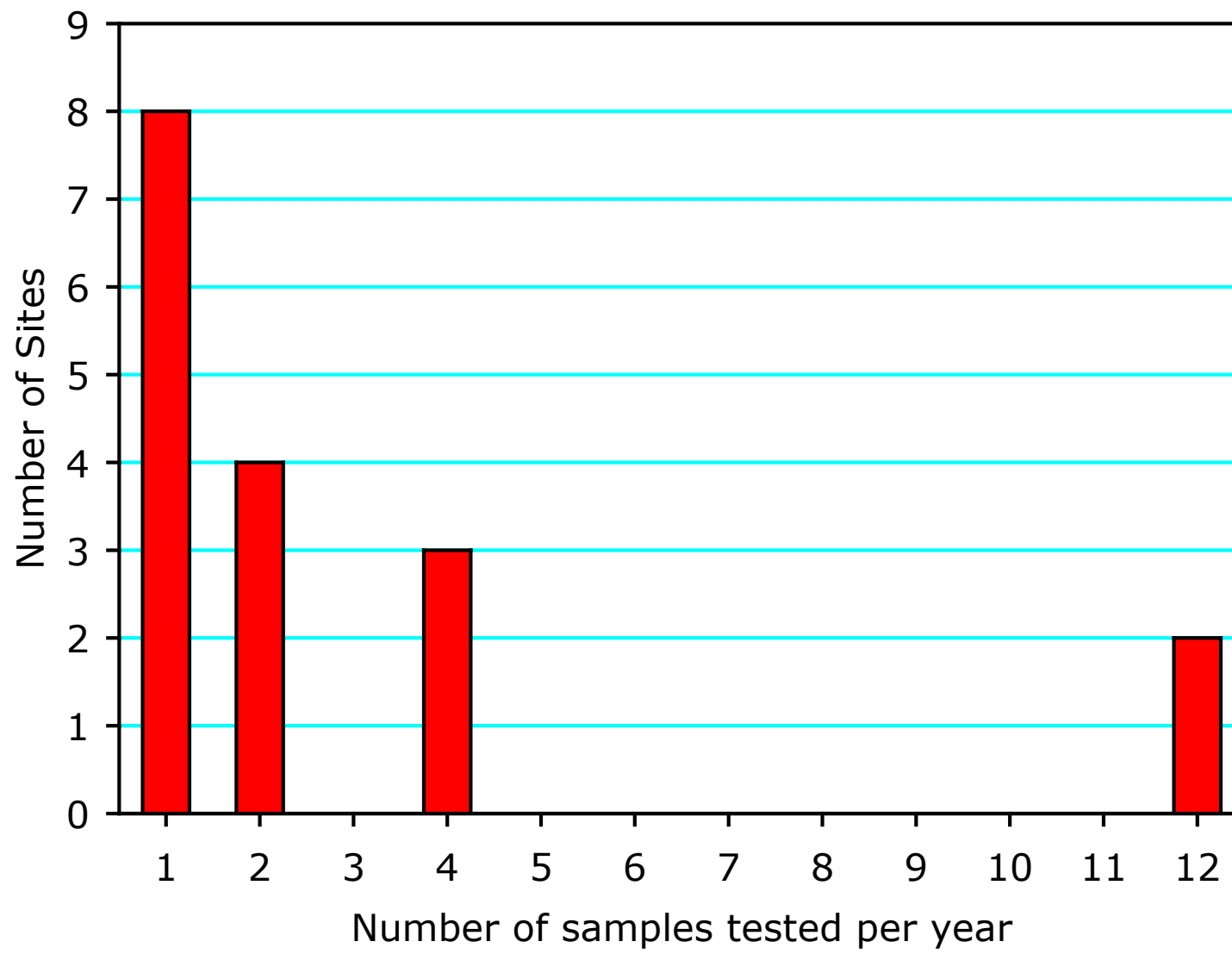


Figure A-13c. Average Concentration of Hg in Ash as a Function of POTW and Year.

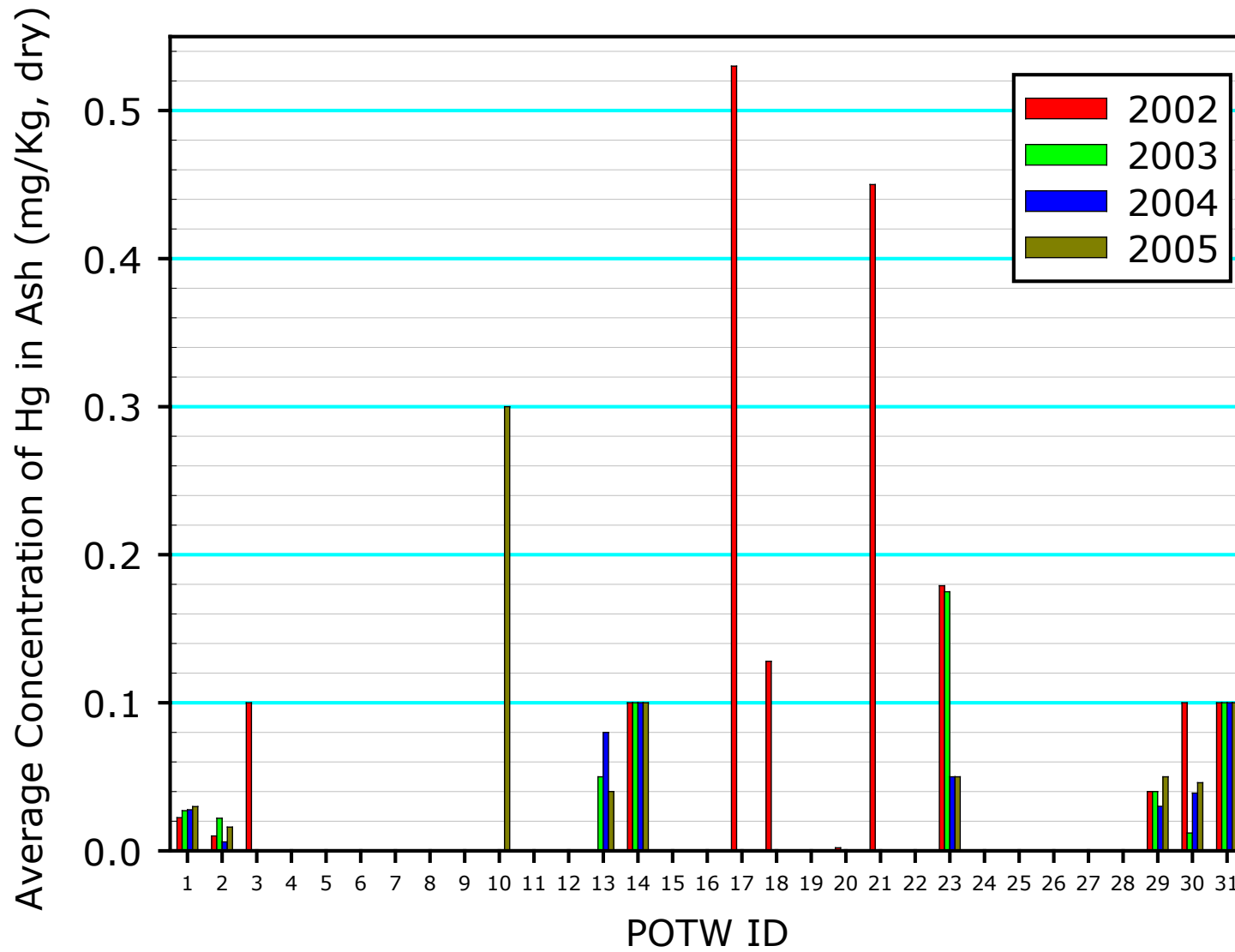


Figure A-14a. Number of Times Per Year that Influent is Tested for Hg as a Function of Location.

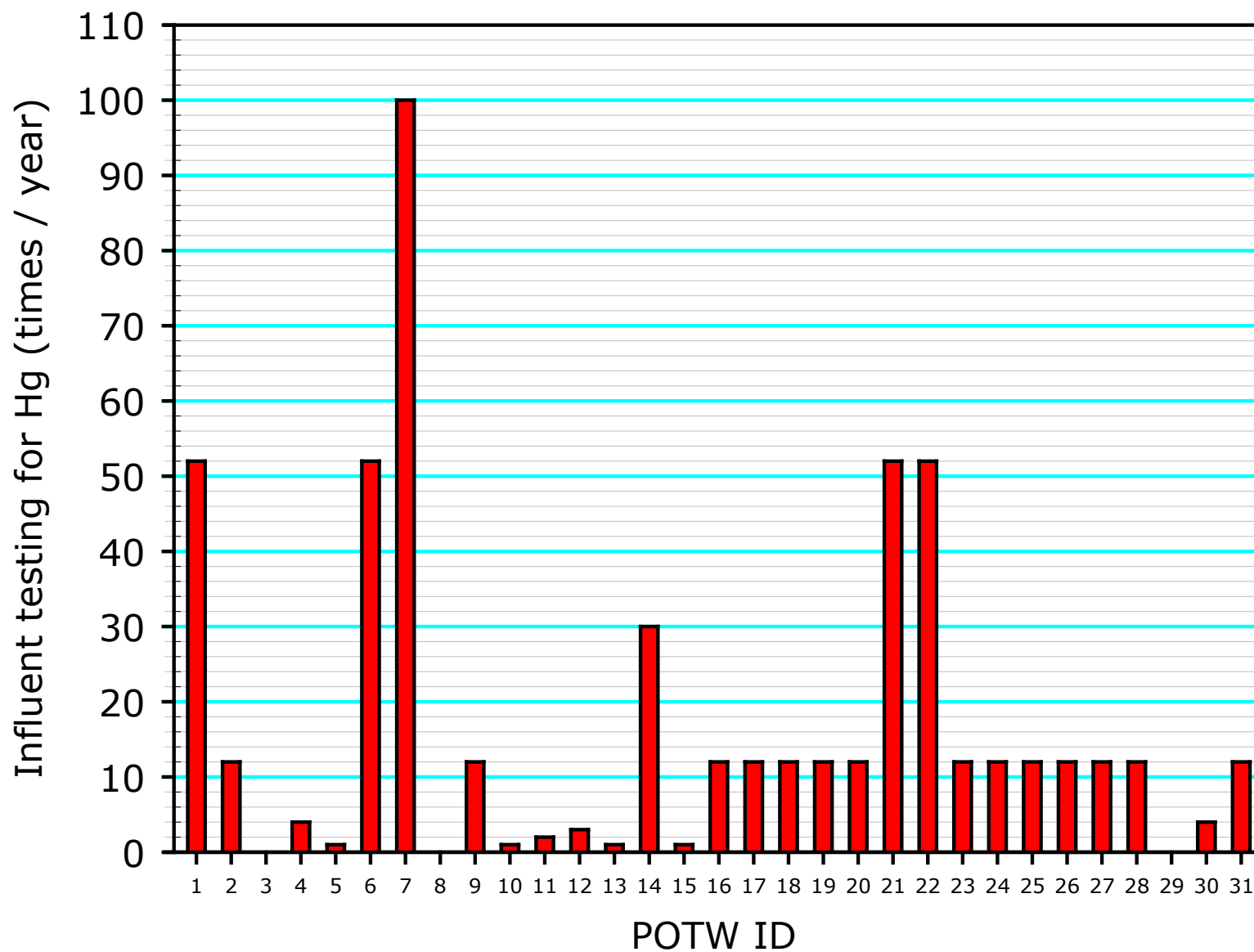


Figure A-14b. Distribution of the Frequency for Testing Influent for Hg.

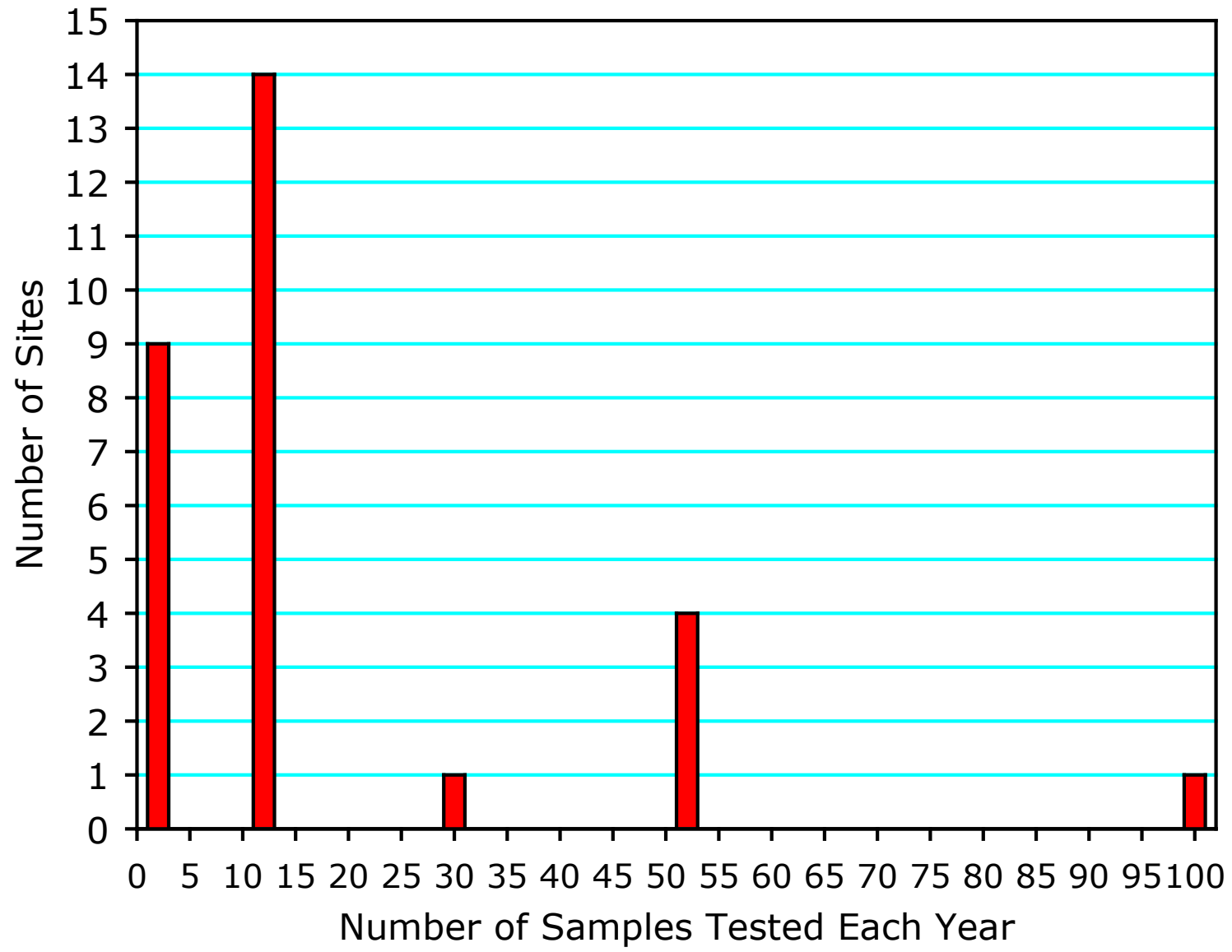


Figure A-14c. Average Concentration of Hg in Influent as a Function of POTW and Year.

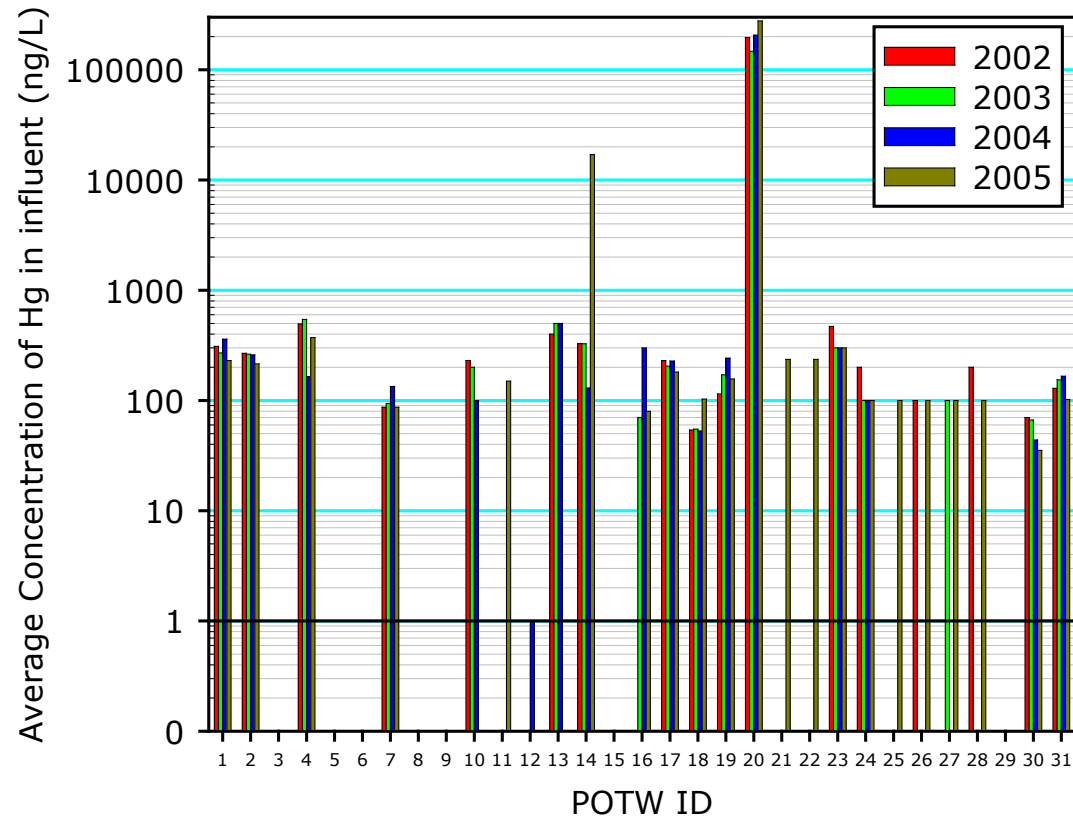


Figure A-14d. Highest Concentration of Hg in Influent as a Function of POTW and Year.

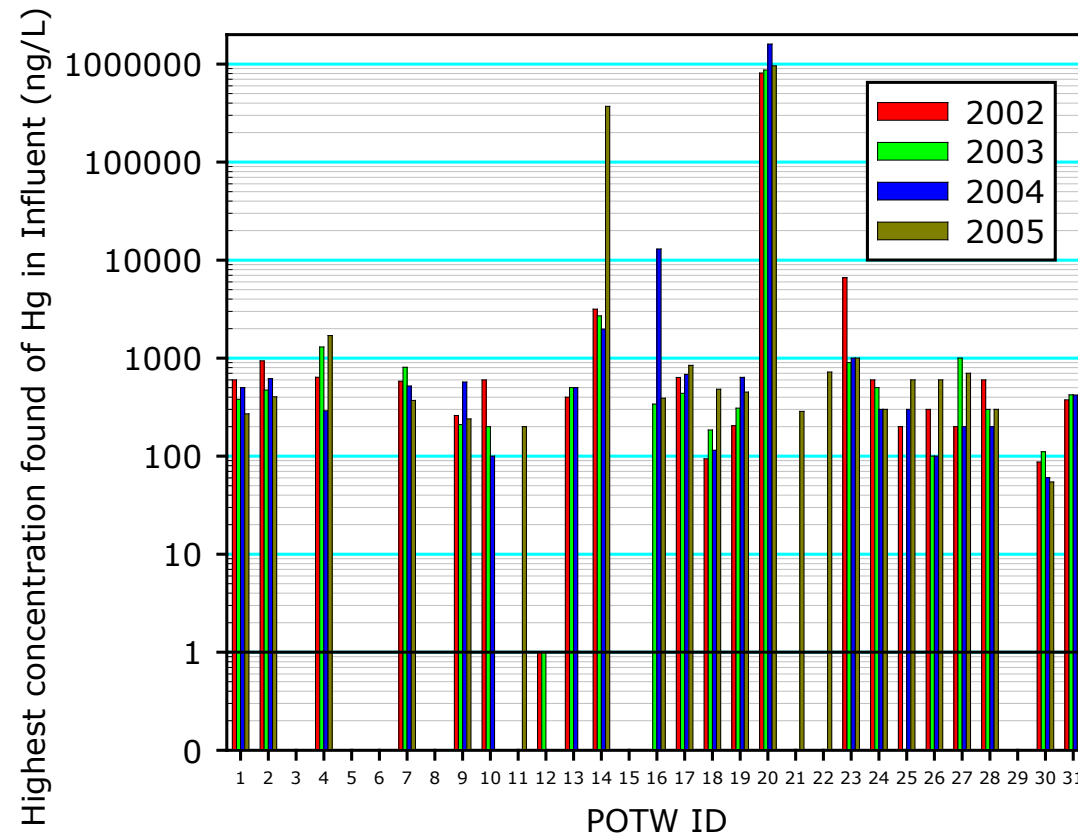


Figure A-15a. Number of Times Per Year That Effluent is Tested for Hg as a Function of Location.

