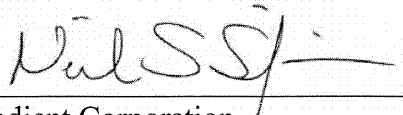


**Air Quality Management
in the 20th Century
and Doe Run's Herculanum
Lead Smelter Activities**

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List of Abbreviations

AAQS	Ambient Air Quality Standards
AAS	Atomic Absorption Spectrophotometry
AISI	American Iron and Steel Institute
AQCRs	Air Quality Control Regions
AQCs	Air Quality Criteria
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BACT	Best Available Control Technology
CAA	Clean Air Act
CMB	Chemical Mass Balance
Cl	Chlorine
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
DHEW	US Department of Health, Education, and Welfare
ESPs	Electrostatic Precipitators
FIP	Federal Implementation Plan
FORTRAN	Formula Translation
GFAA	Graphite Furnace Atomic Absorption
HAPs	Hazardous Air Pollutants
Hi-Vol	High Volume
ICP	Inductively Coupled Argon Plasma
ICP/MS	Inductively Coupled Argon Plasma-Mass Spectrometry
ICP-AES	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
ICP-OES	Inductively Coupled Argon Plasma-Optical Emission Spectrometry
IPFPE	Industrial Process Fugitive Particulate Emissions
ISC	Industrial Source Complex
ISCLT	Industrial Source Complex, Long Term
ISCST	Industrial Source Complex, Short Term
LAER	Lowest Achievable Emission Rate
MACC	Missouri Air Conservation Commission
MACT	Maximum Achievable Control Technology
NAAQS	National Ambient Air Quality Standards
NAMS	National Air Monitoring Stations
NAPCA	National Air Pollution Control Administration
NASN	National Air Sampling Network
NEPA	National Environmental Policy Act
NESHAP	National Emission Standards for Hazardous Air Pollutants
NOAA	National Oceanic and Atmospheric Administration
NRDC	Natural Resources Defense Council
NSPS	New Source Performance Standards
NTIS	National Technical Information Service
OES	Optical Emission Spectroscopy
Pb	Lead
PbS	Galena
PG	Pasquill-Gifford
PGT	Pasquill, Gifford, Turner

PHS	Public Health Service
PTDIS	Point Source: Dispersion
PTMAX	Point Source: Maximum
PTMTP	Point Source: Multiple Point Sources
RACM	Reasonably Available Control Measures
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
SO ₂	Sulfur Dioxide
SOP	Standard Operating Procedures
SPM	Suspended Particulate Matter
SPMs	Special Purpose Monitors
TEOM	Tapered Element Oscillating Microbalance
TSP	Total Suspended Particulates
UNAMAP	User's Network for Applied Modeling of Air Pollution
US EPA	US Environmental Protection Agency
USBM	US Bureau of Mines
VOC	Volatile Organic Compound
XRF	X-Ray Fluorescence Spectrometry

1 Introduction

This report examines the context of air pollution control history and how Doe Run met contemporaneous standards of care at its lead smelter in Herculaneum, Missouri. A casual glance at these events might raise questions about why attainment of Federal air quality standards for lead was not more straightforward, so context must be considered to understand that air quality control evolved over a long period of time. I first describe this context and then describe Doe Run's efforts at lead emission controls.

I am qualified to provide opinions on Doe Run's standards of care due to my education and professional experience. I have been an environmental engineer for 35 years, founded an environmental consulting firm, and serve as President of that firm today. I have a BS in Chemical Engineering from the University of Pennsylvania and a PhD in Environmental Engineering from MIT. In addition to my consulting work on environmental issues, I have extensive experience studying and publishing peer-reviewed papers on pollution management. Elaboration of my qualifications and methods used for this study is provided in Appendix A. Gradient is paid \$450/hr for my services. I reserve the right to alter my opinions if I receive new, pertinent information.

1.1 Genesis of Modern Air Pollution Management

Identifying and solving air pollution problems in the United States has been a slow and arduous process, driven by several landmark events and paradigm changes. Similar to the Shifrin (2005) analysis of the scientific understanding and historical management of water and land pollution, the evolution of air pollution science occurred on a timescale of decades. While some historians suggest that particular events, such as the Donora, Pennsylvania air quality event, single-handedly set the wheels of change into overdrive, it will be shown that progress in our understanding of air pollution and our approaches to mitigating air pollution problems began well before that, and were the product of a series of landmark events (see Table 1-1) with many years of research and scientific debate.

Although significant strides have been made in our understanding of air pollution problems, it is important to emphasize that the science of air pollution still suffers from large uncertainties and major data gaps. Air pollution problems are extremely complex, stretching even our current state-of-the-art

measurement, modeling, and pollution control capabilities. The air pollution field continues to evolve as shown by the current scientific debate concerning the appropriate health-protective form of the lead and particulate matter National Ambient Air Quality Standards (NAAQS). The story of airborne lead in the United States is intricately tied to the evolution of air pollution management, overall.