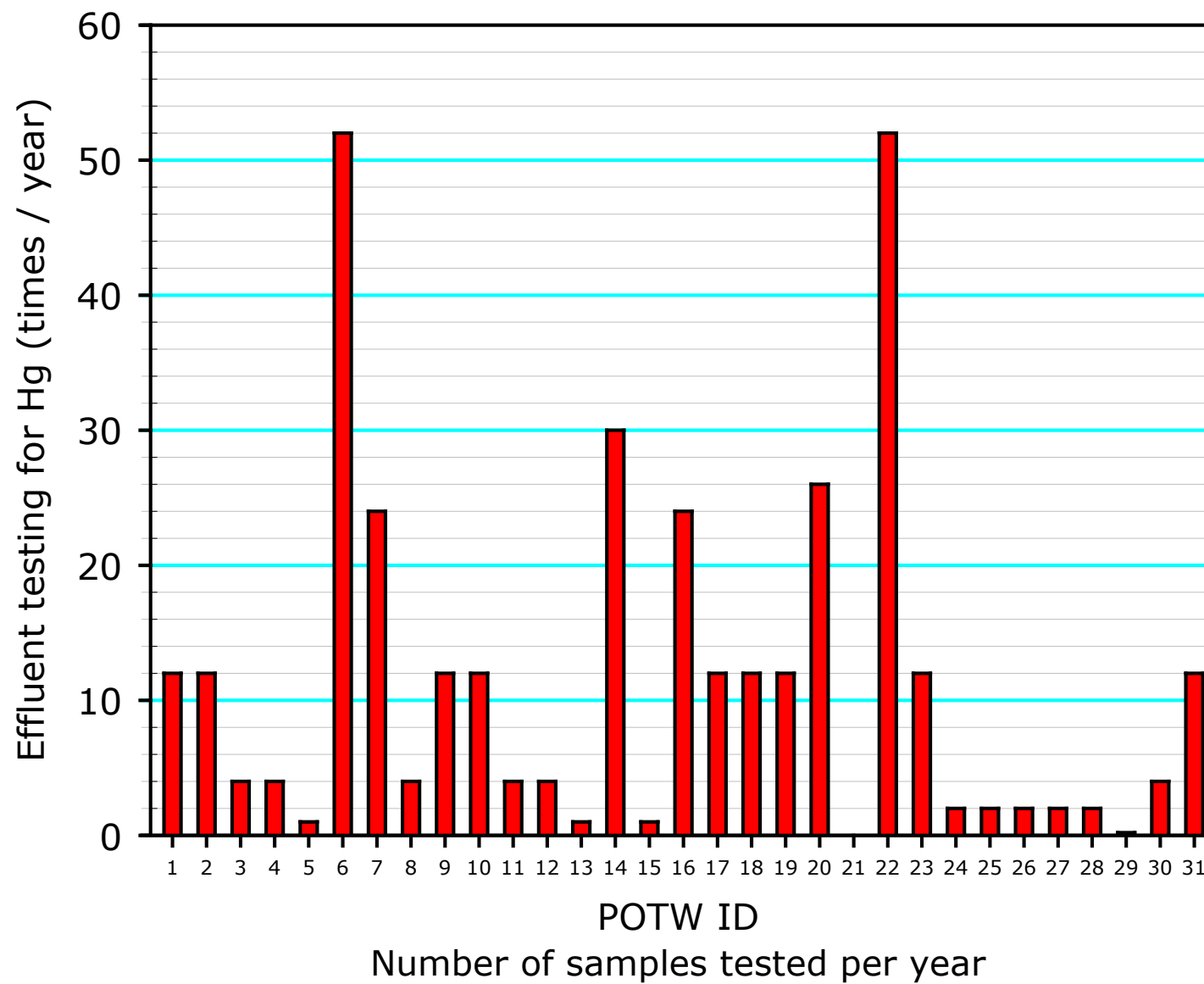


Figure A-15b. Distribution of the Frequency for Testing Effluent for Hg.

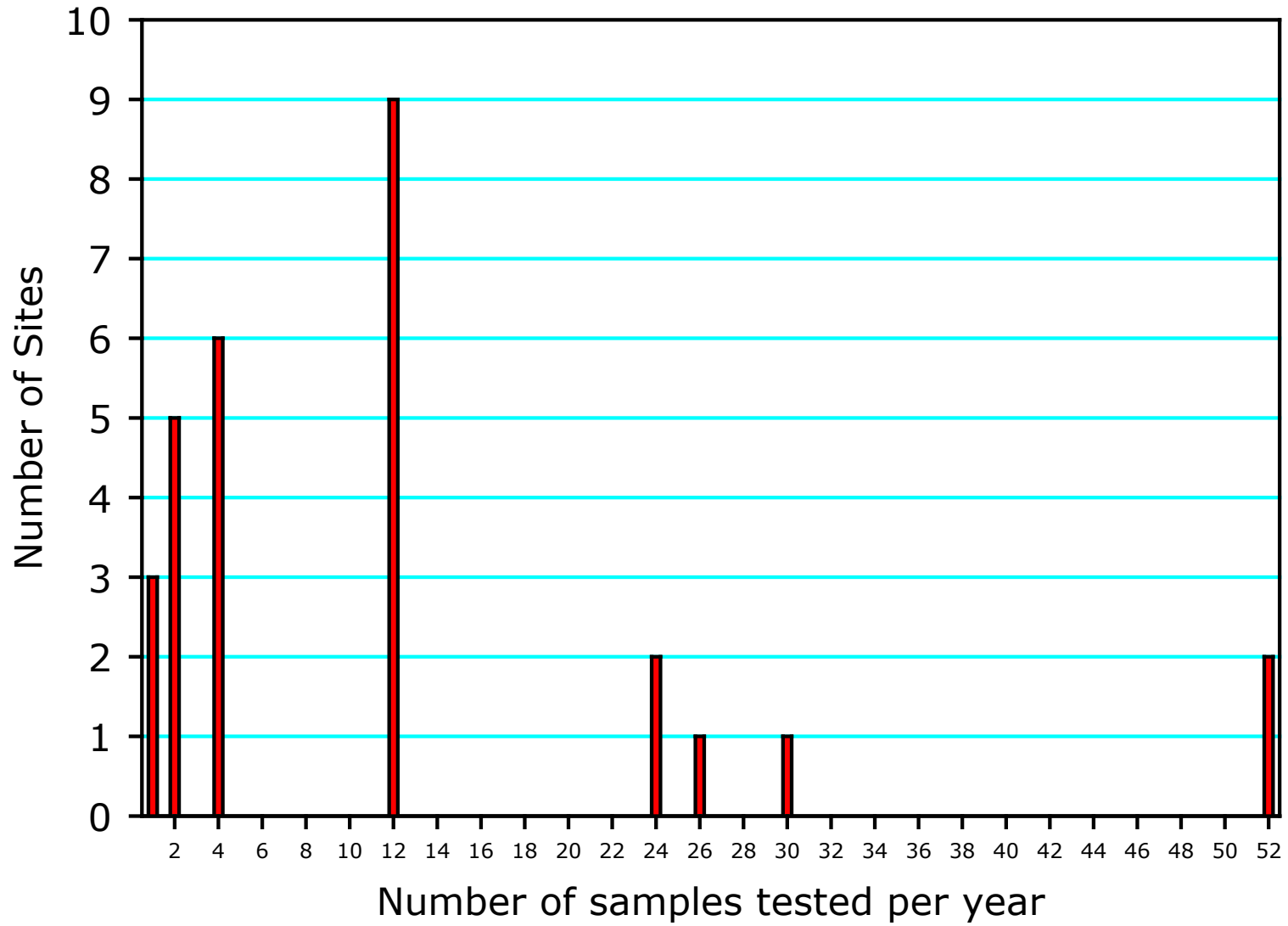


Figure A-15c. Average Concentration of Hg in Effluent as a Function of POTW and Year.

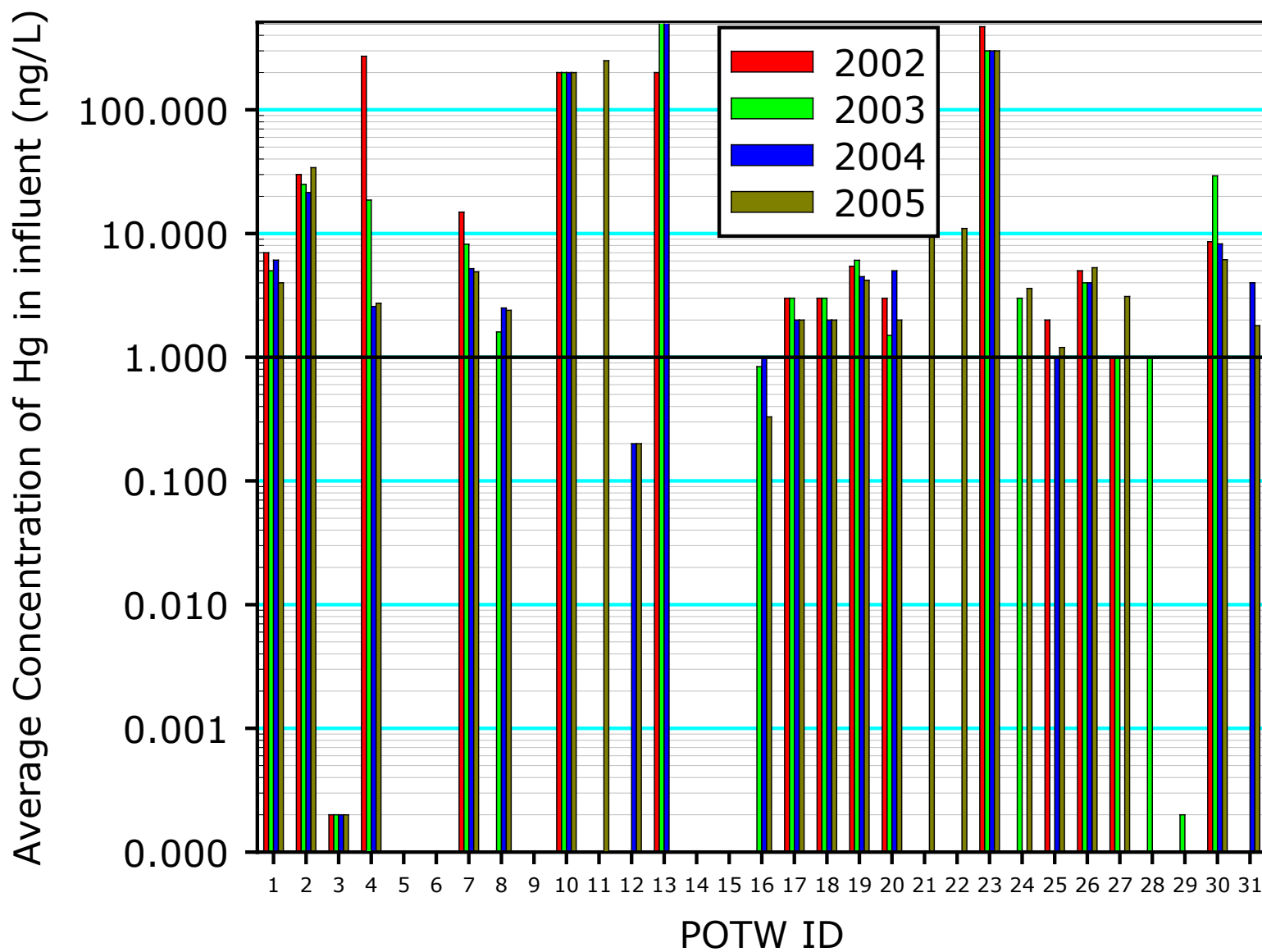


Figure A-15d. Highest Concentration of Hg in Effluent as a Function of POTW and Year.

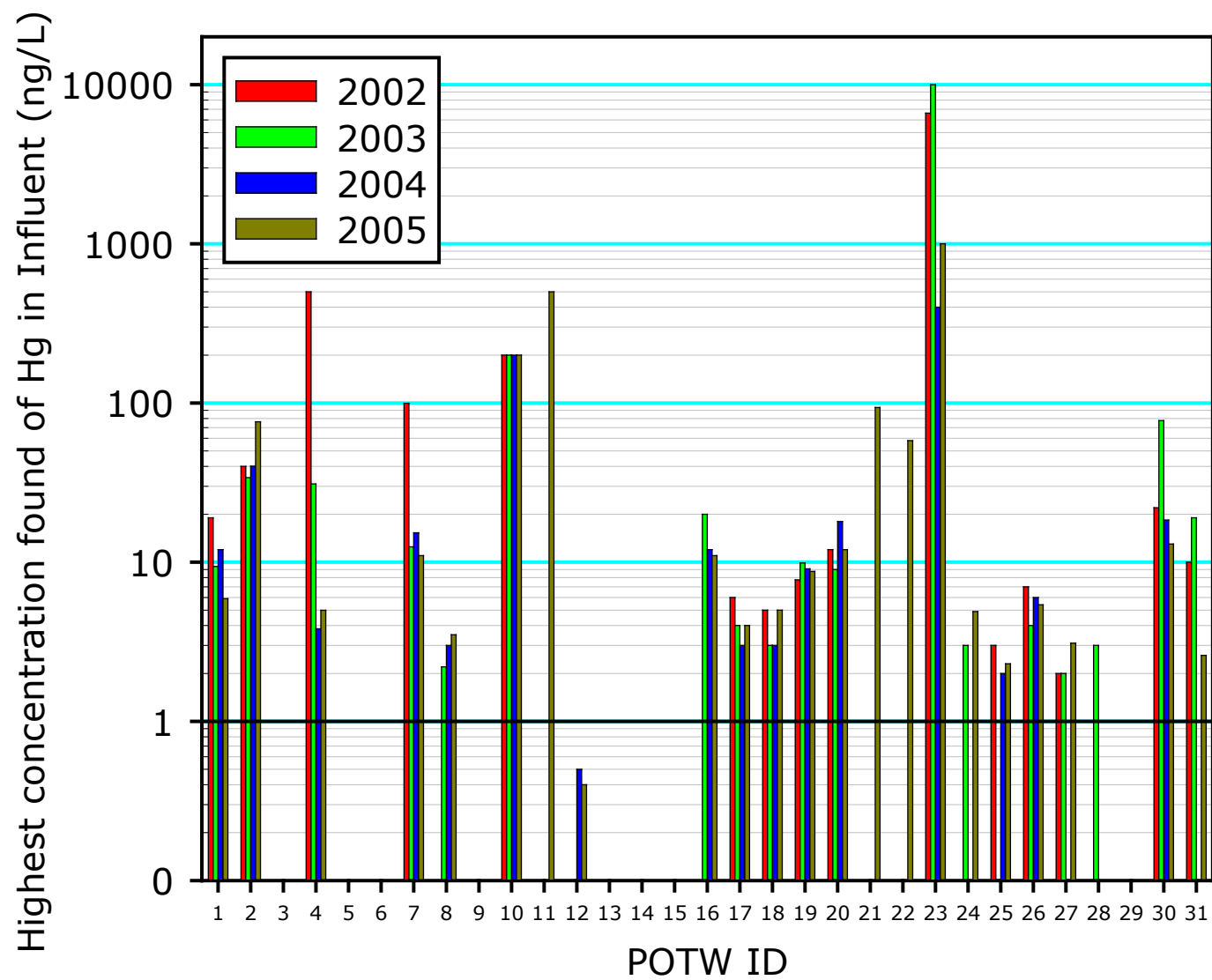


Figure A-16a. Popularity of Emission Test Methods. Other Methods Include CARB 436, EPA Method 101A, and Subsection 3.1 of BIF Methods Manual.

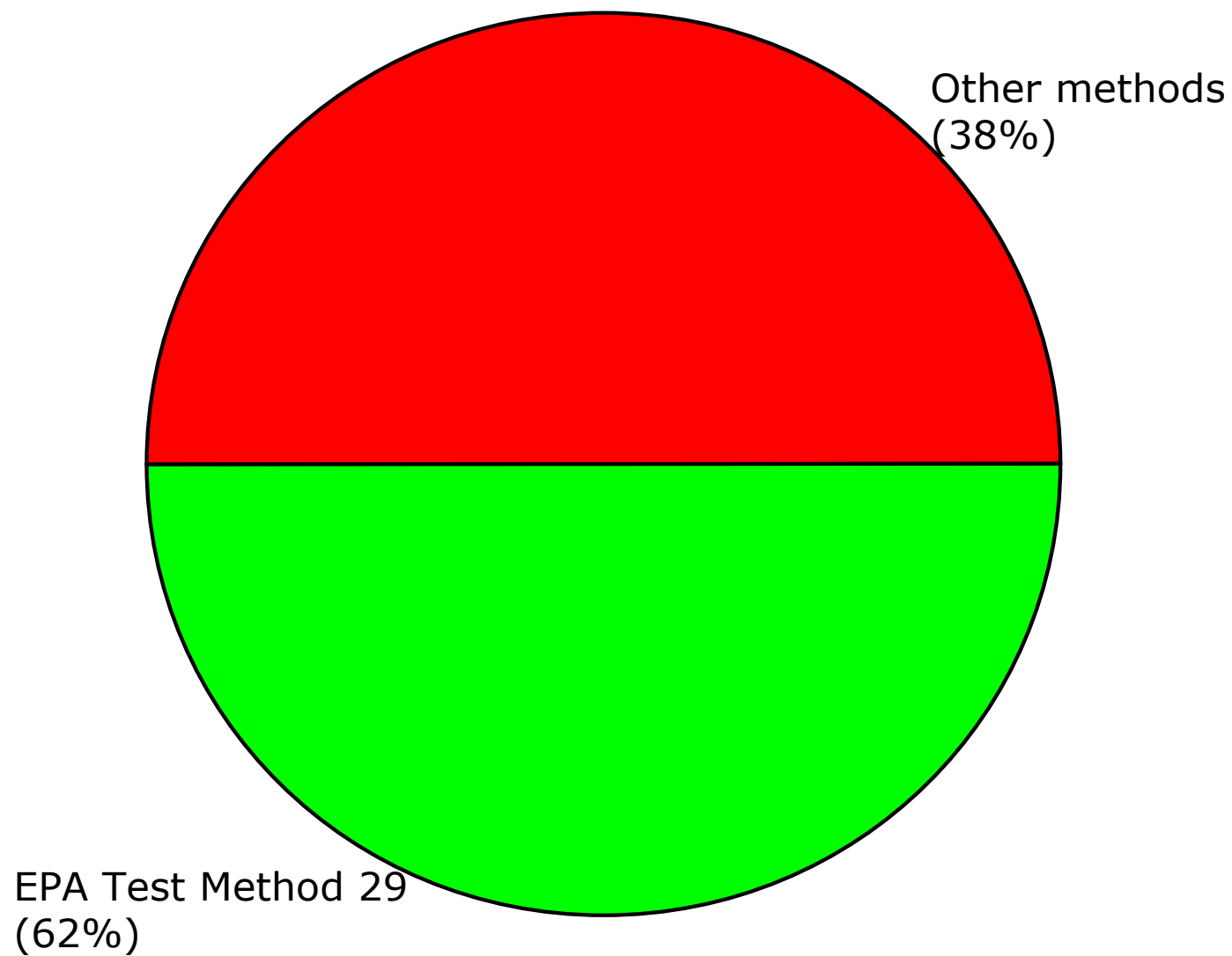


Figure A-16b. Concentration of Hg Measured in Stack Emission Gas as a Function of Year.

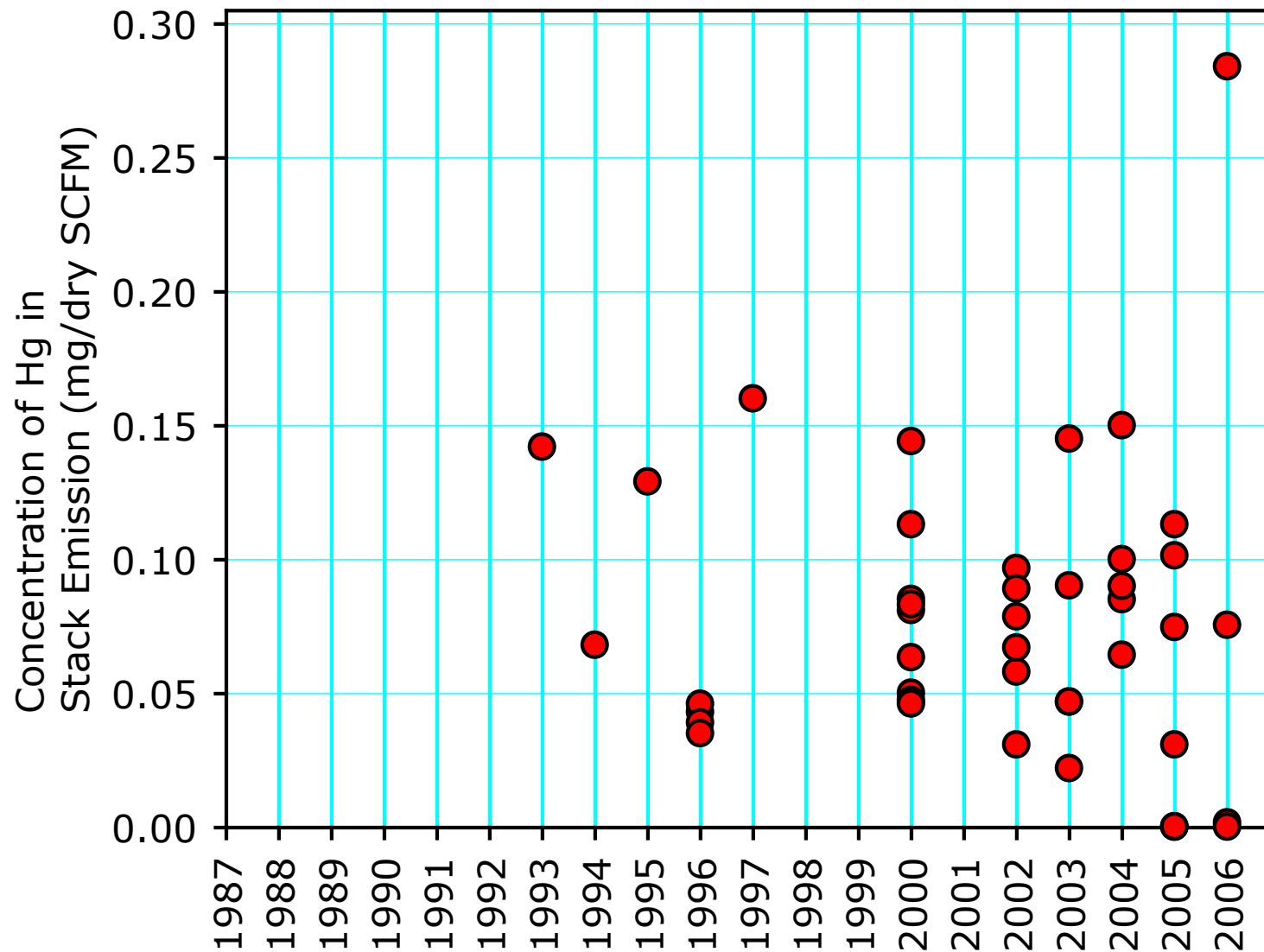
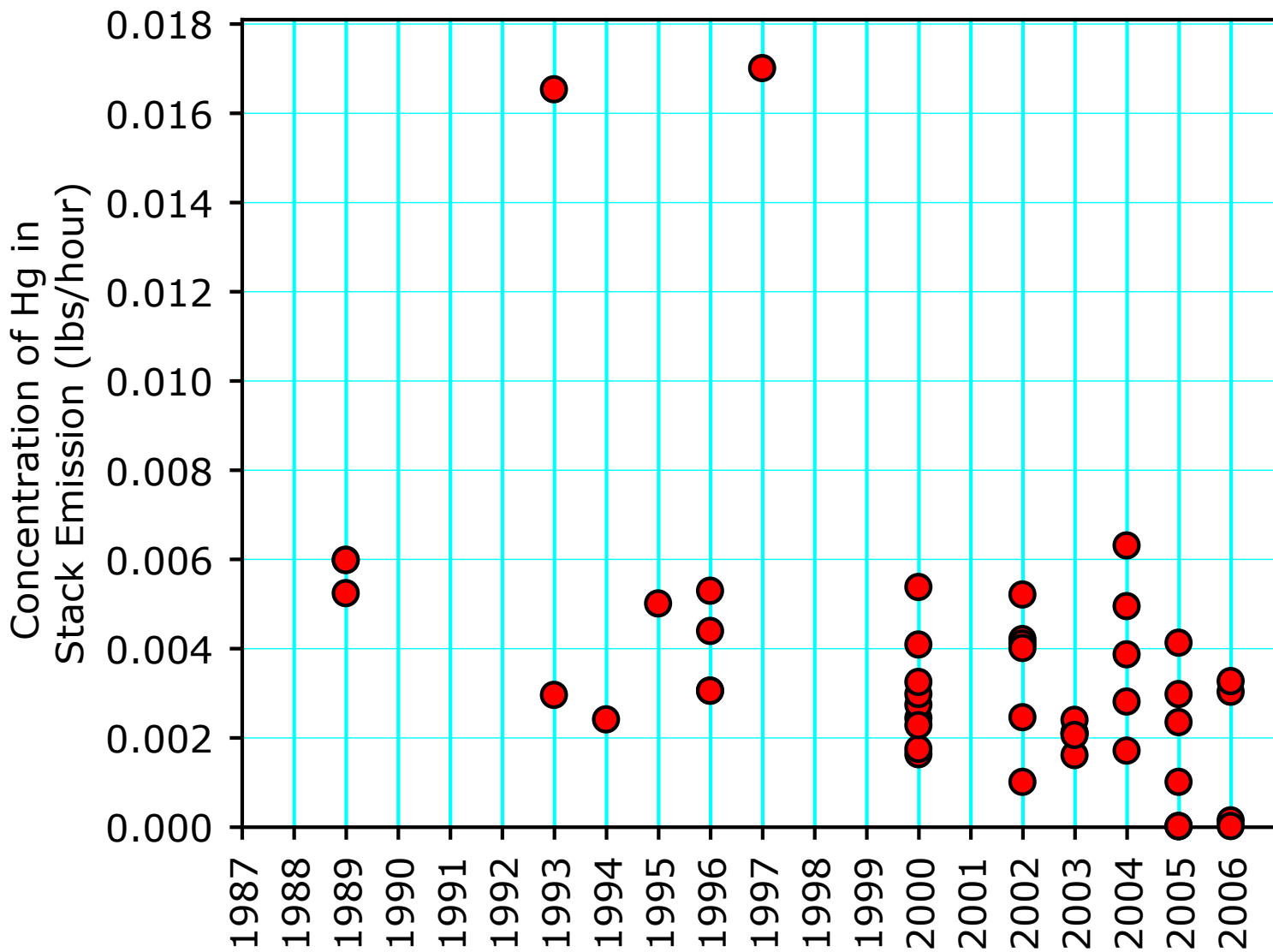


Figure A-16c. Concentration of Hg Measured in Stack Emission Gas as a Function of Year.



Survey Results – Detail

Table A-1. Influent Flow Rates.

POTW ID	Average Daily Flow (MGD)	Average Industrial Loading (% of Average Daily Flow)	Municipal flow (MGD)	Industrial flow (MGD)
1	25.00	17.00	20.75	4.25
2	48.00	0.00	48.00	0.00
3	59.00		59.00	0.00
4	104.00		104.00	0.00
5	41.00	5.00	38.95	2.05
6	22.00	20.00	17.60	4.40
7	190.00	8.20	174.42	15.58
8	24.00	7.20	22.27	1.73
9	10.00	3.00	9.70	0.30
10	40.00	7.00	37.20	2.80
11	100.00	8.80	91.20	8.80
12	125.00	14.00	107.50	17.50
13	10.40	0.00	10.40	0.00
14	90.00	15.00	76.50	13.50
15	39.00	2.00	38.22	0.78
16	93.40	10.00	84.06	9.34
17	120.00	12.00	105.60	14.40
18	25.00	12.00	22.00	3.00
19	30.76	8.00	28.30	2.46
20	77.10	10.00	69.39	7.71
21	125.00	11.70	110.38	14.63
22	33.00	3.90	31.71	1.29
23	225.00	5.00	213.75	11.25
24	12.00	8.00	11.04	0.96
25	14.00	9.00	12.74	1.26
26	20.00	8.00	18.40	1.60
27	29.00	12.00	25.52	3.48
28	15.00	36.00	9.60	5.40
29	42.00	1.00	41.58	0.42
30	27.00	82.50	4.73	22.28
31	30.00	33.00	20.10	9.90

Table A-2a. Biosolids Incinerators, Type and Dewatering Devices.



	Type and Number of Biosolids Incinerators				Type of Biosolids						Type of Biosolids Dewatering Devices		
POTW ID	Multiple Hearth	Fluidized Bed	Other		Chemically Conditioned	Thermally Conditioned	Digested	Other	Other description		Belt Filter Presses	Centrifuges	Plate and Frame Presses
1	2.00				Yes						Yes		
2	2.00							Yes	No Conditioning			Yes	
3	2.00				Yes		Yes		Receive Biosolids from Other POTWs			Yes	
4	4.00				Yes						Yes		
5	2.00				Yes						Yes		
6	10.00				Yes						Yes		
7		3.00			Yes				Ended Nov. 2004			Yes	
8	2.00											Yes	
9		1.00				Yes					Yes		
10		1.00			Yes	Yes					Yes		
11	4.00				Yes						Yes		
12	6.00				Yes						Yes		
13	2.00				Yes						Yes		
14	2.00							Yes	Raw Primary and Secondary Sludge			Yes	
15		3.00			Yes						Yes		
16	2.00				Yes							Yes	
17	4.00				Yes	Yes						Yes	
18	2.00				Yes							Yes	
19	2.00				Yes						Yes		
20	2.00						Yes					Yes	
21	6.00						Yes					Yes	
22	1.00	1.00			Yes						Yes		
23	1.00	2.00						Yes	Waste Activated			Yes	
24	2.00				Yes			Yes	Foreign Biosolids received are digested			Yes	
25	2.00				Yes			Yes	foreign biosolids received are digested			Yes	
26	2.00				Yes							Yes	
27	2.00				Yes			Yes	foreign biosolids received are digested			Yes	
28	2.00				Yes							Yes	
29	6.00				Yes							Yes	Yes
30					Yes			Yes	Dewatered			Yes	
31	2.00				Yes						Yes		

Table A-2b Mass of Biosolids Incinerated Per Year and the Percentage Solids.

POTW ID	Biosolids Incinerated							
	2002		2003		2004		2005	
	US Wet Tons (per Year)	Average % Solids (per Year)	US Wet Tons (per Year)	Average % Solids (per Year)	US Wet Tons (per Year)	Average % Solids (per Year)	US Wet Tons (per Year)	Average % Solids (per Year)
1	23287	29	27338	27	30915	27	31904	27
2	72463	23	69671	23	66017	23	70237	23
3	66478	29	84945	28	88543	27	88952	28
4	215050	25	215951	25	210600	25	207361	24
5	74983	22	57172	22	51430	23	51877	22
6	26476	19	30798	18	31249	18	32123	18
7	224000	32	248000	31	255000	31	278000	30
8	38000	28	36500	28	39500	28	35000	28
9	3351	39	4387	38	4303	41	7614	38
10	413	41	5650	43	8039	42	4676	43
11	65925	30	69866	30	65085	29	53518	29
12	147763	24	142615	23	151766	25	137269	24
13	44500	19	43600	19	52200	19	49900	19
14	23980	29	25341	30	26046	30	20064	29
15	27790	25	28733	24	31817	24	31643	24
16			88641	23	63489	23	61817	25
17	71024	48	75347	47	75503	47	75558	47
18	15915	30	16457	31	16441	31	16029	32
19	34652	21	32602	24	32299	23	29450	24
20	74770	16	83537	17	85404	19	53907	23
21							105683	27
22							24003	20
23	18584	22	17218	27	12800	35	11612	32
24	3130		3168		3581		3892	20
25	6851		7387		8312		8113	20
26	5240		5595		7098		6326	20
27	6732		8408		7193		8419	20
28	6555		7034		7036		6801	20
29	57944	29	57565	29	56583	29	58824	29
30	9007	30	12013	28	13880	26	15760	25
31	49571	24	49484	25	48504	25	38237	25

Table A-3. Supplemental Fuel Used, Reported on a Giga British Thermal Unit Basis.

POTW ID	Supplemental Fuel Used (GBTU)											
	Natural Gas				Fuel Oil				Other			
	2002	2003	2004	2005	2002	2003	2004	2005	2002	2003	2004	2005
1	0.71	0.72	0.72	0.70								
2	1.84	2.56	7.04	10.79					16.50	14.71	14.87	10.79
3	56.10	52.75	44.62	37.50					22.25	10.26	2.95	2.34
4	0.94	1.02	1.09									
5	0.03	0.04	0.04	0.04	19.46	11.94	7.37	9.34				
6	59.04	82.08	32.10	79.63								
7	234.95	417.89	462.93	88.13								
8						19.59	31.47	0.02				
9					3.09	2.56	1.46	3.93				
10									18.75	43.60	39.13	19.40
11	84.60	77.70	59.70	52.40								
12	17.99	14.45	14.27	17.36								
13	0.16	0.16	0.17	0.18								
14	0.16	0.13	0.13	0.10								
15					36.85	36.65	38.04	36.33				
16	0.04	0.07	0.06	0.04								
17	93.06	100.89	80.10	69.37								
18	68.53	68.58	66.48	63.19								
19	28.95	15.63	23.37	20.11								
20	0.13	0.13	0.12	0.06					0.29	0.18	0.29	0.21
21				154.93								
22				63.20								
23							71.45	80.62				
24	23.78	10.47	17.84	15.20		5.91	0.46	0.27				
25	50.12	43.26	41.34	32.26		0.99	4.27	4.00				
26	21.17	21.14	19.50	27.60		2.50	2.09	1.67				
27	39.93	27.72	35.10	28.34		0.19	3.52	4.39				
28	18.33	12.33	13.53	13.25		5.78	1.39	0.65				
29	67.43	65.08	45.44	57.98	0.01	0.54	1.90		123.11	103.62	120.24	105.20
30	27.96	63.22	39.43	45.36								
31	46.41	29.44	33.02	23.21		0.11	6.56	0.19				

Table A-4. Air Pollution Control Devices in Service.

POTW ID	Air Pollution Control Devices Utilized					
	Impingement Tray Scrubber	Venturi Scrubber	Bag House	Wet Electrostatic Precipitator	Other	Other Description
1		Yes				
2	Yes				Yes	Dry Scrubber
3	Yes	Yes				
4		Yes				
5	Yes	Yes		Yes		
6	Yes					
7	Yes	Yes	Yes	Yes		
8		Yes				
9	Yes	Yes				
10	Yes	Yes				
11	Yes	Yes				
12	Yes	Yes				
13	Yes	Yes				
14	Yes					
15	Yes	Yes				
16		Yes				
17	Yes	Yes				
18	Yes	Yes				
19	Yes	Yes				
20		Yes				
21	Yes					
22	Yes	Yes				
23	Yes	Yes	Yes			
24	Yes	Yes			Yes	pre-cooler
25	Yes	Yes			Yes	pre-cooler
26	Yes	Yes			Yes	pre-cooler
27	Yes	Yes			Yes	pre-cooler
28	Yes	Yes			Yes	Pre-cooler
29	Yes	Yes			Yes	afterburner
30	Yes	Yes				
31		Yes				

Table A-5. Scrubber Water Quality and End Use.

POTW ID	Scrubber Water Info					
	End Use					
	Non-Potable	Recycled to Plant Headworks	Used to Transport Ash to Lagoons	Recycled within Scrubber	Other	Other Description
1	Yes	Yes				
2	Yes				Yes	Scrubber Water Recyled to Secondary Process
3	Yes					
4	Yes	Yes				
5	Yes	Yes				
6	Yes	Yes				
7	Yes	Yes		Yes		Scrubber - Absorption Tower
8	Yes	Yes				
9	Yes	Yes	Yes			
10	Yes	Yes			Yes	Discharged to secondary clarifiers
11	Yes	Yes				
12	Yes		Yes			
13	Yes	Yes				
14	Yes	Yes				
15	Yes	Yes	Yes			1. Transport ash to ash lagoons 2. Recycled to plant headworks
16	Yes		Yes			
17	Yes	Yes	Yes			
18	Yes	Yes				
19	Yes	Yes				
20	Yes	Yes			Yes	put into to centrate well to clear up centrates from centrifuges then recycled to headworks
21	Yes		Yes			
22	Yes		Yes			
23	Yes	Yes				
24	Yes	Yes				
25	Yes	Yes				
26	Yes	Yes				
27	Yes	Yes				
28	Yes	Yes				
29	Yes	Yes				
30	Yes	Yes				
31	Yes	Yes				

Table A-6a. Digestion and Analytical Methods for Biosolids.

	Biosolids											
		Test Methods - Digestion						Test Methods - Analytical				
POTW ID	Time Per Year	HNO3	HCL/HNO3/HF Aqua Regia	HCL/HNO3/HF	Other	Other Description		245.X	1631	7471A	Other	Other Description
1	12	Yes								Yes		
2	1							Yes				
3	52									Yes		
4	4	Yes						Yes				
5	2	Yes						Yes				
6	52		Yes							Yes		
7	12		Yes								Yes	245.50
8	12		Yes								Yes	245.50
9												
10	6		Yes							Yes		
11	12	Yes						Yes				
12	12	Yes						Yes				
13	12									Yes		
14	30				Yes	HNO3/H2SO4/KMnO4/K2S2O8		Yes				245.1
15	7									Yes		
16	12		Yes					Yes				245.1
17	52				Yes	3051A & 245.1		Yes				
18	52				Yes	3051A & 245.1		Yes				
19	12									Yes		
20	1		Yes								Yes	method 105
21	52				Yes	HCl/HNO3 =>BrCl			Yes			
22					Yes	HCl/HNO3 followed by BrCl			Yes			
23	12										Yes	SW846-6020 & 245.1
24	12		Yes							Yes		
25	12		Yes							Yes		
26	12		Yes							Yes		
27	12		Yes							Yes		
28	12		Yes							Yes		
29	12		Yes							Yes		
30	12				Yes	H2SO4/HNO3/KMnO4/KSO4					Yes	SW 846/7470-A
31	12				Yes	HCl/HNO3/aqua regia option					Yes	245.5 (see attached email)

Table A-6b. Digestion and Analytical Methods for Ash.

	Ash												
		Test Methods - Digestion							Test Methods - Analytical				
POTW ID	Time Per Year	HNO3	HCL/HNO3/HF Aqua Regia	HCL/HNO3/HF	Other	Other Description		245.X	1631	7471A	Other	Other Description	
1	4	Yes								Yes			
2	2							Yes					
3	1									Yes			
4													
5		Yes						Yes					
6	1		Yes							Yes			
7													
8													
9	2										Yes	SW 7470A	
10	1			Yes						Yes			
11													
12													
13	12									Yes			
14					Yes	HNO3/H2SO4/KMnO4/K2S2O8		Yes			Yes	245.1	
15	1										Yes	SW1311/7470A	
16								Yes			Yes	245.1	
17	1				Yes	3051A & 245.1				Yes			
18	1				Yes	3051A& 245.1				Yes			
19													
20	2										Yes	TCLP SW7470	
21	1		yes		Yes	HCl/HNO3 followed by BrCl			Yes				
22	1										Yes	HCl/HNO3 followed by BrCl	
23	4									Yes			
24													
25													
26													
27													
28													
29	4		Yes							Yes			
30	2				Yes	H2SO4/HNO3/KMnO4/KSO4				Yes			
31	12		yes		Yes	HCl/HNO3/aqua regia option					Yes	245.5	

Table A-6c. Analytical Methods for Influent and Effluent.

POTW ID	Influent						Effluent					
	Time Per Year	Test Methods - Analytical					Time Per Year	Test Methods - Analytical				
		245.X	1631	7471A	Other	Other Description		245.X	1631	7471A	Other	Other Description
1	52	Yes					12			Yes		
2	12	Yes					12			Yes		
3	0						4	Yes				
4	4			Yes			4			Yes		
5	1	Yes					1	Yes				
6	52	Yes					52	Yes				
7	100				Yes	245.70	24				Yes	245.7 with amalgam (alternative method to 1631)
8							4				Yes	245.7 with amalgam (alternative method to 1631)
9	12	Yes					12	Yes				
10	1	Yes			Yes	245.1	12	Yes			Yes	245.1
11	2	Yes					4	Yes				
12	3	Yes					4	Yes				
13	1	Yes					1	Yes				
14	30	Yes			Yes	245.1	30	Yes			Yes	245.1
15	1	Yes			Yes	245.1	1	Yes			Yes	245.1
16	12	Yes			Yes	245.1	24	Yes			Yes	245.1
17	12			Yes			12			Yes		
18	12			Yes			12			Yes		
19	12			Yes			12			Yes		
20	12	Yes			Yes	EPA 245.1	26	Yes			Yes	245.1 EPA
21	52			Yes						Yes		
22	52			Yes			52			Yes		
23	12	Yes			Yes	245.1	12	Yes			Yes	245.1
24	12	Yes			Yes	245.1	2	Yes			Yes	245.1
25	12	Yes			Yes	245.1	2	Yes			Yes	245.1
26	12	Yes			Yes	245.1	2	Yes			Yes	245.1
27	12	Yes			Yes	245.1	2	Yes			Yes	245.1
28	12	Yes			Yes	245.1	2	Yes			Yes	245.1
29	0	Yes					0	Yes				
30	4	Yes				Clean Metals	4	Yes				Clean Metals
31	12	Yes			Yes	245.1	12	Yes			Yes	245.1

Table A-7. Mercury Concentrations in Biosolids.

POTW ID	Biosolids							
	2002		2003		2004		2005	
	Annual Average mg/Kg, Dry	Highest mg/Kg, Dry	Annual Average mg/Kg, Dry	Highest mg/Kg, Dry	Annual Average mg/Kg, Dry	Highest mg/Kg, Dry	Annual Average mg/Kg, Dry	Highest mg/Kg, Dry
1	1.30	1.99	1.42	2.13	1.49	2.03	1.44	2.07
2	0.03		0.34		1.32		2.60	
3							0.10	
4	0.30	0.60	1.18	2.61	0.69	1.52	0.18	0.28
5	1.40	1.90	1.50	1.60	1.30	1.40	1.70	1.80
6	1.33	3.61	1.15	2.67	1.16	2.31	1.10	3.76
7	0.53	0.91	0.73	1.01	0.41	0.90	0.28	0.37
8	0.53	0.91	0.73	1.01	0.41	0.90	0.28	0.37
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.54	0.72	0.61	1.88	0.52	1.20	0.39	0.97
11	0.69	1.02	0.69	1.63	0.49	0.68	0.58	0.91
12	0.51	0.87	0.41	0.65	0.47	0.73	0.26	0.66
13	3.00	5.02	1.60	2.32	0.80	1.38	1.20	2.17
14	0.40	1.37	0.44	1.34	0.39	1.26	0.75	2.50
15	0.61	0.98	0.69	0.88	0.79	1.30	0.74	2.00
16	0.00	0.00	1.43	2.50	1.76	2.80	1.40	1.90
17	1.30	3.30	1.10	2.00	1.10	3.30	1.70	8.80
18	0.70	1.80	0.80	2.20	0.60	2.20	0.70	1.60
19	1.10	1.68	1.21	1.48	1.96	4.99	2.09	6.10
20						3.40		2.40
21							0.52	1.70
22							0.83	2.90
23	0.49	1.10	0.64	1.05	0.59	0.85	1.03	2.30
24	1.02	1.30	1.07	2.50	0.81	1.20	1.23	3.70
25	0.70	0.90	0.70	1.20	0.70	1.20	0.60	0.70
26	1.24	2.30	0.98	2.30	0.86	1.20	0.85	1.20
27	0.49	0.70	0.66	1.10	0.93	1.90	0.75	1.20
28	0.34	0.50	0.43	0.70	0.48	0.80	0.42	0.60
29	0.44	0.58	0.47	0.58	0.43	0.59	0.43	0.55
30	0.59	1.44	0.53	0.96	0.34	0.51	0.48	2.28
31	0.57	0.84	0.74	1.91	0.60	0.82	0.48	0.69

Table A-8. Mercury Concentrations in Influent.