Prior to the 20th century and continuing until approximately the 1950s, air pollution control in the United States focused mainly on gross effects: visible black smoke and other solids (*e.g.*, fly ash) and gaseous by-products of incomplete coal combustion such as sulfur dioxides (Monnett, 1923, as quoted in Briggs, 1941; Meetham, 1952; Faith, 1959). This narrow interest in air pollution was pervasive despite early recognition of other air pollutants and sources, including carbon monoxide and lead from automobile emissions (Bloomfield and Isbell, 1933; Green, 1931) as well as fine dust from sources other than fuel combustion, such as industrial and building operations (Monnett, 1923, as quoted in Briggs, 1941; Green, 1931). Industrial and residential combustion of coal and coke was widely considered to be the primary source of air pollution in urban and industrialized areas in the first half of the 20th century (Meetham, 1952).

Table 1-1
Pre-Clean Air Act Landmark Air Pollution Events

Date	Event
1881	First US municipal smoke abatement legislation enacted in Chicago, IL.
1906	A Utah district court enjoined 4 Utah smelters not to operate in response to litigation launched by farmers alleging injury to crops and livestock.
1907	Municipal smoke inspectors formed the International Association for the Prevention of Smoke, later known as the Air Pollution Control Association and currently the Air & Waste Management Association.
1914	Selby Smelter Commission released its comprehensive report investigating conditions in and around the Selby Smelting and Lead Company smelter in Contra Costa County, California.
1919	US Bureau of Mines launched one of the most comprehensive air pollution studies to date in Salt Lake City, Utah, to identify the sources of the city's smoke problems.
1921	General Motors researchers identified tetraethyl lead as an effective anti-knock agent in gasoline.
1926	Surgeon General's committee affirmed the safety of tetraethyl lead for general use in gasoline, but recommended further federal study (studies never funded).
1927	US Public Health Service (PHS) quantified the loss of daylight due to smoke in New York City, reporting an average loss of 21.5 percent for yearlong measurements in Manhattan.
1930	Strong atmospheric inversion occurred between December 1 and 5 in Belgium's Meuse Valley, trapping industrial air emissions at ground level and contributing to more than 60 deaths and thousands of illnesses.
1943	First smog episodes recognized in Los Angeles, California.
1947	California adopted the Air Pollution Control Act, authorizing the formation of county air pollution control districts.
1948	Acute air pollution episode occurred in the small industrial town of Donora, PA, with an intense temperature inversion trapping particulates and other industrial emissions at ground level over a 4-day period, causing an estimated 20 deaths and between 5,000 and 7,000 illnesses among a population of approximately 14,000.
1950	First US Technical Conference on Air Pollution held in Washington, D.C., with over 750 people attending.
1950	Dr. Arie Haagen-Smit of the California Institute of Technology proposed a photochemical mechanism for smog formation, identifying nitrogen oxides and hydrocarbons from automobiles and the petroleum industry to be key causative agents.
1951	Oregon passed first state law providing statewide authority to a state air pollution control agency.
1952	London "killer fog" event occurred, with official reports blaming the thick sulfur and particulate-laden fog that occurred between December 5 and 9 for over 4,000 deaths over a 2-week period.
1953	New York City experienced its first major acute air pollution episode, with an estimated 160 to 220 deaths.

- 1953 The Public Health Service established the National Air Sampling Network (NASN), later renamed the National Air Surveillance Network.
- 1955 US Air Pollution Control Act of 1955 passed; major provisions provide for federal technical assistance to state air pollution control and funding for Public Health Service to conduct air pollution studies.
- 1955 National Air Pollution Control Administration (NAPCA) founded within the US Department of Health, Education, and Welfare (DHEW).
- 1962 Rachel Carson's *Silent Spring* is published, bringing to the public's attention the unforeseen harm that human actions can have on the environment.
- 1963 Air pollution inversion event resulted in over 400 deaths in New York City.
- 1963 First Federal Clean Air Act enacted, giving the federal government enforcement authority to combat both interstate and intrastate air pollution problems and providing grants for initiation and development of local or state air pollution control programs.
- 1965 Motor Vehicle Air Pollution Control Act enacted, authorizing the development of federal emissions standards for new motor vehicles.
- 1965 Dr. Clair Patterson of the California Institute of Technology published the seminal paper "Contaminated and Natural Lead Environments of Man," challenging the current paradigm that human exposures to lead were in large part natural in origin and that the body had adapted over time to handle chronic lead exposure.
- 1967 Federal Air Quality Act of 1967 enacted, with key provisions authorizing the federal government to define the atmospheric areas of the nation, designate air quality control regions (AQCRs), publish Air Quality Criteria (AQC)s and Control Technology Documents for use by the states in setting air quality standards, require the development of state implementation plans (SIPs), and expand ongoing air pollution control research.
- 1969 National Environmental Policy Act (NEPA) passed in Congress.
- 1970 US Environmental Protection Agency (US EPA) established.
-

By the early 1900s, smoke from smelters had become an issue for both science and government (Swain, 1949). Complaints arose concerning crop and livestock damage in Utah, Montana, and California (Baskerville, 1910; Ebaugh, 1907; 1910; Westby, 1912; Selby Smelter Commission, 1915; Wells, 1917).¹ Smelters were recognized to be sources of sulfur dioxide and trace metals such as arsenic and lead at this time (Ebaugh, 1907; Selby Smelter Commission, 1915; Swain, 1939; 1949).