POTW ID	Influent							
	2002		2003		2004		2005	
	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L
1	310	600	270	380	360	500	230	270
2	268	939	263	472	260	617	215	404
3								
4	494	639	543	1300	164	290	372	1700
5	500<	500<	500<	500<	400<	400<	200<	200<
6	500<	500<	500<	500<	500<	500<	500<	500<
7	87	581	94	806	134	520	87	370
8								
9	200<	260	200<	210	200<	570	200<	240
10	230	600	200	200	100	100	0	0
11	0	0	0	0	0	0	150	200
12	0	1	0	1	1	0	0	0
13	400	400	500	500	500	500		
14	328	3160	327	2700	130	1980	16988	370000
15	0	200<	0	200<	0	200<	0	200<
16			70	340	300	13000	80	390
17	230	636	205	438	228	683	181	844
18	54	94	55	185	53	115	103	481
19	115	205	171	309	242	638	157	450
20	196200	810000	147100	870000	206300	1600000	277400	960000
21							236	286
22							236	721
23	470	6620	300	900	300	1000	300	1000
24	200	600	100	500	100	300	100	300
25	0	200	0	0	0	300	100	600
26	100	300	0	100	0	100	100	600
27	0	200	100	1000	0	200	100	700
28	200	600	0	300	0	200	100	300
29			0	0<				
30	70	87	67	111	44	60	35	55
31	129	376	154	422	166	420	102	140

Table A-9. Mercury Concentrations in Effluent.

POTW ID	Effluent							
	2002		2003		2004		2005	
	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L	Annual Average ng/L	Highest ng/L
1	7	19	5	9	6	12	4	6
2	30	40	25	34	22	40	34	76
3	0	0	0	0	0	0	0	0
4	271	500	19	31	3	4	3	5
5	500<	500<	500<	500<	200<	200<	200<	200<
6	500<	500<	500<	500<	500<	500<	500<	500<
7	15	100	8	13	5	15	5	11
8			2	2	3	3	2	4
9	200<	200<	200<	200<	200<	200<	200<	200<
10	200	200	200	200	200	200	200	200
11	0	0	0	0	0	0	250	500
12	0	0	0	0	0	1	0	0
13	200		500		500			
14	1000<	1000<	1000<	1000<	62	2240	57	1320<
15	0	200<	0	200<	0	1<	0	200<
16			1	20	1	12	0	11
17	3	6	3	4	2	3	2	4
18	3	5	3	3	2	3	2	5
19	5	8	6	10	4	9	4	9
20	3	12	2	9	5	18	2	12
21							33	94
22							11	58
23	470	6620	300	10000	300	400	300	1000
24	0	0	3	3	0	0	4	5
25	2	3	0	0	1	2	1	2
26	5	7	4	4	4	6	5	5
27	1	2	1	2	0	0	3	3
28	0	0	1	3	0	0	0	0
29			0	0.0002<				
30	9	22	29	78	8	18	6	13
31	7<	10	19<	19	4	11.7<	2	3

Table A-10. Test Date, Methods, and Hg Emission Concentrations.

POTW ID	Mercury Incinerator Emissions Test			
	Test Date	Test Method Utilized	Mercury Emissions mg / dry SCM	Mercury Emissions lbs / hr
1	Nov. 2000	CARB 436	0.1441	4.08E-03
1	April 2000	CARB 436	0.0851	0.00243
1	August 2002	CARB 436	0.0786	0.00245
2	June 2003	EPA Test Method 29	0.0468	0.0021
2	December 2002	EPA Test Method 29	0.0308	0.001
3	No Data			
4	2003	EPA Test Method 29	0.0468	0.0021
4	2005	EPA Test Method 29	0.0308	0.001
5	April 1997	EPA Test Method 29	0.16	0.017
6	No Data			
7	May 2005	101A	0.00024	1.30E-05
7	May 2005	101A	0.00005	4.40E-06
7	May 2005	101A	0.00022	8.80E-06
7	March 2006	101A	0.00171	1.38E-04
7	February 2006	EPA Test Method 29		
7	March 2006	101A	0.00011	8.80E-06
8	August 2006	EPA Test Method 29		
9	June 1993	EPA Test Method 29	0.142	0.00295
10	January 2002	EPA Test Method 29	0.096705	4.20E-03
10	October 2006	EPA Test Method 29	0.0754614	3.02E-03
11	June 15, 1993	Method 29 CVAAS		0.0165235
12	No Data	No Data		
13	No Data	No Data		
14	No Data	No Data		
15	No Data	No Data		
16	No Data	No Data		
17	September 2002	25A(?)	0.089	0.0041
17	September 2002	25A(?)	0.058	0.004
17	September 2002	25A(?)	0.067	0.0052
17	June 2003	SW-8460012(?)	0.022	0.0016
17	July 2004	25A(?)	0.085	0.0063

Mercury Incinerator Emissions Test				
POTW ID	Test Date	Test Method Utilized	Mercury Emissions mg / dry SCM	Mercury Emissions lbs / hr
18	October 1994	Draft Method 29	0.068	0.0024
18	September 1995	Draft Method 29	0.129	0.005
19	August 2004	EPA Test Method 29	0.15	0.0028
19	September 2004	EPA Test Method 29	0.09	0.0017
20	April 2006	EPA Test Method 29	0.284	0.00326
21	July 2005	EPA Test Method 29	0.07464	0.00412
22	August 2000	EPA Test Method 29	0.113	0.00537
23	No Data			
24	June 2000	EPA Test Method 29	0.081	0.00273
24	June 2000	EPA Test Method 29	0.0634	0.00162
25	June 2000	EPA Test Method 29	0.0501	0.00174
25	June 2000	EPA Test Method 29	0.0832	0.00297
26	March 2003	EPA Test Method 29	0.0902	0.00239
26	March 2003	EPA Test Method 29	0.145	0.00205
27	June 2000	EPA Test Method 29	0.0474	0.00227
27	June 2000	EPA Test Method 29	0.0461	0.00324
28	June 2005	EPA Test Method 29	0.1014	0.00234
28	June 2005	EPA Test Method 29	0.113	0.00297
29	June 20, 1996	Subsection 3.1 of BIF methods Manual, EPA/530 = SW91-010	0.043	0.003046
29	June 18, 1996	Subsection 3.1 of BIF methods Manual, EPA/530 = SW91-010	0.046	0.003046
29	June 21, 1996	Subsection 3.1 of BIF methods Manual, EPA/530 = SW91-010	0.039	0.005284
29	June 26, 1996	Subsection 3.1 of BIF methods Manual, EPA/530 = SW91-010	0.035	0.004383
29	September 2004	EPA Test Method 5/29	0.1	0.00386
29	September 2004	EPA Test Method 5/29	0.0643	0.00494
30	No Data			
31	September 1989		0	0.00523
31	September 1989		0	0.00598
31	September 1989		0	0.00597

APPENDIX B

FRONTIER FSTMTM SORBENT GAS SAMPLING

This sampling guide is intended to provide an abbreviated technique for total gaseous mercury collection in combustion flue. This guide is applicable to short term monitoring projects only. If long-term emission compliance monitoring is required, please refer to EPA Appendix K.

Definition of Terms:

Sampling Console: An integrated gas sampling unit that contains the dry gas meter, pump, flow control, and probe temperature controller.

Control Panel Faceplate: The front panel of the sampling console that houses all of the dials, toggle switches, and displays.

Sample Line: A 1/4" Polypropylene line that contains all fittings between the sample console and the sample trap.

Water Trap: A Teflon water trap designed to remove water from the flue gas stream before it enters the sampling console. The water trap is placed between the sample trap and sampling console.

Sample Trap: The solid sorbent trap used to trap and capture total Hg from a gaseous sample stream.

Probe: The unit used to keep the temperature of the solid sorbent trap above the dew point. This is to ensure that water does not condense out in the solid sorbent trap and thus compromising the sample.

Getting Power to the Sample Box:

- ◆ Remove the cover from the face of the sampling console. Pull out on the silver cleats and rotate them counterclockwise. Remove the lid.
- ◆ The power cord for the sampling console connects to the outlet marked 115VAC/15A-60 Hz. The standard three-prong cord can then be plugged into a standard power outlet.
- ◆ Place the air-sampling unit on some sort of pad or clean surface to help minimize the potential for contamination.

Power On the Console:

- ◆ Once power cord is plugged in, turn on the unit. This is the toggle switch marked "Main".

- ◆ Turn on the sampling pump by turning on the toggle switch marked “Pump”. There should be an audible hum if the pump is operating.
- ◆ Open the coarse flow control to the fully open position by turning ¼ turn counter-clockwise. The flow is then set using the “Fine Control” valve. Turning the “Fine Control” clockwise will increase the gas sampling flow rate.
- ◆ Check to make sure that the flowmeter registers gas flow. When a reasonable flow is set, check to make sure that the check meter wheel on the dry gas meter is advancing as well as the totalizer readout (just above the dry gas meter).

Turn On the Probe:

- ◆ Prior to sampling, it is important to allow the probe to come fully up to temperature. This is to ensure that the sample trap temperature is above the dew point to prevent condensation on the trap.
- ◆ After the securing the probe, power up the temperature controller by flipping the “Temp. Cont.” toggle switch. The temperature controller will light up.
- ◆ Attach a Type-K thermocouple extension to the probe, and plug the other end of the thermocouple extension into the yellow port marked “Probe”.
- ◆ Using an electrical extension cord, plug the probe into the outlet on the box labeled “T/C Load”.
- ◆ Turn the black toggle switch to the “Probe” position. If everything is connected properly, the large temperature display will read the temperature of the probe, and will closely follow the temperature readout on the temperature controller.

Warning: The probe maintains constant temperature by a continuous temperature feedback loop with the thermocouple. The thermocouple must have a secure connection to the probe, and the probe heater must only be plugged into “T/C Load” outlet for proper functioning. Never plug the probe directly into an electrical outlet. This will cause runaway heating and permanently damage the probe.

Perform a Leak Check of the System:

- ◆ Assemble the sampling train using clean sampling techniques that are appropriate to the level cleanliness desired (see U.S. EPA Method 1669). Extra care should be exercised to the sampling train components upstream of the sample trap as these have the greatest potential of sample contamination.
- ◆ After assembly of the sampling train, securely seal the inlet end of the sample train.
- ◆ Turn on the pump and open the “Coarse” valve. Turn the “Flow Control” valve clockwise until the vacuum gage reads at least as high as the expected back-pressure during sampling.

- ◆ Observe the flow meter, volume totalizer, or dry gas meter to determine if that the systems are not registering any flow.
- ◆ Turn the “Flow Control” counter-clockwise, and close the coarse valve.
- ◆ There will now be negative pressure in the sample lines. This should be released at the sample inlet. The pressure must be released slowly to prevent upset of the sorbent beds of the sample traps.
- ◆ After the Pre-Leak Check is complete, turn off the pump power.

Preparations to Begin Sampling:

- ◆ Double check to ensure the pump is OFF.
- ◆ Check to be sure that the “Flow Control” valve has been turned a couple of times counter-clockwise. This assures that the desired sample rate is not exceeded at the start of sampling.
- ◆ Press the reset button on the volume totalizer, and press the reset button on the elapsed sampling time (optional).
- ◆ Record the readout of the dry gas meter. Make sure to record this number as accurately as possible. You should get a number like 1.234(5) m³ where the (5) is estimated.

Begin Sampling:

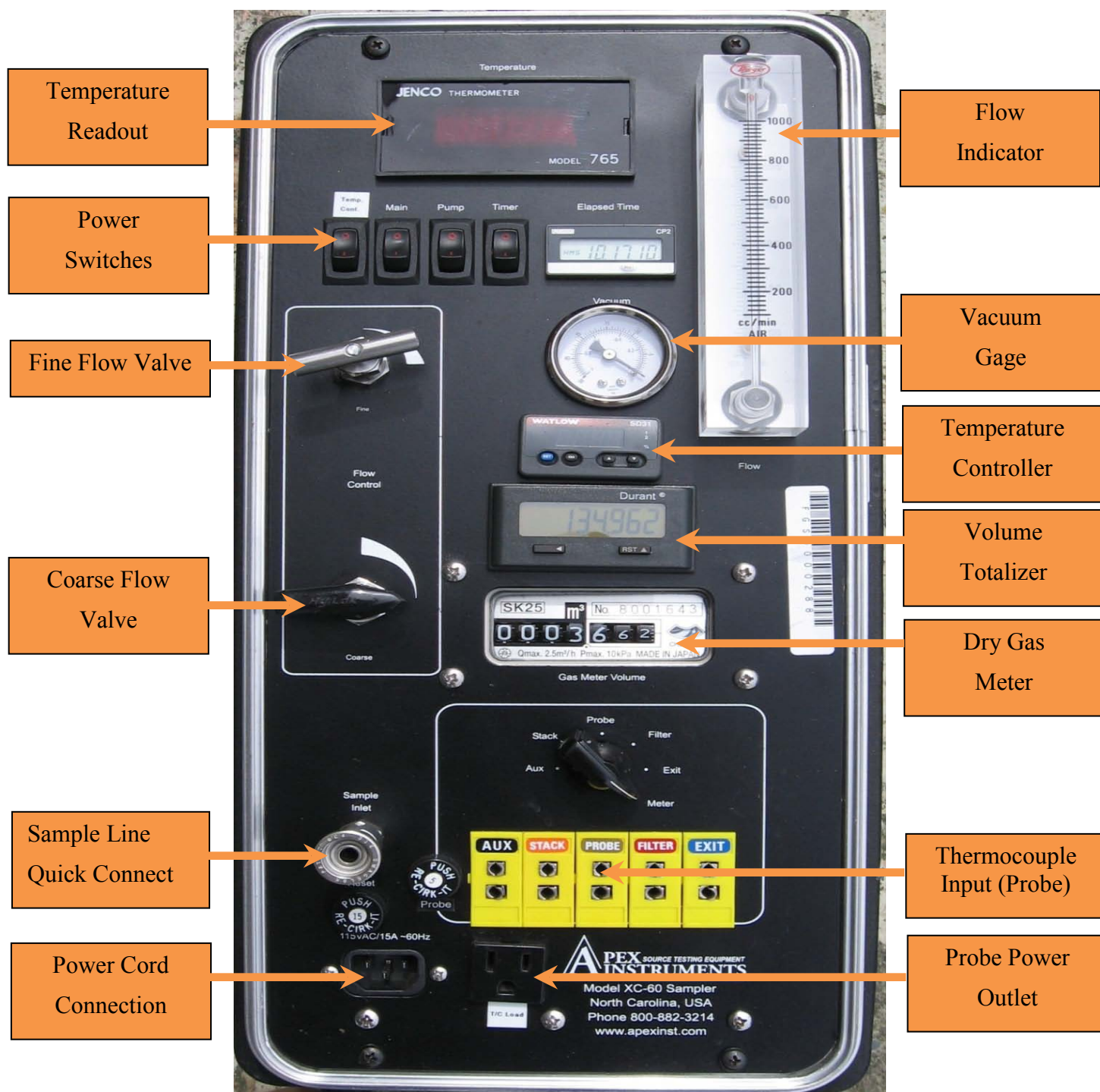
On the field data sheet record the following:

- ◆ Sample Date
- ◆ Sampling Location
- ◆ Sample Trap ID
- ◆ Sample Matrix
- ◆ Install the probe into the sampling duct and assure that the interface is secure and leak tight.
- ◆ Turn on the pump power.
- ◆ Open the “Coarse Valve” and turn the “Flow Control” valve clockwise to obtain desired flow.
- ◆ Record the sampling start time on the field data sheet, and the sampling flow rate.
- ◆ Periodically record the sampling flow rate and with the elapsed sampling interval.
- ◆ Do a quick calculation: Figure out how long the sample has been running. Using the flow rate, calculate the interim volume collected [Y(slpm) X time(minutes) = liters]. This value should be fairly close to the value on the Totalizer.

Ending Sampling:

- ◆ After desired volume is collected, close the “Coarse” valve and turn off the pump using the “Pump” toggle switch.
- ◆ Perform a “Post-Sample Leak Check” in the same manner as the pre-leak check.
- ◆ Collect the sample using the same clean techniques as were used to assemble the sampling train.
- ◆ Remove the trap from the sample train and replace the original end caps to seal the trap.
- ◆ Place trap in the original inner Ziploc bag.
- ◆ Place the Field Data Sheet in the outer Ziplock bag with the sample.

Figure B-1. Gas Sampling Console Control Panel Faceplate.



APPENDIX C

CLEAN SAMPLING TECHNIQUES

Introduction

The following comments are based on U.S. EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. This method was designed to support water quality monitoring programs authorized under the Clean Water Act, specifically created for measuring toxic metals at ultra-trace levels (low part per trillion to low part per billion range). Although primarily designed for ambient water research, these ultra-clean methodologies are now used extensively for sampling all types of matrices.

Preventing samples from being contaminated during sampling and analysis is imperative. It has been recently shown that many of the historical trace metal concentrations in ambient waters were erroneously high, because samples were contaminated during sampling and analysis. To prevent such errors, this method describes reliable sample collection with the necessary steps to preclude contamination in nearly all situations. Although clean-sampling technique is often described as a “method,” it is better viewed as a flexible “philosophy,” which requires biogeochemical and analytical understanding by the practitioner, as well as a good dose of common sense.

Method Summary

All sampling equipment and sample containers used for metals determination must be nonmetallic and free from any material that may contain metals. A sampling kit consisting of proper containers, bags, clean-room gloves, and instructions for the “clean hands/dirty hands” collection method should be pre-built or purchased. Containers for the “clean hands/dirty hands” collection method should be double-bagged. It is advised to submit a sample blank with the samples.

For total mercury analysis, sample containers should be either Teflon or borosilicate glass.

Ideally, at least two persons wearing fresh clean-room gloves at all times are required on a sampling crew. The person designated “clean hands” is responsible for all operations involving direct contact with the sample container and transfer of the sample from the collection device to the container. The person designated “dirty hands” is responsible for the preparation of the sampler, operation of any machinery, and all other activities that do not involve direct contact with the sample.

- ◆ “Dirty hands” pulls a bagged container from the cooler and opens the outer, dirty bag, avoiding touching inside that bag.
- ◆ “Clean hands” reaches in, opens the inner bag (if present), and pulls out the sample container. “Clean hands” should not touch anything but the sample container, its cap, and the sample stream.
- ◆ The container is opened and the sample collected.

- ◆ The top is replaced and the container rebagged in the opposite order from which it was removed.
- ◆ Clean-room gloves are changed between samples for both parties.

Aqueous Sampling

- ◆ The container (including its cap) is rinsed three times with the sample water, and then filled almost completely.
- ◆ Leaving a small headspace (e.g. 1% of bottle volume) is acceptable and provides space for subsequent acid preservation at the laboratory.

Sediment Sampling

- ◆ The container is filled almost completely with sediment using a non-metallic utensil known to be free from trace metal contamination.
- ◆ The sampler should ensure that the sampling site is representative of the bulk stream.

Samples should be sent overnight to the analytical laboratory without preservative to minimize contamination in the field. The samples will be preserved as required by the method after arrival at the laboratory. Samples for total mercury can be shipped at ambient temperature.

Whenever possible, samples should be collected facing upstream and upwind to minimize contamination. Surface samples are collected using a grab technique. The principle is to fill a sample bottle by rapid immersion of the collection bottle in water capping immediately to minimize exposure to airborne particulate matter. Care must be taken to submerge the mouth of the bottle quickly and fully to minimize contamination from the surface micro-layer. Samples are collected by a surface-activated discrete sampler (e.g., Go-Flo), or by pumping the sample to the surface. Either a rigorously cleaned Teflon and silicone peri-staltic pumping system (low flow), or a cleaned submergible pumping system (high flow) can be used.

QA/QC Procedures

To ensure accuracy, it is critical that the sampling team also employ quality assurance/quality control (QA/QC) procedures. At least one field blank should be processed per site, or one per every ten samples, to confirm that contamination has not occurred during collection or processing. Before using any sampling equipment on site, equipment blanks (container blanks and sampling equipment blanks) should be collected from each item that will be used in the field. To assess the precision of the field sampling and analysis, a field duplicate should also be collected at each site, or one field duplicate per every ten samples. In addition and if possible, extra samples should be collected to allow for necessary quality control analyses, such as matrix spike and matrix spike duplicate analyses.

Table C-1. Equipment Used for Collecting Sewage Sludge Samples.¹

Equipment	Description
Composite Liquid Waste Sampler (Collwasa)	The Collwasa is a device employed to sample free-flowing sewage sludges contained in drums, shallow tanks, pits and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases. The Collwasa consists of a glass, plastic or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled.
Weighted Bottle	This sampling device consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise and open the bottle. The weighted bottle is used for sampling free flowing sewage sludges and is particularly useful for obtaining samples at different depths in a lagoon. A weighted bottle with line is built to the specifications in ASTM Method D270 and E300
Dipper	The dipper consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper is used for obtaining samples of free difficult to access free flowing sewage sludge. Dippers are not typically available commercially and are normally fabricated in-house
Sampling Thief	A thief consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample high solids content materials such as composted and heat dried biosolids for which particle diameter is less than one-third the width of the slots. Thief samplers are available from laboratory supply companies
Trier	A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky materials such as dewatered cake and lime stabilized biosolids. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm and 1.27 to 2.54 cm in diameter are available from laboratory supply companies.
Auger	An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger can be used to obtain samples through a cross-section of biosolids stockpile. Augers are available at hardware and laboratory supply stores.
Scoops and Shovels	Scoops are used to collect samples from sewage sludge or biosolids stockpiles, shallow containers, and conveyor belts. Stainless steel or disposable plastic scoops are available at laboratory supply houses. Due to the difficulty of sterilizing shovels and other large sampling equipment, this type of equipment should only be used for accessing the center of stockpiles and should not be used for collecting the actual sample.

¹ EPA/625/R-92/013 "Environmental Regulations and Technology: Control of Pathogens and Vector Attraction in Sewage Sludge (PDF)" Revised July 2003 – Chapter 9
<http://www.epa.gov/nrmrl/pubs/625r92013/625R92013chap1.pdf>

Table C-2. Sampling Scheme Used in Their Mercury Mass Balance of Their Treatment Plant and Biosolids Incinerator.

Input/Output	Sampling Method	Analytical Method	Notes
Raw Influent	Discrete Sampler	EPA 245.2	2-4 samples per hour for 7 consecutive days
Grit	Not disclosed	EPA 7471	2 samples per day for 5 days during the 7 day period
Ash	Not disclosed	EPA 7471	Each ash load hauled from site sampled
Scum	Not disclosed	EPA 7471	1 sample per day for 5 days during the 7 day period
Final Effluent	Discrete Sampler	EPA 245.2	2-4 samples per hour for 7 consecutive days
Stack Emissions	Not Applicable	Not Applicable	Values estimated from historical data
WAS	Discrete Sampler	EPA 7471	2-4 samples per hour for 7 consecutive days
Scrubber Effluent	Discrete Sampler	EPA 245.2	2 samples per hour for 7 consecutive days
DAF Underflow	Not Disclosed	EPA 7471	2 samples per hour for 7 consecutive days. Sample was composited
Primary Effluent	Discrete Sampler	EPA 245.2	2 samples per hour for 7 consecutive days
Centrate	Not Disclosed	EPA 7471	1 samples per day for 7 consecutive days. Sample was composited
Cake	Not Disclosed	EPA 7471	1 samples per day for 7 consecutive days. Sample was composited

APPENDIX D

PALO ALTO REGIONAL WATER QUALITY CONTROL PLANT MERCURY MASS BALANCE



Technical Memorandum

DATE: March 24, 2003 [Modified & Reissued 4/2/03]

TO: Phil Bobel, City of Palo Alto
Karin Didriksen, City of Palo Alto
Stephanie Hughes, City of Palo Alto

CC: Monica Oakley, LWA

FROM: Brian Laurenson
Everest Yan

SUBJECT: **Palo Alto Regional Water Quality Control Plant Mercury Loading Mass Balance**

509 4th Street
Davis, CA 95616
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(530) 753-7030 fax

As requested by the City of Palo Alto, Larry Walker Associates (LWA) has performed a Mercury Loading Mass Balance of monitoring data from the City of Palo Alto Regional Water Quality Control Plant Influent, Effluent, Incinerator and Sludge Flows. This memo presents and reviews the results of the mass balance.

Introduction

The City of Palo Alto Regional Water Quality Control Plant (RWQCP) has an average dry weather flow of 25 million gallons of per day (MGD) of domestic and industrial wastewater. The plant uses physical, biological and chemical treatment techniques. Sludge removed from sedimentation is thickened, dewatered through a belt press and incinerated. The incineration of sludge also requires scrubbers for air pollution control as well as fly ash disposal. A schematic of the plant processes related to this study is provided as Figure 1.

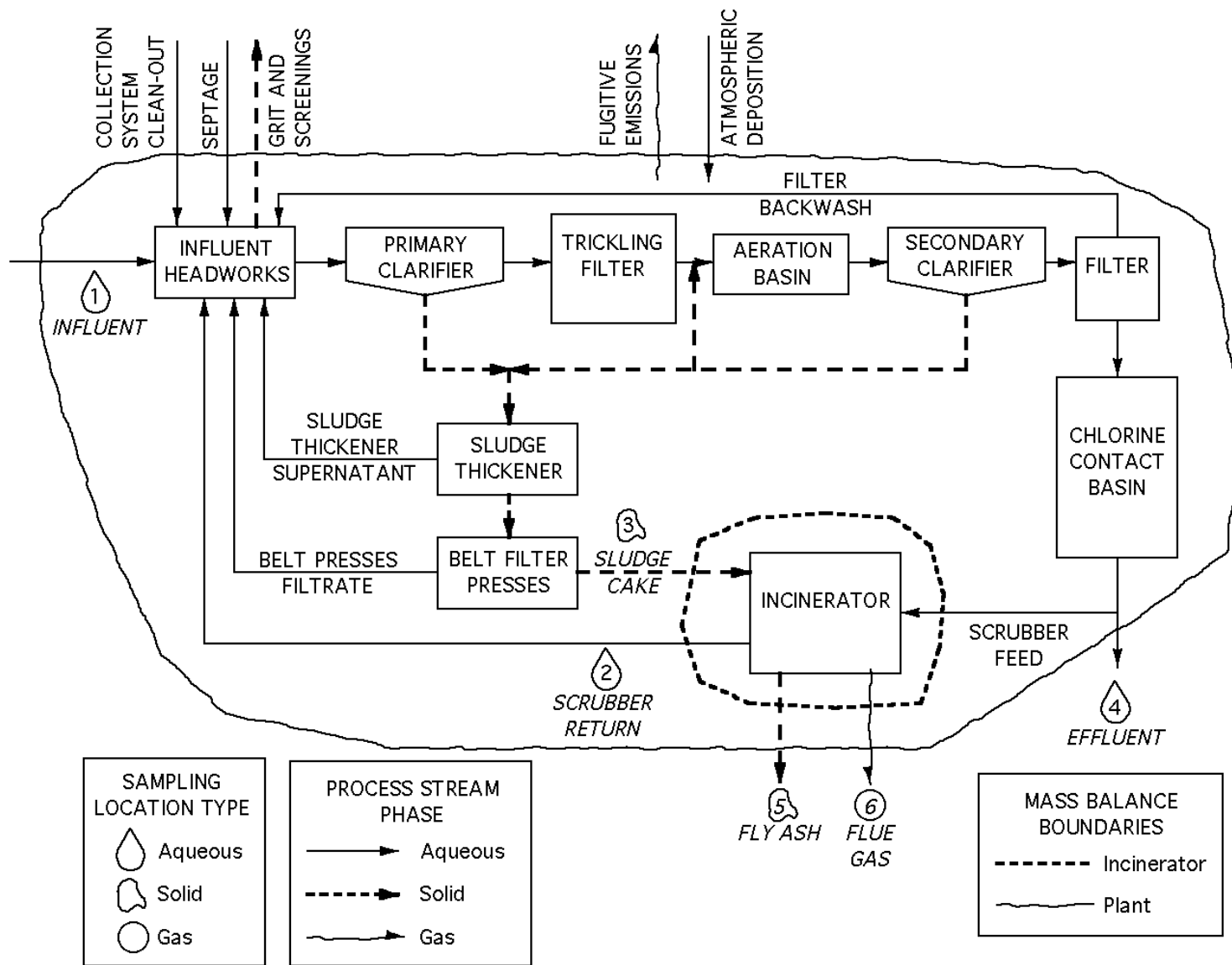


Figure 1. RWQCP Process Schematic and Mass Balance Boundaries

Objective

The objective of this study was to characterize typical plant mass transfer of mercury (Hg) across the treatment plant and incinerator mass balance “boundaries” (see Figure 1), as well as account for all known significant mass flows in and out of the mass balance boundaries. The incinerator stack sampling and characterization was particularly important because a significant fraction of the mercury leaving the plant was expected to be released through the stack.

Methods

The characterization was performed during a three-day period under normal dry weather operating conditions. A combined total of six aqueous, gas, and solid phase process flows were monitored for flow volume and concentration, including the influent and effluent aqueous sites. The influent and effluent sites were collected according to the RWQCP’s normal sampling schedule and all other samples conducted as a part of this study coincided with the plant schedule when possible. With the exception of the incinerator stack monitoring, existing plant equipment was used to record flow volumes. Composite and grab sampling of the streams were used to determine pollutant concentrations.

Sampling Locations

The sampling locations were selected to characterize the mass balance for the incinerator and total plant boundaries as shown in Figure 1. The first boundary encompasses all mass inputs and outputs for the entire treatment plant. The second boundary accounts for all incinerator inputs and outputs. Based on the mass flows within the plant and incinerator, six locations were selected for sampling.

The selected locations are numbered 1 through 6 in Figure 1. The sample locations are:

1. Influent (scheduled treatment plant sampling and historical data)
2. Scrubber return water
3. Sludge cake (input to incinerator)
4. Effluent (scheduled treatment plant sampling and historical data)
5. Fly ash
6. Flue gas

The collection system clean-out, septage and atmospheric depositions are not considered significant inputs based on estimated plant volumes and typical concentrations from other plants. Based on literature research, grit, screening and fugitive emissions are not considered significant plant outputs.

Sampling Methods

Sampling was performed simultaneously at all sites using methods to collect samples most representative of daily averages, whenever feasible. All samples were collected and handled to minimize contamination. Sampling location and frequency are listed below:

- Influent and effluent were sampled as grabs by treatment plant staff as is done for standard treatment plant monitoring.
- Scrubber water samples were collected by plant staff as six hour composite samples for each of the 3 days (one composite aliquot per hour).
- Fly ash and thickened sludge feed samples were collected six times daily and composited into a daily sample.
- Flue gas was collected as a partial day (6-hour) composite.

Calculation Methodology

Several calculation methods were used to convert flow and concentration into mercury mass transfer rates. Multiple calculation methods are necessary because the mercury load is converted to solid, aqueous, and gas phases through the plant processes. Example calculations for each type of mass transfer are shown below. Detailed calculations for the 3-day period of the study are shown in Attachment A.

Example 1. Liquid Phase (Influent, Effluent, and Scrubber Flows) Mass Transfer

Mass transfer of mercury for the aqueous phase, low solids process streams was calculated directly as the mass concentration ($\mu\text{g/L}$) of mercury multiplied by the volumetric flow rate (million gallons per day), with corresponding unit conversions.

$$\text{Flow Rate } \left(\frac{1 \times 10^6 \text{ gal}}{\text{day}} \right) \times \text{Hg Concentration } \left(\frac{\mu\text{g Hg}}{\text{L}} \right) \times \frac{3.78 \times 10^6 \text{ L}}{1 \times 10^6 \text{ gal}} \times \frac{1 \text{ lb Hg}}{0.45 \times 10^9 \mu\text{g Hg}} =$$

$$\text{Hg Loading } \left(\frac{\text{lb Hg}}{\text{day}} \right)$$

Example 2. Gas Phase Mass Transfer (Flue Gas)

Mass transfer of the incinerator stack gas was calculated as the dry standard volumetric air transfer rate (dscfm) multiplied by the dry weight concentration.

$$\text{Flow Rate } \left(\frac{\text{ft}^3}{\text{min}} \right) \times \text{Hg Concentration } \left(\frac{\mu\text{g Hg}}{\text{m}^3} \right) \times \frac{1 \text{ m}^3}{35.31 \text{ ft}^3} \times \frac{1440 \text{ min}}{\text{day}} \times \frac{1 \text{ lb Hg}}{0.45 \times 10^9 \mu\text{g Hg}} =$$

$$\text{Hg Loading } \left(\frac{\text{lb Hg}}{\text{day}} \right)$$

Example 3. Sludge Mass Transfer Thickened Sludge and Sludge Cake

Sludge loading was calculated using a solids balance across the belt-press just prior to sludge cake incineration. It is expected that 96% of the solids are retained for incineration. The mass rate of solids to the incinerator was calculated using the thickened sludge mass transfer rate times the percent solids of the thickened sludge. The wet weight concentration was converted to a dry weight and multiplied by the mass transfer rate of solids. The solids balance technique was used, as there was no direct manner to calculate the sludge mass loading rate to the incinerator. Sludge calculations perform the volume to mass conversion using the density of water (62.4 lb/ft³) and the specific gravity of the sampled sludge (1.02). Percent solids were measured each minute and the average over 3 days was used in the balance. Solids capture through the belt press was assumed to be 96% based on typical belt press performance.¹

Convert the sludge flow rate to a solids transfer rate:

$$\text{Sludge Flow Rate (gpm)} \times \frac{1440 \text{ min.}}{\text{day}} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \times \frac{62.4 \text{ lb}}{\text{ft}^3} \times 1.02 \times \text{Percent Solids (\%)} \times \left(\frac{0.96 \text{ lb solids out of belt press}}{1 \text{ lb solids in to belt press}} \right) = \text{Solids Transfer Rate} \left(\frac{\text{lb solids}}{\text{day}} \right)$$

Convert the solids transfer rate to a mercury loading:

$$\text{Solids Transfer Rate} \left(\frac{\text{lb solids}}{\text{day}} \right) \times \text{Dry Weight Hg Concentration} \left(\frac{\text{mg Hg}}{\text{kg solids}} \right) \times \frac{0.4536 \text{ kg solids}}{\text{lb solids}} \times \frac{\text{lb Hg}}{453600 \text{ mg Hg}} = \text{Hg Loading} \left(\frac{\text{lb Hg}}{\text{day}} \right)$$

Example 4. Solid Phase Mass Transfer (Fly Ash)

Fly ash mass transfer was calculated as the mass rate of solids multiplied by the dry weight concentration. The mass rate of solids was not measured directly and was estimated based on historical plant performance. Mercury was not always detected in the fly ash samples, so the reporting limit was used as upper limit on the fly ash mercury mass transfer (i.e., the actual concentration is less than the reporting limit and the mass calculation is conservative). Using these assumptions the fly ash mass transfer is a negligible fraction (<0.05%) of the total incinerator mass transfer and so the conservative assumption of using the reporting limit does not affect the overall result.

$$\text{Fly Ash Solids Transfer Rate} \left(\frac{\text{lb solids}}{\text{day}} \right) \times \text{Hg Concentration} \left(\frac{\text{mg Hg}}{\text{kg solids}} \right) \times \frac{0.4536 \text{ kg solids}}{\text{lb solids}} \times \frac{\text{lb Hg}}{453600 \text{ mg Hg}} = \text{Hg Loading} \left(\frac{\text{lb Hg}}{\text{day}} \right)$$

¹ Wastewater Engineering. Third Edition. 1991. Metcalf & Eddy. pp. 892

Results

Mass balances were calculated across the entire plant and the incinerator. Results are shown in Table 1.

Table 1. Mass Balance Results

	Load (lb/day)	%	Notes
Treatment Plant			
Input			
Influent	0.062	100%	Average of 2001-02 Monthly Sampling
Total	0.062		
Output			
Effluent	0.0013	2.21%	Average of 2001-02 Monthly Sampling
Flue Gas	0.059	97.75%	Avogadro 3-day average.
Fly Ash	0.000021	0.03%	Estimated based on previous mass flow rate estimates and 3-day concentration average upper limit.
Total	0.060		
Closure Difference	0.0020	3.2%	
Incinerator			
Input			
Sludge Cake	0.056	99.93%	Solids load to incinerator based on thickened sludge and percent solids
Scrubber Feed	0.000039	0.07%	Average of 2001-02 Monthly Sampling
Total	0.056		
Output			
Flue Gas	0.059	95.33%	Avogadro 3-day average.
Fly Ash	0.000021	0.03%	Estimated based on previous mass flow rate estimates and 3-day concentration average upper limit.
Scrubber Return	0.0029	4.64%	RWQCP 3-day average
Total	0.062		
Closure Difference	-0.0057	-9.7%	

Discussion

The mass transfer balances across both the entire plant and the incinerator were closed within 4% and 10%, respectively. Lack of complete closure is attributed to sampling and analytical error, process efficiency assumptions, and the inherent variability of environmental monitoring over short periods of time (i.e., limited data set). However, this mass closure analysis is an improvement over previous studies due to a reduced number of assumptions and because the analysis was performed during more typical plant conditions. The results of the study confirmed the expected results and previously performed study results. The largest fraction of mercury leaves the plant boundary through the incinerator flue gas; the effluent and fly ash contribute only a small fraction of the total mass of mercury leaving the plant. Mercury concentrates in the plant solids, and primarily comes to the plant through the influent headworks (i.e., septage, collection system clean-out, air deposition, and other inputs are negligible). The newly installed scrubbers remove a small fraction of the volatilized mercury and do not significantly affect overall effluent concentrations of mercury.

Future studies could improve the mass balance as follows:

- Long-term monitoring would allow for an analysis of the variability of mass transfer rates. Two years of monthly influent and effluent data were used in this study because one of the reported effluent concentrations during the three-day sampling period was above the 95th percentile value observed at the plant. This high value was more likely due to sample contamination and the long-term average is more representative of actual conditions. Similarly, long-term flue gas and sludge monitoring would provide a better measure of process variability. The variability of plant performance is useful for regulatory purpose, as this information is critical for determining the statistical range of likely mass transfer rates rather than a just three-day “snapshot”.
- Sludge cake mass loading data collection would enable a direct calculation of the incinerator loading, eliminating the belt press solids removal assumptions.

Please contact us if you would like additional information on the mercury mass balance study.

Attachment A. Mercury Mass Balance Worksheet

Input	Date	Flow	Flow Units	Hg Concentration	Units	Percent Solid	Load	Load Units	Notes
Influent	2001-02	23.07	MGD	0.6	ug/L		0.12	lb/day	2001-02 average
Effluent	2001-02	22.95	MGD	0.0082	ug/L		0.0016	lb/day	2001-02 average
Scrubber Return	8/13/02	387	GPM	0.52	ug/L		0.0024	lb/day	
Scrubber Return	8/14/02	392	GPM	0.88	ug/L		0.0041	lb/day	
Scrubber Return	8/15/02	401	GPM	0.42	ug/L		0.0020	lb/day	
Scrubber Feed	8/13/02	387	GPM	0.0082	ug/L		3.81E-05	lb/day	Assuming 2001-02 average effluent concentration and no scrubber evaporation
Scrubber Feed	8/14/02	392	GPM				3.85E-05	lb/day	
Scrubber Feed	8/15/02	401	GPM				3.95E-05	lb/day	
Fly Ash	8/13/02	7000	lb/day	0.003	mg/kg		2.098E-05	lb/day	Mass rate estimated by Bill Miks (Plant Supervisor), concentrations assumed to be below detection limit of 0.003 mg/kg
Fly Ash	8/14/02								
Fly Ash	8/15/02								
Flue Gas	8/13/02	10,433	dscfm	64.77	ug/m^3		0.061	lb/day	
Flue Gas	8/14/02	10,397	dscfm	62.53	ug/m^3		0.058	lb/day	
Flue Gas	8/15/02	10,481	dscfm	60.59	ug/m^3		0.057	lb/day	
Thickened Sludge	8/13/02	107.70	GPM			2.91%	36,889	lb solids/day	Assumes 96% retention of solids in belt press based on typical values in Metcalf & Eddy, <i>Wastewater Engineering. Third Edition</i> . 1991 pp. 892
Thickened Sludge	8/14/02	107.33	GPM			3.37%	42,522	lb solids/day	
Thickened Sludge	8/15/02	110.04	GPM			2.86%	37,024	lb solids/day	
Sludge Cake	8/13/02	36,889	lb solids/day	1.61	mg/kg DW	27.9%	0.059	lb/day	2002 average percent solids for sludge cake
Sludge Cake	8/14/02	42,522	lb solids/day	1.33	mg/kg DW	27.9%	0.056	lb/day	
Sludge Cake	8/15/02	37,024	lb solids/day	1.40	mg/kg DW	27.9%	0.052	lb/day	

APPENDIX E

NORTHEAST OHIO REGIONAL SEWER DISTRICT SOUTHERLY WASTEWATER TREATMENT CENTER MERCURY MASS BALANCE

TO: Scott Broski
Supervisor of Enforcement

DATE: November 9, 2006

FROM: Tiffany Moore
WQIS Investigator

RE: 2005 Southerly Wastewater
Treatment Center Mercury Mass
Balance Study

Introduction

The Northeast Ohio Regional Sewer District (NEORSD) owns and operates three wastewater treatment plants in the Greater Cleveland area. Southerly Wastewater Treatment Center (SWWTC) has a long-term average flow of 122 million gallons per day (MGD), based on 2003-2005 monthly averages, and it discharges effluent to the Cuyahoga River. Westerly Wastewater Treatment Plant and Easterly Wastewater Treatment Plant, treat smaller quantities, with long-term average flows of 30 and 105 MGD respectively based on 2003-2006 monthly averages, and they discharge effluent to Lake Erie. While the three wastewater treatment plants were not designed, nor have specific equipment, for removal of mercury, it is incidentally removed from the wastewater through the biological/sludge handling processes at each plant at a removal efficiency of greater than 95 percent. Due to the high density of mercury, it tends to become incorporated in the settleable solids that make up the sludge.

The current National Pollutant Discharge Elimination System (NPDES) permit for SWWTC expired in July 2005. Although no numeric effluent limit exists under this permit, it does require a local limit for mercury discharged from indirect sources. A numeric local limit calculated to achieve the applicable water quality criterion of 1.3 ppt (parts per trillion) in the Cuyahoga River was infeasible, so a narrative local limit was instead adopted. The narrative local limit contains a requirement for indirect sources of mercury to perform Best Management Practices (BMPs) for mercury discharge minimization. Sources and/or sectors determined to be significant sources of mercury are required to submit and implement BMP plans. These BMPs include, but are not limited to, mercury inventories, proper housekeeping, and proper disposal of mercury-containing equipment/products, in order to minimize the amount of mercury entering the sewer system.

Upon renewal of the NPDES permit, the NEORSD is anticipating, as a result of the Great Lakes Initiative, a numeric effluent limit of 1.3 ppt for mercury. According to current and past monthly sampling of SWWTC effluent, this limit is

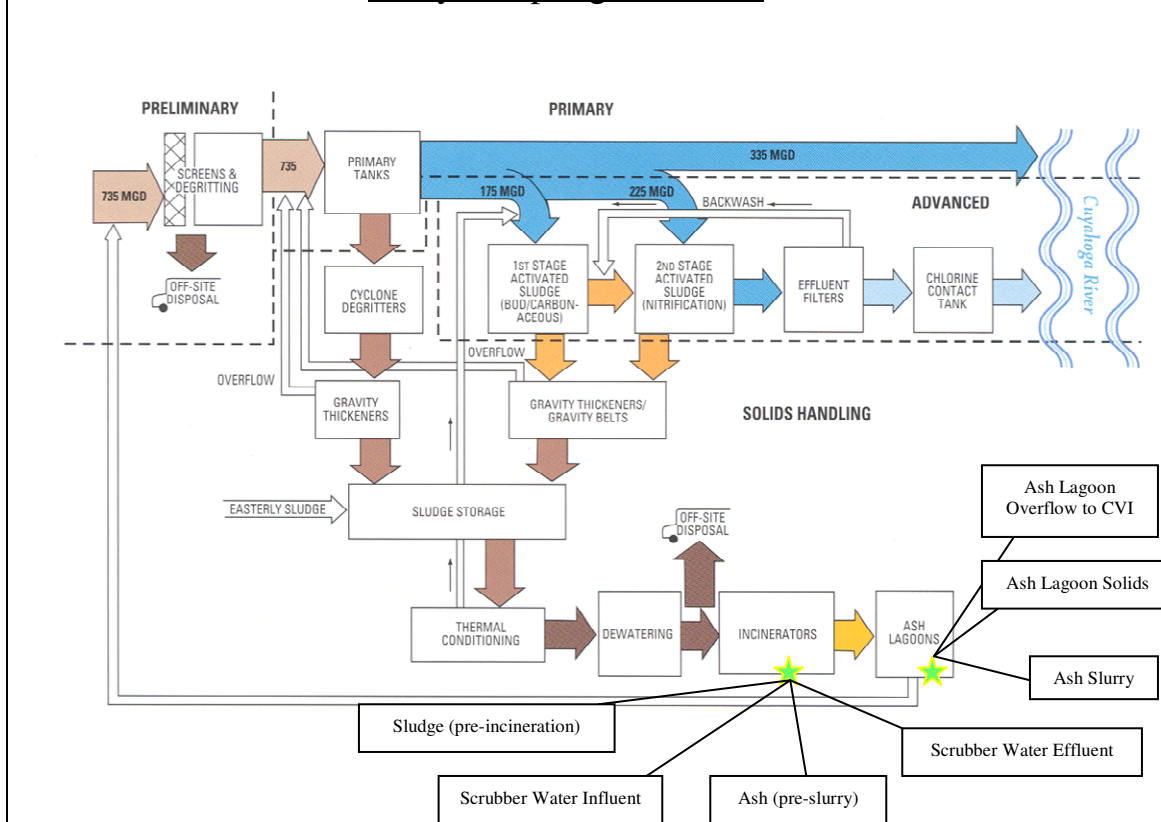
continually exceeded. It is expected that SWWTC effluent will continue to exceed this limit. Additional source identification and subsequent BMP implementation could, in theory, decrease the mercury concentration in the influent and, in turn, decrease the mercury concentration in the effluent. Until that sufficiently occurs to produce an effluent mercury concentration consistently lower than 1.3 ppt, the NEORSD will need to apply for, obtain, and maintain a variance from the numeric effluent limit for mercury. One of the conditions required under a variance is development and implementation of a pollutant minimization program in which all potential sources of mercury are examined with the goal of meeting the numeric effluent limit.

The purpose of this study was to conduct a mercury mass balance within the SWWTC by quantifying the mercury concentrations in multiple wastestreams of the treatment process. It has been hypothesized that wastestreams that return to the SWWTC may contain significant amounts of mercury, thereby increasing mercury concentrations throughout the treatment process. By conducting sampling, including within the solids handling process, decisions could be made as to whether or not these returned wastestreams are significantly affecting mercury concentrations in SWWTC influent and/or effluent. This could thereby direct future NEORSD efforts to reduce/eliminate mercury sources.

Sampling

Currently and throughout the study period, monthly sampling of the raw influent, final effluent and filter cake was and continues to be routinely conducted at SWWTC. In addition to these efforts, samples were taken for this study from the sludge before incineration, the scrubber water influent (sampled once during the study), the scrubber water effluent, the ash (pre-slurry), the ash/scrubber water slurry, ash lagoon solids and the ash lagoon overflow water to the Cuyahoga Valley Interceptor (CVI) (Figure 1).

Figure 1: Southerly Wastewater Treatment Center Mercury Mass Balance Study Sampling Locations



Grit samples were not taken for this study, as the raw influent sampling occurs downstream of the grit removal process and the representativeness of sampling for mercury in grit is questionable, given its extreme heterogeneity.

U.S. EPA Method 1669 clean sampling was performed by trained personnel at each sample location for each weekly sampling event, from July 6, 2005 to September 28, 2005, for a total of 13 sampling events. All 13 sampling events occurred during late morning, between the hours of 9:00am and 12:00pm. This sampling time was concurrent with the monthly U.S. EPA Method 1669 clean sampling performed by NEORSD Analytical Services at the SWWTC raw influent and final effluent. This sampling was done only during weather conditions conducive to clean sampling for U.S. EPA Method 1669, to reduce the possibility of preventable sample contamination. Therefore, these results do not represent effects of wet weather conditions, such as high plant flow or rainwater contamination, but they do represent normal plant conditions.

One duplicate per matrix (aqueous and solid) was taken during each sampling event. Field blanks (one per sample site) and trip blanks (one per sampling event) were used according to U.S. EPA Method 1669. Solids samples were grab samples placed in plastic bags and aqueous samples were grab samples taken directly into the glass sample bottle. Field blanks were filled with blank water at the sampling location and then held at the sampling site for approximately 10 seconds. Samples were labeled with sample tags immediately and then placed on ice.

During a typical sampling event, two to three incinerators of the three available (#2, #3 and #4) were in service. This meant that corresponding samples of sludge, ash and scrubber water effluent would be taken in that order, with approximately 15 minutes between sludge sampling and ash sampling, and with approximately 15 minutes between ash sampling and scrubber water effluent sampling. Ash samples from the ash lagoons were composed of ten grab samples taken around the perimeter of Ash Lagoon B and combined into one sample.

Sample matrices, methods and laboratories used for this study are shown in Table 1.

Table 1			
Sample	Matrix	U.S.EPA Method	Laboratory
Raw Influent	Aqueous	1631	Battelle
Scrubber Water Influent	Aqueous	245.2	NEORSD
Sludge	Solid	245.7	NEORSD
Scrubber Water Effluent	Aqueous	245.2	NEORSD
Ash	Solid	245.7	NEORSD
Scrubber Water Slurry	Aqueous	245.2	NEORSD
Lagoon Ash	Solid	245.7	NEORSD
Overflow to CVI	Aqueous	245.2	NEORSD
Final Effluent	Aqueous	1631	Battelle

Total mercury was determined for all aqueous samples, as was dissolved mercury except in field and trip blanks. Total mercury and percent total solids were measured for all solids samples. Flow/mass measurements were taken, where applicable, for each sampling location during each sampling period.

A mass balance of total mercury and dissolved mercury, from the influent, through the treatment process, to the effluent, through the ash lagoons and including the return ash lagoon overflow water to the CVI, was developed using

results specifically from the Southerly Mercury Mass Balance Study conducted in 2005 and from the following additional sampling efforts:

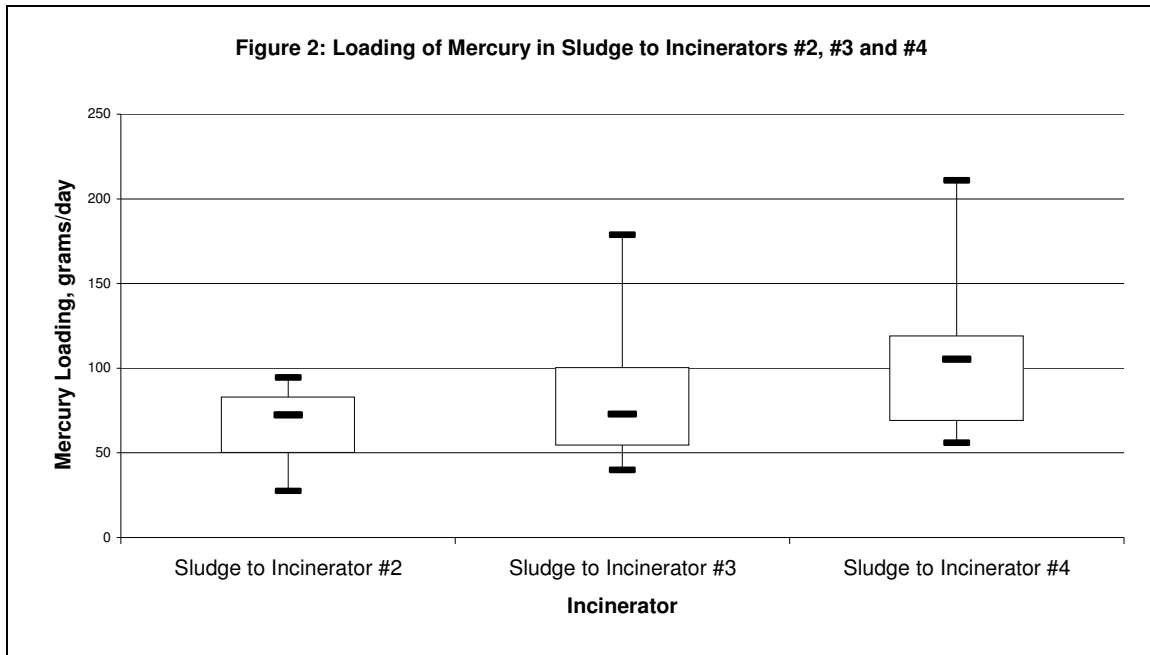
- Total mercury data for Incineration was based on 48 biosolids samples taken weekly in 2005, which are used to determine compliance with the National Emission Standards for Hazardous Air Pollutants (NESHAP) limit. The average mercury concentration of these samples was calculated with the average biosolids feed rate to determine the maximum mercury emissions per day, assuming 100% of the mercury was volatilized and emitted to the atmosphere.
- Total mercury data for Sludge was based on the samples taken for the 13-week mercury mass balance study and was supplemented with 13 SWWTC NPDES permit-required sludge samples taken during the study period.
- Total and dissolved mercury data for the Raw Influent was based on three sets of composite sampling, while Treated Effluent total and dissolved mercury data was based on monthly U.S. EPA Method 1669 sampling by Analytical Services.
- The Easterly Pumped Sludge total mercury was based on average sludge loading for 2005.

Loading throughout the SWWTC was calculated using mercury concentration(s) and flow/mass measurements.

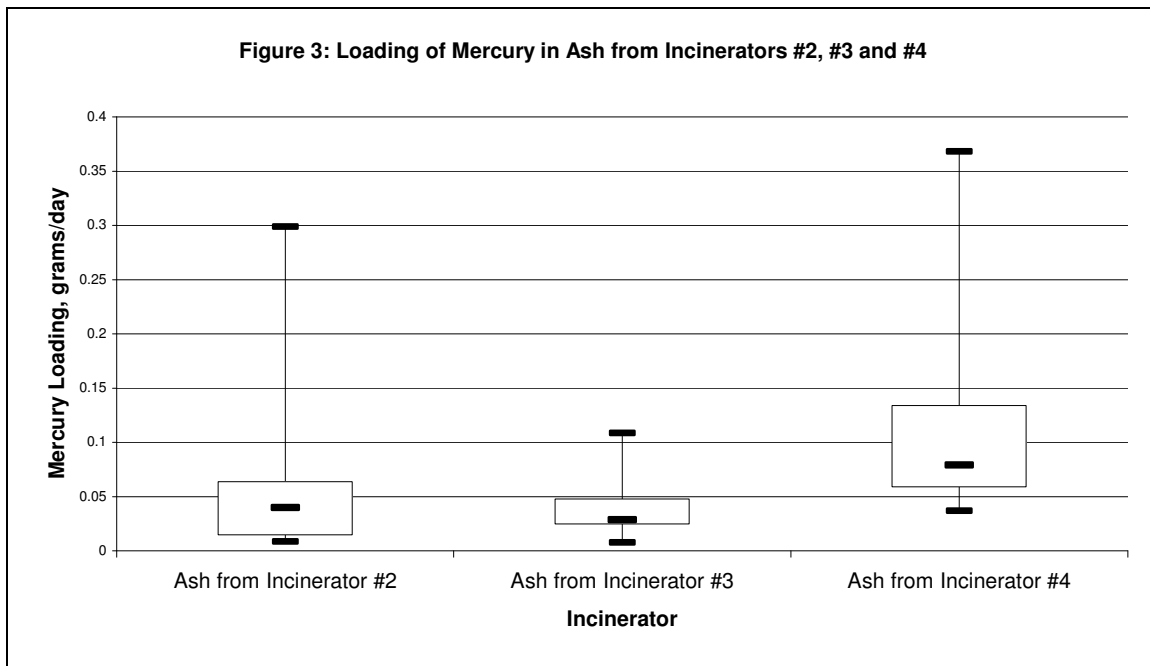
Results

A complete dataset, including sample date, sample location, Total Mercury, Dissolved Mercury (where applicable) and Flow for the project, is located in Appendices A and B.

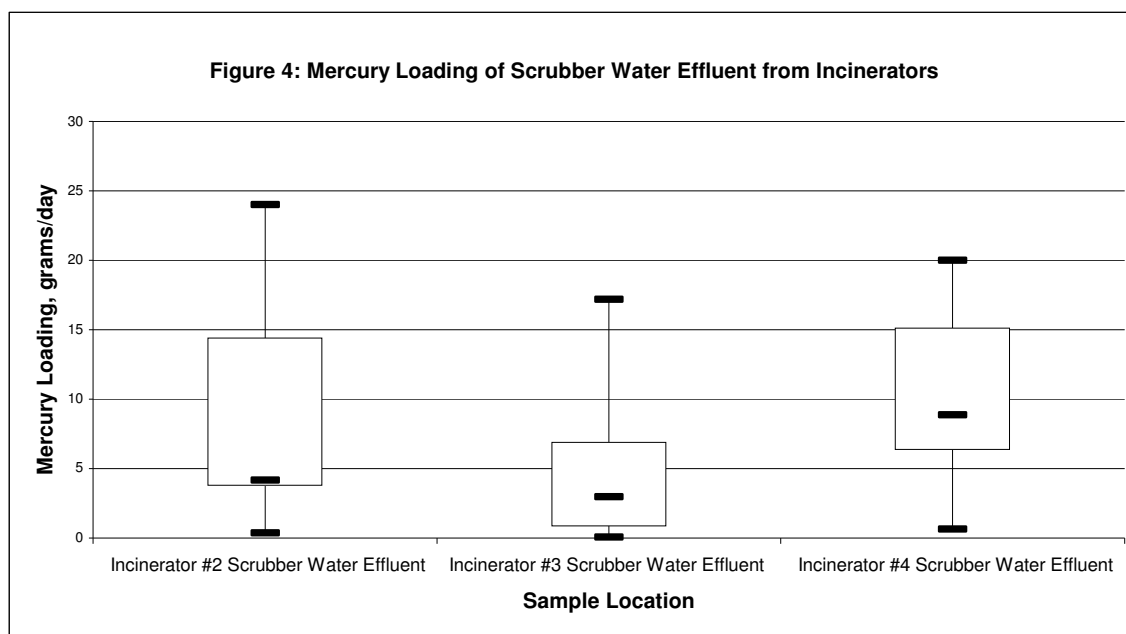
Figure 2 presents the mercury loading in the sludge to each incinerator over the 13-week sampling period. As indicated by the chart in Figure 2, mercury loading in the sludge to Incinerators #2, #3 or #4 did not appear to substantially differ between incinerators during the sampling period.



Similarly, Figure 3 demonstrates that there appears to be no major difference in the mercury loading in the ash produced from each incinerator.

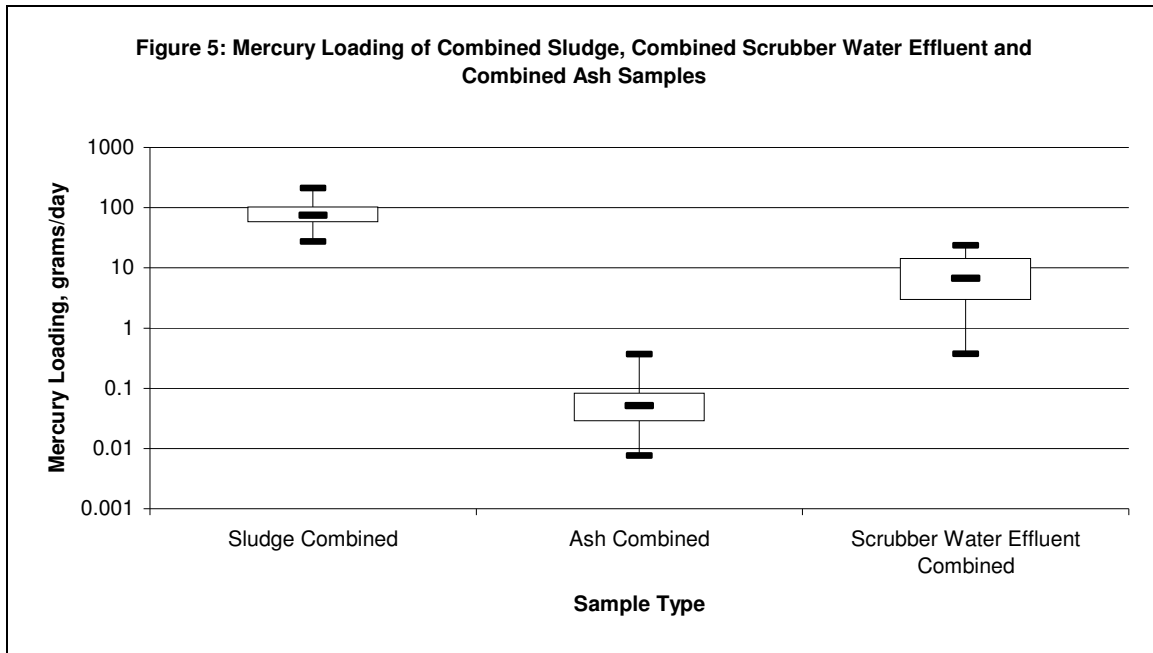


Likewise, Figure 4 shows there appears to be no major difference between incinerators in the mercury loading in the scrubber water effluent from the incinerators.

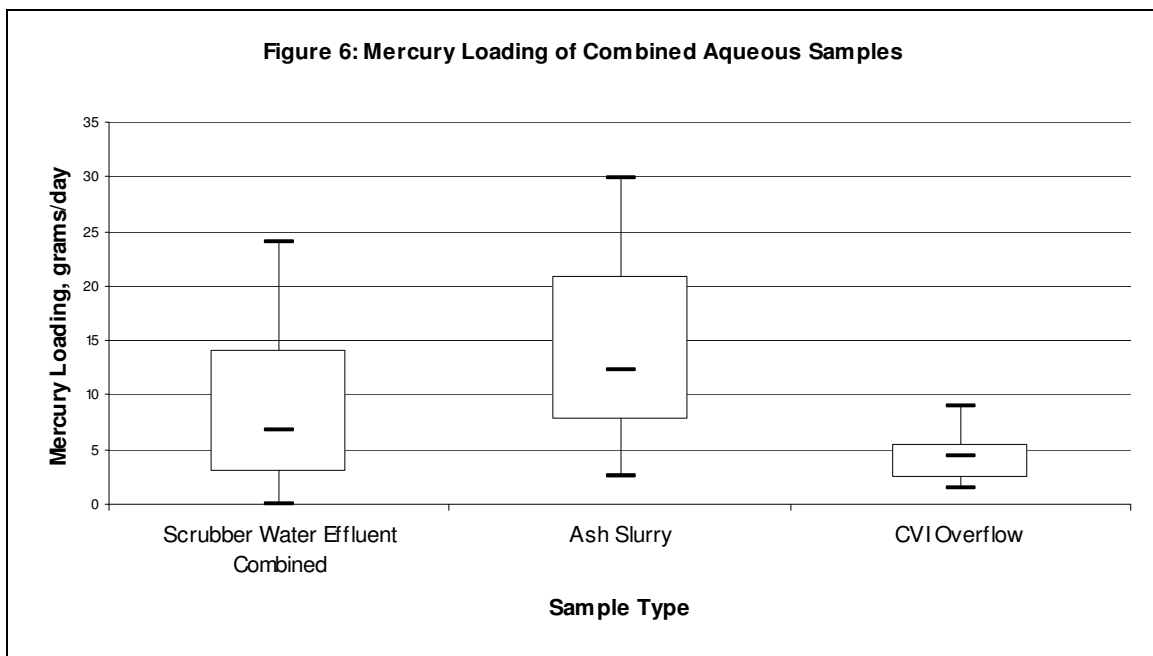


An average mercury concentration from the three incinerators was determined and was calculated with each daily flow to produce an average daily mercury loading. These average daily mercury loadings were then averaged to produce a single average mercury loading. This approach was taken as opposed to determining an average mercury loading from each incinerator.

Figure 5 shows the relationship between the mercury loading in the sludge from all of the incinerators combined, the ash produced from all of the incinerators combined and the scrubber water effluent produced from all of the incinerators combined. The data ranges indicate that the overall performance of each incinerator was similar and that no single incinerator produced ash or scrubber water effluent containing disproportionate amounts of mercury compared to the other incinerators. Figure 5 also depicts the substantial difference in mercury loading between the sludge and the ash.



Mercury loadings from the scrubber water effluent (combined), the ash slurry and the Overflow to CVI are shown in Figure 6. While variation is generally high, the Overflow to CVI had the lowest mercury loading, while the ash slurry had the highest mercury loading. The amount of mercury deposited in the ash lagoon solids can be determined as the difference between the mercury loading of the ash slurry and the mercury loading in the Overflow to CVI.

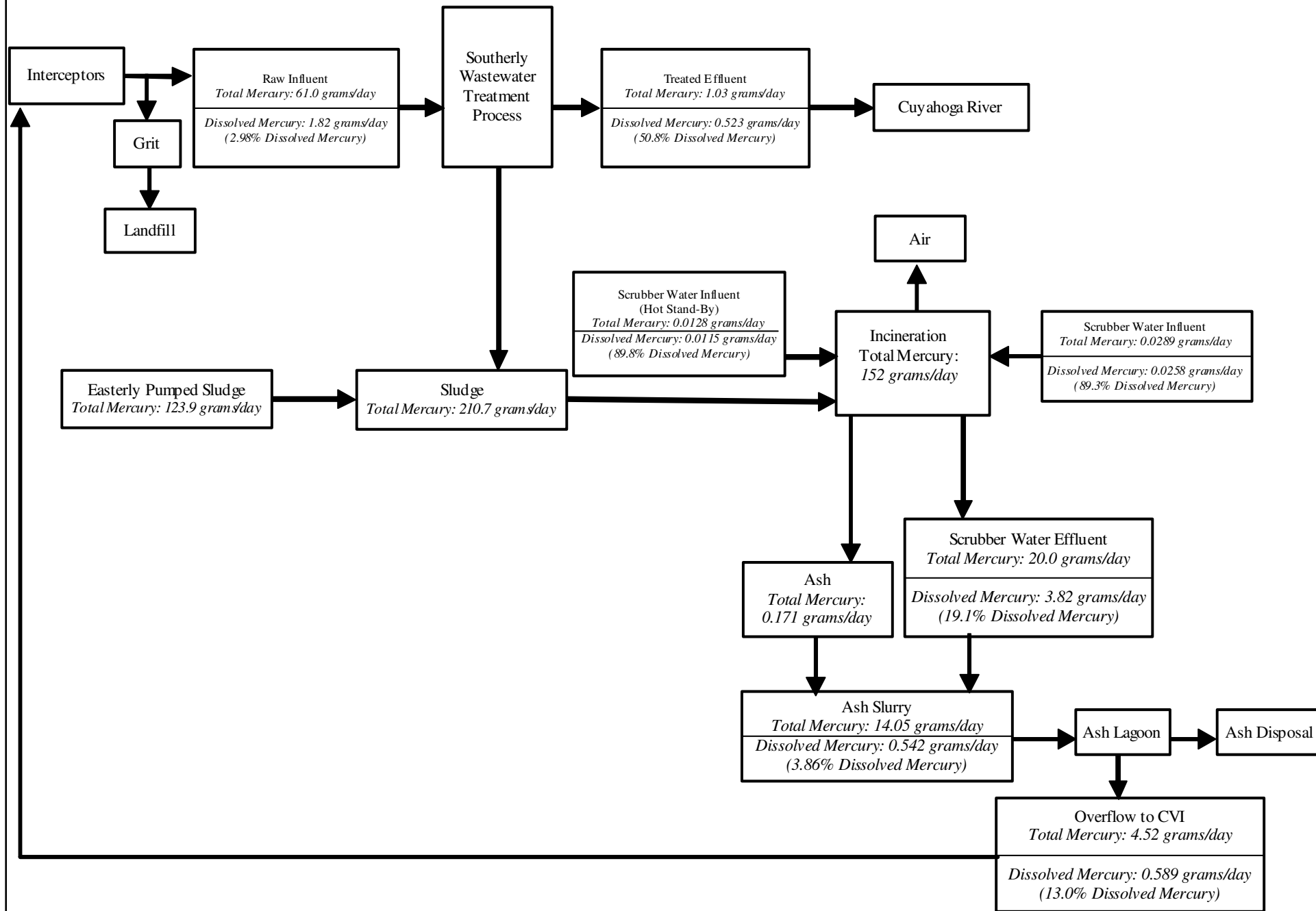


Ash samples from the ash lagoons were also analyzed during this project but were not included in the mass balance, due to the great variation in ash mercury concentrations and the inability to quantify the rate of ash accumulation in each lagoon. Of the 13 composite samples taken, the minimum mercury concentration was 0.036 mg/Kg, the maximum mercury concentration was 0.62 mg/Kg, and the average mercury concentration was 0.21 mg/Kg.

Given the extremely high variability of mercury in raw influent, the initial raw influent samples, collected monthly as grab samples, were determined to be inadequate for calculating an average raw influent mercury loading, as only three grab samples were analyzed throughout the duration of the project. As a grab sample is only a measure of the level of mercury at a single point in time, it is not sufficiently representative of the continuous flow of SWWTC raw influent over extended periods, especially where the variability is high. These sampling “snapshots” are required under the SWWTC NPDES permit, but a more accurate loading would be calculated using data from composite sampling. Therefore, flow-proportionate, composite raw influent sampling was conducted for 13 consecutive days in April 2006, 10 consecutive days in June/July 2006, and 14 days in August/September 2006. Because of the relatively high levels of mercury in raw influent, these additional sampling events did not need to fully comply with U.S. EPA Method 1669 clean sampling protocols and, therefore, they also took into account mercury entering the plant during wet weather events, constituting another respect in which they were more representative than the grab sampling. The resulting average total mercury loading in the raw influent, as determined from the April 2006, June/July 2006 and August/September 2006 sampling events, was 61.0 grams per day, in contrast to the 54.4 grams per day total mercury loading average determined using the monthly grab sampling results.

A mass balance flow chart is presented in Figure 7, where average concentrations and average flows were used to estimate average loadings for total mercury and dissolved mercury (where applicable) for each sample location. The percent of the total mercury composed of dissolved mercury is also indicated for each location, where applicable. The Sludge loading calculation was based on the 13 samples taken specifically for the study and the 13 supplemental samples taken in accordance with the SWWTC NPDES permit. Total mercury data for Incineration was based on 48 biosolids samples taken weekly in 2005, which are used to determine compliance with the NESHAP limit. Raw Influent data was based on the three flow-proportionate, composite sampling episodes previously mentioned. Treated Effluent data was based on the monthly U.S. EPA Method 1669 grab sampling conducted throughout the duration of the study by Analytical Services. The average mercury loading for Easterly Pumped Sludge was based on the monthly samples taken during 2005. All other data was collected specifically for the study as previously discussed in the Sampling section.

Figure 7. Flow Chart of Average Mercury Loading Throughout SWWTC



QA/QC

As earlier stated, field duplicate samples, field blanks and trip blanks were all taken during each sampling event as necessary for U.S. EPA Method 1669. A Relative Percent Difference (RPD) of greater than 20 percent is an indication of unsatisfactory sampling precision and accuracy according to NEORSD Analytical Services protocol and U.S. EPA Method 1631. As seen in Table 2, there were a total of 13 sample events, four of which had solids sample field duplicates with a RPD of greater than 20 percent for total mercury. Because, when analyzing for mercury in solids samples such as sludge, there is typically a high variability in mercury concentration due to the expected heterogeneity of mercury in the matrix, the associated data were not excluded in these cases.

While no aqueous sample field duplicates had a RPD of greater than 20 percent for total mercury, three had a RPD value of greater than 20 percent for dissolved mercury. This exceedence of the RPD limit may be due to the heterogeneous nature of the sample taken. Another source of uncertainty potentially causing the exceedence could be the sample filtration necessary for dissolved mercury analysis. In addition, due to the especially low detection levels for U.S. EPA Method 1631, slight differentiations in sample composition could result in a RPD greater than 20 percent. Therefore, the associated data were not excluded in these cases. All trip blanks had results of less than the detection limit, and one field blank had a result greater than the minimum level of quantitation, 0.5 nanograms per liter, but it was less than one-fifth the level in the associated sample, and therefore the sample remains usable.

Table 2. Relative Percent Difference Values for Duplicate Samples									
Date	Solids Samples			Aqueous Samples					
	Total Mercury			Total Mercury			Dissolved Mercury		
	Sample	Duplicate	RPD	Sample	Duplicate	RPD	Sample	Duplicate	RPD
7/6/2005	0.0006	0.0005	18.18	0.25	0.24	4.08	38.7	40.9	5.53
7/13/2005	1.22	1.08	12.17	0.74	0.78	5.26	58	58	0.00
7/20/2005	3.47	1.63	72.16	1.12	1.09	2.71	0.25	0.26	3.92
7/26/2005	1.52	1.37	10.38	1.74	1.71	1.74	0.52	0.47	10.10
8/2/2005	0.38	0.3	23.53	1.62	1.54	5.06	0.06	0.079	27.34
8/10/2005	4.18	3.86	7.96	4.52	3.9	14.73	0.35	0.28	22.22
8/17/2005	0.22	0.25	12.77	0.38	0.38	0.00	63	57	10.00
8/23/2005	0.0043	0.00412	4.28	2.54	2.64	3.86	0.064	0.073	13.14
8/31/2005	7.3	3.35	74.18	0.62	0.63	1.60	0.095	0.097	2.08
9/7/2005	3.04	2.78	8.93	4.76	4.94	3.71	1.14	1.16	1.74
9/13/2005	2.84	2.73	3.95	0.8	0.8	0.00	0.12	0.1	18.18
9/21/2005	1.92	2.46	24.66	0.48	0.48	0.00	0.071	0.073	2.78
9/28/2005	1.69	1.39	19.48	6.04	5.86	3.03	0.97	1.27	26.79

Conclusions

After constructing the mass balance of mercury throughout the wastewater treatment process, using raw influent and final effluent data from the April 2006, June/July 2006 and August/September 2006 composite sampling episodes, data showed that the average total mercury loading attributable to the raw influent was 61.0 grams/day. An average mercury loading of 123.9 grams/day from the Easterly Pumped Sludge (EPS) enters the SWWTC treatment process at the gravity thickeners. Therefore, the sludge going to the incinerators, incorporating both the raw influent and the EPS, results in an average total mercury loading of 184.9 grams/day before subtracting the effluent loading. This indicates a relatively accurate mercury mass balance as the sludge sampled prior to incineration, which would include the EPS and solids from the raw influent, resulted in an average mercury loading of 210.7 grams/day.

The relatively large loading of mercury from the EPS may be attributed to the ongoing cleaning of the Easterly Interceptor. The process of cleaning the Easterly Interceptor results in the disturbance of accumulated sediments in the bottom of the sewer. In order to conduct a mass balance during more typical plant conditions, the study would need to be repeated in the future, once activity from all cleaning projects within the Easterly service area has ceased. In addition, future sampling should include grit analysis to determine the potential loading of mercury to the environment, via landfills, due to the grit disposal.

As seen in Figure 7, the majority of mercury is lost through the incineration process and released to the atmosphere. Nonetheless, regulatory requirements necessitate that opportunities to reduce mercury in the treated effluent remain a priority.

The following information is based on the April 2006, June/July 2006 and August/September 2006 composite sampling events. Assuming that the dissolved fraction of each contributing flow's mercury remains relatively constant after their confluence (i.e., dissolved mercury remains dissolved, and particulate mercury remains particulate), the following estimates can be made:

- 0.97% of the total mercury in the raw influent is attributable to the dissolved mercury coming from the CVI Overflow.
- 7.4% of the total mercury in the raw influent is attributable to the total mercury coming from the CVI Overflow.
- 32% of the dissolved mercury in the raw influent is attributable to the dissolved mercury coming from the CVI Overflow.

- 57% of the total mercury in the treated effluent is attributable to the dissolved mercury coming from the CVI Overflow.

Although based on an admittedly dubious assumption, these estimates nonetheless suggest that future mercury reduction opportunities may include the implementation of additional cost-effective practices and/or control technologies for specific wastestreams, biosolids and/or air emissions. Mercury reduction throughout the SWWTC may be possible specifically within the incineration process and/or within the return flow from the ash lagoon overflow back to the influent via the CVI. The feasibility of rerouting the return flow from the CVI Overflow and/or implementing additional/alternative treatment for it should be investigated to possibly reduce the dissolved mercury in the influent, and ultimately, the total mercury in the final effluent. Further investigation should also include the potential impact of the Zimpro return wastewater and the effect of other return wastestreams within the treatment process.

cc: R. Connelly
F. Foley
K. Linn
S. Zych
C. Soltis-Muth
E. Toot-Levy
E. Hinton

	APPENDIX A Aqueous Samples																				
	Scrubber Water from Incinerator 2		Scrubber Water from Incinerator 2	Scrubber Water from Incinerator 3		Scrubber Water from Incinerator 3	Scrubber Water from Incinerator 4		Scrubber Water from Incinerator 4	Influent Hg	Effluent Hg	Scrubber Water Influent, ng/L	Scrubber Water from Incinerators on Hot Stand-By, MGD	Scrubber Water Influent to Scrubbers, MGD	Ash/Scrubber Water Slurry Hg Concentration, ng/L	Ash/Scrubber Water Slurry Flow, MGD	Overflow to CVI Hg Concentration, ng/L	Overflow to CVI Hg Flow, MGD			
	Hg Concentration ng/L		Effluent Flow MGD	Hg Concentration ng/L		Effluent Flow MGD	Hg Concentration ng/L		Effluent Flow MGD	Concen tration, ng/L	Concen tration, ng/L										
Date	total	dissolved		total	dissolved		total	dissolved		total	total	total	dissolved		total	dissolved	total	dissolved			
7/6/2005	1030	220	1.00944	1280	110	0.97776				137				0.98784	1.99	690	35.2	2.33	250	38.7	2.99
7/13/2005	1080	390	0.9288	350	69	0.89712	1390	240	0.94464					2.77		740	58	2.12	210	36	2.96
7/20/2005	1120	250	1.04256	150	43.4	0.91872	1960	200	0.99648					2.96		920	24	2.33	170	28.6	3.02
7/26/2005	940	360	1.05264				1740	520	1.01376					0.9648	2.07	860	86	2.33	250	49.1	3.07
8/2/2005				2390	300	1.01808	2980	400	1.0512		844			1.0392	2.07	1620	60	3.31	210	21.2	3.05
8/10/2005				4520	350	1.008	4650	690	1.09008					2.1		3390	57	2.33	750	63	2.10
8/17/2005	190	84	1.01088				170	7.03	1.0224					0.9792	2.03	290	57	2.39	380	63	3.01
8/23/2005	6180	810	1.02096				2770	610	0.95472					1.00512	1.98	2540	64	2.16	420	48.1	2.98
8/31/2005	4240	1220	1.03392				5060	1150	1.0512					2.09		3500	91	1.58	620	95	2.09
9/7/2005	99	23.6	1.0008				4760	1140	1.01376			3.41	3.05	0.99792	2.01	2110	60	1.70	900	98	2.01
9/13/2005				800	120	0.9792	790	110	0.9936		91.9			1.97		420	18.4	2.28	130	22.3	3.00
9/21/2005	1950	1060	1.00224	480	150	1.02816	2070	300	0.99792					3.03		1360	130	2.39	480	71	3.08
9/28/2005	6040	970	1.00368				3690	730	1.0152					0.99792	2.02	2890	83	2.16	780	89	3.02

Appendix B Solids Samples												
Date	Ash from Incinerator 2 Hg Concentration, mg/kg (dry weight)	Ash from Incinerator 2 Production Rate, tons of ash/day	Ash from Incinerator 3 Hg Concentration, mg/kg (dry weight)	Ash from Incinerator 3 Production Rate, dry tons/day	Ash from Incinerator 4 Hg Concentration, mg/kg (dry weight)	Ash from Incinerator 4 Production Rate, dry tons/day	Sludge from Incinerator 2 Hg Concentration, mg/kg (dry weight)	Sludge from Incinerator 2 Production Rate, dry tons/day	Sludge from Incinerator 3 Hg Concentration, mg/kg (dry weight)	Sludge from Incinerator 3 Production Rate, dry tons/day	Sludge from Incinerator 4 Hg Concentration, mg/kg (dry weight)	Sludge from Incinerator 4 Production Rate, dry tons/day
7/6/2005	0.00292	11.9	0.0006	14.1			1.02	29.8	1.25	35.2		
7/13/2005	0.00103	13.1	0.00183	15.6	0.00274	15.6	1.22	34.3	1.48	41.1	1.5	41.1
7/20/2005	0.00379	19.7	0.00586	7.4	0.00302	26.9	1.79	45.9	3.47	17.1	1.6	62.7
7/26/2005	0.00119	19.2			0.00357	19.2	1.94	42.2			1.52	42.2
8/2/2005			0.0054	22.2	0.01	22.2			2.68	40.3	1.9	40.3
8/10/2005			0.00101	25.5	0.00576	25.5			4.18	47.2	4.93	47.2
8/17/2005	0.017	19.4			0.017	23.9	2.29	34			3.04	41.9
8/23/2005	0.0043	18.1			0.00431	19.1	2.26	42			2.79	44.4
8/31/2005	0.00354	16.1			0.0073	20.7	3.16	33			3.58	42.3
9/7/2005	0.00117	8			0.0071	20.5	3.33	15.2			3.04	39
9/13/2005			0.00273	22.8	0.00178	22.8			2.84	40	2.84	40
9/21/2005	0.00292	18.1	0.00163	19.4	0.00474	19.4	1.92	36.2	2.07	38.8	1.92	38.8
9/28/2005	0.00169	8			0.00252	21	2.47	41.5			3.44	41.5

APPENDIX F

DESCRIPTION OF QUALITY CONTROL SAMPLES

F.1 Laboratory Quality Control

The laboratory and field quality control samples detailed below are common to analysis of total mercury in biosolids. However, the QC samples actually employed should reflect the requirements of the analytical technique and/or instrument manufacturer's specifications.

F.1.1 Standards

All calibration standards should be traceable to a certified standard obtained from a reputable organization. If traceable standards are not available, procedures should be implemented to standardize the utilized calibration solutions (e.g., comparison to a certified reference material (CRM – see below). Standardization of calibration solutions should be thoroughly documented and acceptable only when pre-certified standard solutions are not available.

Working standards are dilutions of stock standards prepared for daily use in the laboratory. Working standards are used to calibrate instruments or prepare matrix spikes, and may be prepared at several different dilutions from a common stock standard. Working standards are diluted with solutions that ensure the stability of the target analyte. Preparation of the working standard should be thoroughly documented such that each working standard is traceable back to its original stock standard. Finally, the concentration of all working standards should be verified by analysis prior to use in the laboratory.

F.1.2 Instrument Calibration

Prior to sample analysis, utilized instruments should be calibrated following the procedures outlined in the relevant analytical method or manufacturer's specifications. Each method specifies acceptance criteria that demonstrate instrument stability and an acceptable calibration. If instrument calibration does not meet the specified acceptance criteria, the analytical process is not in control and should be halted. The instrument should be successfully recalibrated before samples may be analyzed.

Calibration curves should be established for each analyte covering the range of expected sample concentrations. Only data that result from quantification within the demonstrated working calibration range may be reported unflagged by the laboratory. Quantification based on extrapolation is not acceptable. Data reported outside of the calibration range should be flagged

as “Detected not Quantified”. Alternatively, if the instrumentation is linear over the concentration ranges to be measured in the samples, the use of a calibration blank and one single standard that is higher in concentration than the samples may be appropriate. Samples outside the calibration range will be diluted or concentrated, as appropriate, and reanalyzed.

F.1.3 Initial Calibration Verification

The initial calibration verification (ICV) is a mid-level standard analyzed immediately following the calibration curve. The source of the standards used to calibrate the instrument and the source of the standard used to perform the ICV must be independent of one another. This is usually achieved by the purchase of standards from separate vendors. Since the standards are obtained from independent sources and both are traceable, analyses of the ICV functions as a check on the accuracy of the standards used to calibrate the instrument. The ICV is not a requirement of all methods, particularly if other checks on analytical accuracy are present in the sample batch (e.g., the analysis of reference materials).

F.1.4 Continuing Calibration Verification

Continuing calibration verification (CCV) standards are mid-level standards analyzed at specified intervals during the course of the analytical run. CCVs are used to monitor sensitivity changes in the instrument during analysis. In order to properly assess these sensitivity changes, the standards used to perform CCVs should be from the same set of working standards used to calibrate the instrument. Use of a second source standard is not necessary for CCV standards, since other QC samples are designed to assess the accuracy of the calibration standards. Analysis of CCVs using the calibration standards limits this QC sample to assessing only instrument sensitivity changes. If a CCV falls outside the acceptance limits, the analytical system is not in control, and requires immediate corrective action.

Data obtained while the instrument is out of control is generally considered not reportable, and all samples analyzed during this period should be reanalyzed. If reanalysis is not an option, the original data should be flagged with the appropriate qualifier and reported. A narrative should be submitted listing the results that were generated while the instrument was out of control, in addition to corrective actions that were applied.

F.1.5 Laboratory Blanks

Laboratory blanks (also called extraction blanks, procedural blanks, or method blanks) are used to assess the background level of the target analyte resulting from sample preparation and analysis. Laboratory blanks are carried through precisely the same procedures as the field samples. It is recommended that a minimum of one laboratory blank be prepared and analyzed in every analytical batch (20 or fewer field samples). Some methods may require more than one laboratory blank with each analytical run.

Improvements in analytical sensitivity have pushed detection limits down to the point where some amount of analyte will be detected in even the cleanest laboratory blanks. The magnitude of the blanks must be evaluated against the concentrations of the samples being analyzed and against project objectives. Blanks that are too high require corrective action to bring the concentrations down to acceptable levels. This may involve changing reagents, cleaning equipment, or even modifying the utilized methods.

F.1.6 Reference Materials and Demonstration of Laboratory Accuracy

Evaluation of the accuracy of laboratory procedures is achieved through the preparation and analysis of reference materials with each analytical batch. Ideally, the reference materials selected are similar in matrix and concentration range to the samples being prepared and analyzed. The accuracy of the results is assessed through the calculation of a percent recovery.

Where:

$$\% \text{ recovery} = \frac{V_{\text{analyzed}}}{V_{\text{certified}}} \times 100$$

V_{analyzed} : the analyzed concentration of the reference material

$V_{\text{certified}}$: the certified concentration of the reference material

The accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the target analytes. When possible, reference materials that have certified values for the target analytes should be used. This is not always possible, and often times certified reference values are not available for all target analytes. Many reference materials have both certified and non-certified (or reference) values listed on the certificate of analysis. Certified reference values are clearly distinguished from the non-certified reference values on the certificate of analysis.

F.1.7 Reference Materials vs. Certified Reference Materials

The distinction between a reference material and a certified reference material does not involve how the two are prepared, rather with the way that the reference values were established. Certified values are determined through replicate analyses using two independent measurement techniques for verification. The certifying agency may also provide “non-certified or “reference” values for other target analytes. Such values are determined using a single measurement technique that may introduce bias.

When available, it is preferable to use reference materials that have certified values for all target analytes. This is not always an option, and therefore it is acceptable to use materials that have reference values for these analytes.

Note: Standard Reference Materials (SRMs) are essentially the same as CRMs. The term “Standard Reference Material” has been trademarked by the National Institute of Standards and Technology (NIST), and is therefore used only for reference materials distributed by NIST.

F.1.8 Laboratory Control Samples

While reference materials are not available for all analytes, a way of assessing the accuracy of an analytical method is still required. Laboratory control samples (LCSs) provide an alternate method of assessing accuracy. An LCS is a specimen of known composition prepared using contaminant-free reagent water or an inert solid spiked with the target analyte at the midpoint of the calibration curve or at the level of concern. The LCS must be analyzed using the same preparation, reagents, and analytical methods employed for regular samples. If an LCS needs to be substituted for a reference material, the acceptance criteria are the same as those for the analysis of reference materials.

F.1.9 Prioritizing Certified Reference Materials, Reference Materials, and Laboratory Control Samples

Certified reference materials, reference materials, and laboratory control samples all provide a method to assess the accuracy at the mid-range of the analytical process. However, this does not mean that they can be used interchangeably in all situations. When available, projects should require the analysis of one certified reference material per analytical batch (20 field samples). Certified values are not always available for all target analytes. If no certified reference material exists, reference values may be used. If no reference material exists for the target analyte, an LCS must be prepared and analyzed with the sample batch as a means of assessing accuracy.

The hierarchy is as follows: analysis of a CRM is favored over the analysis of a reference material, and analysis of a reference material is preferable to the analysis of an LCS. It must be stressed that substitution of an LCS is not acceptable if a certified reference material or reference material is available.

F.2 Matrix QC

F.2.1 Matrix Spikes

A matrix spike (MS) is prepared by adding a known concentration of the target analyte to a field sample, which is then subjected to the entire analytical procedure. If the ambient concentration of the field sample is known, the amount of spike added is within a specified range (2-5 times the ambient concentration). Matrix spikes are analyzed in order to assess the magnitude of matrix interference and bias present. Because matrix spikes are analyzed in pairs, the second spike is called the matrix spike duplicate (MSD). The MSD provides information regarding the precision of the matrix effects. Both the MS and MSD are split from the same original field sample.

The success or failure of the matrix spikes is evaluated by calculating the percent recovery.

Where:

$$\% \text{ recovery} = \frac{(V_{MS} - V_{\text{ambient}})}{V_{\text{spike}}} \times 100$$

v_{MS} : the concentration of the spiked sample

$v_{ambient}$: the concentration of the original (unspiked) sample

v_{spike} : the concentration of the spike added

In order to properly assess the degree of matrix interference and potential bias, the spiking level should be approximately 2-5 times the ambient concentration of the spiked sample. If the MS or MSD is spiked too high or too low relative to the ambient concentration, the calculated recoveries are no longer an acceptable assessment of analytical bias. In order to establish spiking levels prior to analysis of samples, the laboratories should review any relevant historical data. In many instances, the laboratory will be spiking the samples blind and will not meet a spiking level of 2-5 times the ambient concentration. However, the results of affected samples will not be automatically rejected.

In addition to the recoveries, the relative percent difference (RPD) between the MS and MSD is calculated to evaluate how matrix affects precision.

$$RPD = \left| \frac{(v_{MS} - v_{MSD})}{mean} \right| \times 100$$

There are two different ways to calculate this RPD, depending on how the samples are spiked.

- 1) The samples are spiked with the same amount of analyte. In this case,

v_{MS} : the concentration for the matrix spike

v_{MSD} : the concentration of the matrix spike duplicate

mean: the mean of the two concentrations ($MS + MSD$)

- 2) The samples are spiked with different amounts of analyte. In this case,

v_{MS} : the recovery associated with the matrix spike

v_{MSD} : the recovery associated with matrix spike duplicate

mean: the mean of the two recoveries ($recovery_{MS} + recovery_{MSD}$)

The MQO for the RPD between the MS and MSD is the same regardless of the method of calculation.

Recovery data for matrix spikes provides a basis for determining the prevalence of matrix effects in the samples collected and analyzed. If the percent recovery for any analyte in the MS or MSD is outside of the limits specified, the chromatograms (in the case of trace organic analyses) and raw data quantitation reports should be reviewed. The data should be scrutinized for evidence of sensitivity shifts (indicated by the results of the CCVs) or other potential problems with the analytical process. If other QC samples analyzed with the batch (reference materials or LCSs) are in control, matrix effects may be the source of the problem. If the

standard used to spike the samples is different from the standard used to calibrate the instrument, it should be checked for accuracy prior to attributing poor recoveries to matrix effects.

F.2.2 Laboratory Duplicates

In order to evaluate the precision of an analytical process, a field sample is selected and digested or extracted in duplicate. Following analysis, the results from the duplicate samples are evaluated by calculating the RPD.

$$RPD = \left| \frac{(v_{\text{sample}} - v_{\text{duplicate}})}{\text{mean}} \right| \times 100$$

Where:

v_{sample} : the concentration of the original sample digest

$v_{\text{duplicate}}$: the concentration of the duplicate sample digest

mean: the mean concentration of both sample digests

Specific requirements pertaining to the analysis of laboratory duplicates vary depending on the type of analysis.

In order for the RPD to be an indicator of precision, the concentration of the duplicate samples must be higher than the detection limit of the utilized analytical method (typically 5 times the MDL). If the sample concentration is low, and if the difference between duplicate concentrations is approximately 3-5 times the MDL, the resulting RPD may be higher than the associated MQO. When this occurs, unacceptable results should be appropriately flagged.

F.2.3 Laboratory Duplicates vs. Matrix Spike Duplicates

Although the laboratory duplicate and matrix spike duplicate both provide information regarding precision, they are unique measurements. Laboratory duplicates provide information regarding the precision of laboratory procedures. The matrix spike duplicate provides information regarding how the matrix of the sample affects both the precision and bias associated with the results. It also determines if the matrix affects the results in a reproducible manner. Because the two concepts cannot be used interchangeably, it is insufficient to analyze only an MS/MSD when a laboratory duplicate is required.

F.2.4 Replicate Analyses

Replicate analyses are distinguished from duplicate analyses based simply on the number of involved analyses. Duplicate analyses refer to two sample digests, while replicate analyses refer to three or more. Analysis of replicate samples is important to establish a consistent method of evaluating these analyses. The method of evaluating replicate analysis is by calculation of the relative standard deviation (RSD). Expressed as a percentage, the RSD is calculated as follows:

$$RSD = \frac{\text{Stdev}(v_1, v_2, \dots, v_n)}{\text{mean}} \times 100$$

Where:

$\text{Stdev}(v_1, v_2, \dots, v_n)$: the standard deviation of the values (concentrations) of the replicate analyses.

mean: the mean of the values (concentrations) of the replicate analyses.

F.2.5 Dilution of Samples

Final reported results must be corrected for dilution carried out during the process of analysis. In order to evaluate the QC analyses associated with an analytical batch, corresponding batch QC samples should be analyzed at the same dilution factor. For example, the results used to calculate the results of matrix spikes should be derived from results for the native sample, matrix spike, and matrix spike duplicate analyzed at the same dilution. Results derived from samples analyzed at different dilution factors should not be used to calculate QC results.

F.3 Field Quality Control

Specific field quality control samples may also be required by the method or SOP selected for sample collection and analysis. If MQOs conflict with those prescribed in the utilized analytical method, the more rigorous of the objectives should be met.

F.3.1 Travel Blanks

Travel blanks are used to determine if there is any cross-contamination of volatile constituents between sample containers during shipment from the field to the laboratory. Travel blanks are not required unless explicitly required by the utilized analytical method.

F.3.2 Equipment Blanks

Equipment blanks are generated by the personnel responsible for cleaning sampling equipment. Equipment blanks must be analyzed before the equipment is shipped to the sampling site. In order to accommodate any necessary corrective action, equipment blank results must be available well in advance of the sampling event.

To ensure that sampling equipment is contaminant-free, water known to be low in the target analyte(s) must be processed through the equipment as during sample collection. The specific type of water used for blanks (e.g., American Society for Testing and Materials (ASTM) Type II water, Deionized (DI) water) is selected based on the information contained in the relevant sampling or analysis methods. The water should be collected in an appropriate sample container, preserved, and analyzed for the target analytes (in other words, treated as an actual sample).

The inclusion of field blanks is dependent on the requirements specified in the relevant MQO tables, or in the sampling method. Typically, equipment blanks are collected when new equipment, equipment that has been cleaned after use at a contaminated site, or equipment that is not dedicated for surface water sampling is used.

F.3.3 Field Blanks

A field blank is collected to assess potential sample contamination levels that occur during field sampling activities. Field blanks are taken to the field, transferred to the appropriate container, preserved (if required by the method), and treated the same as the corresponding sample type during the course of a sampling event. The inclusion of field blanks is dependent on the requirements specified in the sampling method.

Field blanks for other media and analytes should be conducted upon initiation of sampling. If field blank performance is acceptable, further collection and analysis of field blanks for these other media and analytes need only be performed on an as-needed basis or during field performance audits.

The water used for field blanks must be free of target analyte(s) and appropriate for the analysis being conducted. For trace metals samples, DI water that has been confirmed to be low in metals must be used.

F.3.4 Field Duplicates

Field samples collected in duplicate provide precision information as it pertains to the sampling process. The duplicate sample should be collected in the same manner and as close in time as possible to the original sample. This effort is an attempt to examine field homogeneity as well as sample handling, within the limits and constraints of the situation. The precision of field duplicates is evaluated by calculating the RPD between the involved samples.

$$RPD = \left| \frac{(V_{\text{field sample}} - V_{\text{field duplicate}})}{\text{mean}} \right| \times 100$$

Where:

$V_{\text{field sample}}$: the concentration of the original field sample

$V_{\text{field duplicate}}$: the concentration of the field duplicate

mean: the mean of the concentrations of both field samples

F.4 List of Abbreviations and Acronyms

CCV	Continuing Calibration Verification
CRM	Certified Reference Material
DI	Deionized
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
MDL	Method Detection Limit
ML	Minimum Level
MQO	Measurement Quality Objective
MS	Matrix Spike
MSD	Matrix Spike Duplicate
PI	Principle Investigator
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
U.S. EPA	U.S. Environmental Protection Agency

F.5 Resources and Web Links

F.5.1 EPA Quality Assurance/Quality Control Links

- ◆ **EPA Requirements for Quality Management Plans; EPA QA/R-2:**
<http://www.epa.gov/quality/qs-docs/r2-final.pdf>
- ◆ **Guidance for the Data Quality Objectives Process; EPA QA/G-4:**
<http://www.epa.gov/quality/qs-docs/g4-final.pdf>
- ◆ **EPA Region Nine Guidance for Quality Assurance Program Plans:**
http://www.epa.gov/region09/qa/pdfs/qaprp_guidance3.pdf
- ◆ **Guidance for Quality Assurance Project Plan; EPA QA/G-5:**
<http://www.epa.gov/quality/qs-docs/g5-final.pdf>
- ◆ **EPA Requirements for Quality Assurance Project Plan; EPA QA/R-5:**
<http://www.epa.gov/quality/qs-docs/r5-final.pdf>
- ◆ **Guidance for Preparing Standard Operating Procedure; EPA QA/G-6:**
<http://www.epa.gov/quality/qs-docs/g6-final.pdf>
- ◆ **Guidance on Environmental Data Verification and Validation; EPA QA/G-8:**
<http://www.epa.gov/quality/qs-docs/g8-final.pdf>
- ◆ **Guidance for Data Quality Assessment: Practical Methods for Data Analysis; EPA QA/G-9:** *<http://www.epa.gov/quality/qs-docs/g9-final.pdf>*
- ◆ **Guidance on Developing a Training Program for Quality Systems; EPA QA/G-10:**
<http://www.epa.gov/quality/qs-docs/g10-final.pdf>
- ◆ **EPA Training Courses on Quality Assurance:**
<http://www.epa.gov/quality/trcourse.html>

◆ F.5.2 Methods Selection Links

- **National Water Quality Monitoring Council, Methods and Data Comparability Board:**
<http://wi.water.usgs.gov/methods/index.html>
- **Guide to Method Flexibility and Approval of EPA Water Methods:**
http://www.swrcb.ca.gov/swamp/docs/guidelines_pbms_program.pdf
- **National Environmental Methods Index (NEMI):**
http://www.nemi.gov/servlet/page?_pageid=179&_dad=portal30&_schema=PORTAL30
- **American National Standards Institute:**
<http://www.ansi.org/>
- **International Atomic Energy Agency:**
<http://www.iaea.org/>
- **Shareware: Visual Sample Plan:**
<http://dgo.pnl.gov/vsp/>

APPENDIX G

BIOSOLIDS INCINERATORS LOCATIONS (2004)

STATE	Electric Arc	Fluidized Bed	Multiple Hearth	Total	No. of POTWs that Incinerate
Alaska	1	1	1	3	3
California	0	0	4	4	2
Connecticut	0	2	7	9	5
Georgia	0	0	8	8	4
Indiana	0	0	4	4	1
Iowa	0	2	1	3	2
Kansas	0	2	0	2	1
Louisiana	0	1	1	2	1
Maryland	0	2	2	4	2
Massachusetts	0	2	4	6	3
Michigan	0	1	25	26	9
Minnesota	0	0	8	8	2
Missouri	0	2	13	15	5
New Hampshire	0	1	0	1	1
New Jersey	0	11	8	19	10
New York	0	13	25	38	20
North Carolina	0	2	1	3	3
Ohio	0	1	28	29	12
Pennsylvania	0	5	8	13	10
Puerto Rico	0	0	1	1	1
Rhode Island	0	0	4	4	3
South Carolina	0	1	3	4	3
Virginia	0	2	16	18	9
Washington	0	4	2	6	5
West Virginia	0	1	0	1	1
Wisconsin	0	0	3	3	2
TOTAL	1	56	177	234	120

APPENDIX H

A PRIMER ON BIOSOLIDS MANAGEMENT AND INCINERATION

Background

16,500 publicly owned municipal wastewater treatment plants (WWTPs) in the United States treat 40 billion gallons of wastewater each day.^{1,2} Organic matter removed from the wastewater is processed (e.g., digested; chemically conditioned with lime, polymers, and other products; thermally conditioned) and dewatered by vacuum filters, plate and frame presses, belt filter presses or centrifuges to produce biosolids (sewage sludge).

Biosolids Management Practices in the United States

U.S. EPA estimates that a total of 5-6 million dry metric tons (5.5-6.6 million dry U.S. tons) of biosolids are generated each year in the United States, and managed in the following manner:

1. Land Application, by which biosolids are applied to agricultural land or reclamation sites.
2. Distribution and Marketing, which includes composting, pelletizing, packaging for commercial and home use.
3. Incineration
4. Landfilling
5. Surface Disposal, by which biosolids are applied to dedicated sites under restrictions of public access and crop.

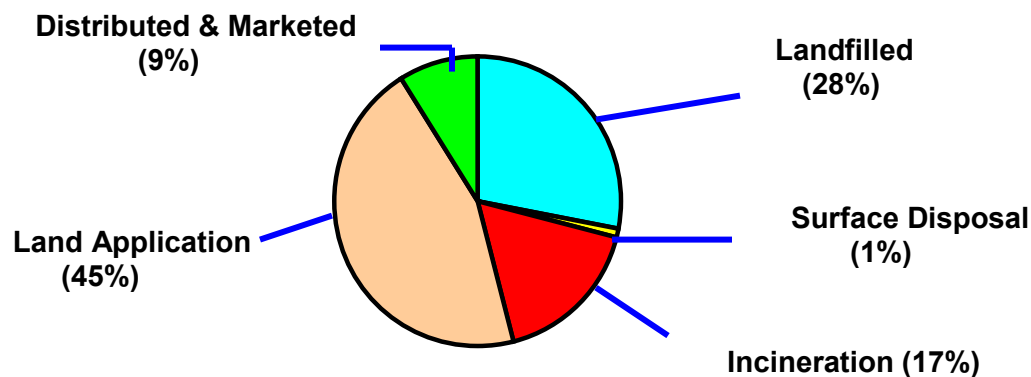
The selection and implementation of a biosolids management strategy is a choice made at the local level, within a framework of national and state regulations. The choice is driven by many variables and site-specific factors. Each of these options is protective of human health and the environment as long as compliance is maintained with applicable regulatory requirements.

The following illustration highlights the percentage of U.S. biosolids managed by each of the five aforementioned practices³.

¹ U.S. EPA. (2003)

² U.S. EPA (2000a)

³ National Association of Clean Water Agencies. (2006).



Biosolids Regulations

Federal regulation of biosolids commenced, under the Clean Water Act in the 1970s, with the promulgation of 40 CFR Part 257 and in 1987, Section 405 was added to the Clean Water Act to govern the disposal and use of biosolids.

In February, 1993 U.S. EPA promulgated biosolids regulations at 40 CFR Part 503 for the land application, distribution & marketing, incineration and surface disposal of biosolids, while landfilling remained regulated under 40 CFR Part 258.

In addition, biosolids incinerators are also regulated under the Clean Air Act.

The Incineration of Biosolids

In 2004, approximately 234 multiple hearth and fluidized bed incinerators were used to combust biosolids. Located at 120 WWTPs in 26 states, their operation results in the following benefits:

- ◆ Evaporation of water and combustion of organic matter resulting in a 80-95% reduction in volume
- ◆ Degradation of potentially toxic organic chemical compounds
- ◆ Destruction of all pathogens
- ◆ Production of inert non-toxic/non-hazardous ash

The hot gases in the a number of biosolids incinerator exhaust gas systems are used to produce steam which can be used for building comfort heating and in various plant processes. At other locations, the hot exhaust gases are used to pre-heat the incinerator's combustion air or fluidizing air. The beneficial reuse of the heat in the hot exhaust gases substantially reduces the use of auxiliary fossil fuels (e.g., natural gas, fuel oil) and, thus, the cost of incineration.

A number of WWTPs that practice incineration beneficially reuse their ash. Biosolids incinerator ash is used to make bricks, as a soil supplement, as an additive for cement, concrete, or asphalt, for the reclamation of strip mines, and as clean daily cover at municipal solid waste landfills.

Figure H-1. Cross Section of a Multiple Hearth Incinerator.

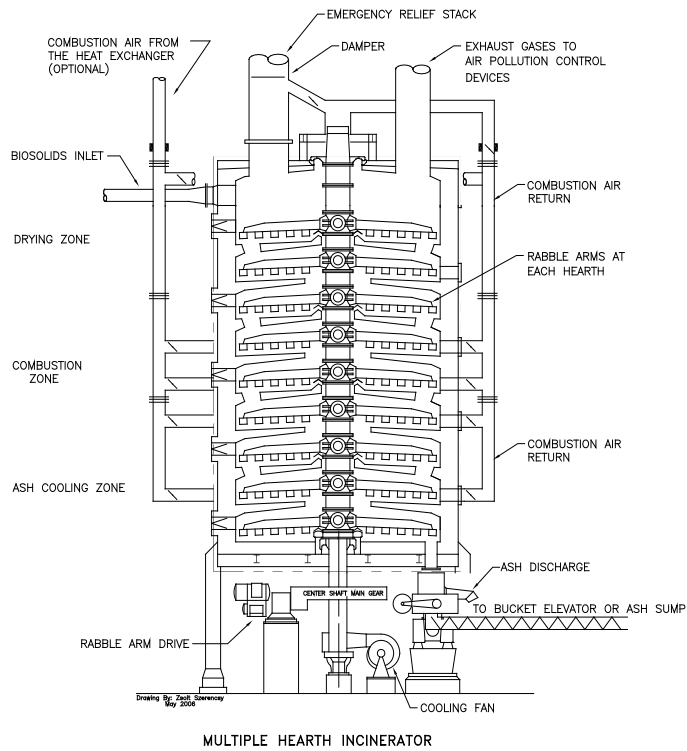
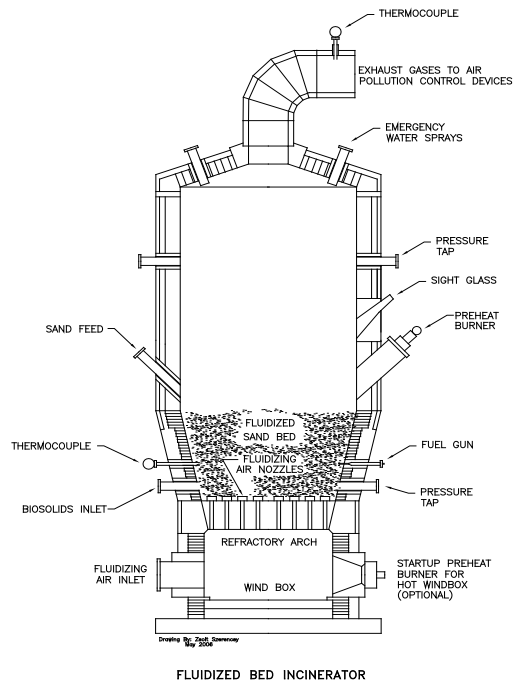


Figure H-2. Cross Section of a Fluidized Bed Incinerator.



The U.S. EPA has established a goal of reducing levels of in the environment. Mercury is classified as a Persistent Bio-accumulative Toxicant (PBT), thus underscoring the emphasis on its reduction across nearly all industrial sources. An estimated 144-189 metric tons (158-207 U.S. tons) of mercury are emitted into the atmosphere annually in the United States by anthropogenic (i.e., derived from human activity) sources ^(ref). Most emissions inventories conducted by and for U.S. EPA use the National Emissions Standard for Hazardous Air Pollutants (NESHAP) emission ceiling limit for biosolids incinerators rather than site-specific information. This simplification results in a conservative estimate. Emission estimates based upon biosolids analysis of total mercury, without accounting for removal through the incinerator APCDs, are shown to be significantly less than the ceiling method. More significantly, emission estimates based upon actual mercury incinerator stack emissions are generally even less than the biosolids methods, but such calculations are generally too intricate to serve as a basis for national emission inventories.

Based upon the most conservative (high) estimate, biosolids incinerators collectively emit less than 0.9 metric tons (1 U.S. ton) of mercury to the atmosphere each year, which is roughly 0.5% of the total amount of mercury annually emitted to the atmosphere in North America.

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Las Virgenes Municipal Water District
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Los Angeles County, Sanitation Districts of
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San Francisco, City & County of
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Santa Cruz, City of
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South Coast Water District

South Orange County Wastewater Authority
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Sunnyvale, City of
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