Smoke was primarily viewed as a public nuisance (*e.g.*, soiling of merchandise, buildings, and clothes; injuring vegetation and animals; impacting visibility and loss of sunlight) (PHS, 1936; Meller, 1931). Human health impacts were also considered, but the relationship between smoke and health was not established at this time (PHS, 1936). As stated by Drinker (1939), air pollution was viewed more as a nuisance than a health hazard to the "average man." Black smoke from incomplete fuel combustion remained the primary focus of scientists and governmental officials through the 1940s and into the 1950s, in part because other forms of air pollution, including non-fuel dust from industrial emissions, were considered to be less harmful to health and property (Monnett, 1923, as quoted in Briggs, 1941; Meetham, 1952; Faith, 1959).

As smoke abatement became a greater priority of the public and government in the early 1900s, so did the study of air pollution problems (Schueneman, 1955). The air pollutants of interest in these early air pollution measurement studies included total airborne suspended particles, total dustfall, and sulfur dioxide (Schueneman, 1955; PHS, 1936). Among the early large-scale air pollution studies of note was a 1913-1914 investigation conducted by the Selby Smelter Commission in the vicinity of the Selby Smelting and Lead Company in Contra Costa County, California. Sulfur dioxide was measured in the "smoke zone" of the smelter (Selby Smelter Commission, 1915). Other early major studies included a 1919-1920 study conducted by the US Bureau of Mines to characterize the factors affecting smoke levels in Salt Lake City. The US Public Health Service emerged as the federal research authority on air pollution in the 1920s and 1930s, conducting such important work as a 1927 study quantifying loss of daylight due to smoke in New York City and the 1931-1933 atmospheric pollution study of 14 of the largest US cities (PHS, 1936). In addition to these large-scale studies, a number of cities, including

¹ McKee (1969) noted that few damage claims or reports of problematic smelter emissions have become a matter of public record since approximately 1940. McKee (1969) attributed this to the successful responses of smelter companies to address these early air quality problems, both through engineering measures (*e.g.*, use of tall stacks and stringent pollution control equipment) and through purchase of adjacent lands.

Pittsburgh, Chicago, Cleveland, and St. Louis, sponsored air pollution measurement studies prior to 1930 to investigate their smoke problems (PHS, 1936; Meller, 1931).

It was not until the post-World War II years that the potential health impacts of air pollution became a significant source of public and governmental concern. As detailed in Table 1-1, several landmark air pollution events occurred in the US and in Europe in the late 1940s and early 1950s, contributing to a greater awareness and increased scientific interest in atmospheric pollution at this time (McCabe, 1954). Among these acute air pollution events was the 1948 Donora, Pennsylvania event, which precipitated a formal inquiry by the US Public Health Service and others that has been cited as the first organized effort in the US to investigate the health impacts of air pollution (Helfand *et al.*, 2001). Although several acute air pollution events had occurred in Europe prior to the Donora event, there was an opinion among leading US air pollution scientists that these incidents were the products of unusual meteorological and geographical circumstances that could not happen in the US (Drinker, 1939).

In this same time period, a new form of air pollution was being investigated in the Los Angeles area: smog. In the summer of 1943, smog clouds descended on the city, reducing visibility to 3 blocks and eliciting reports of smarting eyes, respiratory discomfort, nausea, vomiting, and vegetative damage (SCAQMD, 1997; CARB, 2004). A local butadiene plant was originally blamed for this "gas attack" but, following the plant shutdown, these extreme air pollution events continued. The repeated occurrence of smog events prompted both heightened scientific and regulatory air pollution activity in the Los Angeles basin in the 1940s. In 1947, the nation's first air pollution district was formed in Los Angeles County. In 1950, Dr. Arie Haagen-Smit of the California Institute of Technology proposed a photochemical mechanism for smog formation, identifying nitrogen oxides and hydrocarbons from automobiles and the petroleum industry to be key causative agents (Haagen-Smit, 1950). This was a significant breakthrough with sweeping ramifications for the emerging air pollution field, as it highlighted air pollutants other than smoke as threats to public health and welfare.

Approximately 1950 thus represents the emergence of the modern air pollution field and its focus on potential health implications and the levels and effects of specific air pollution constituents. At that time, following the occurrence of several air pollution events, scientific interest in air pollution increased (Clayton, 1949; McCabe, 1954) with a shift to other forms of air pollution beyond smoke and fly ash from coal combustion sources. Air pollution was redefined, with air pollutants such as oxidants,

hydrocarbons, and sulfur dioxide becoming the subject of increased attention and research activity (Lagarias, 1982). Nevertheless, many scientists at this time viewed air pollution incidents as providing only limited evidence for the acute health effects of major air pollution events, which they relegated to an unusual set of meteorological and geographical conditions (Clayton, 1949; Nord, 1951; Foulger, 1952a). In fact, Nord (1951) concluded: "In view of the fact that tobacco smoking- which is a highly intense form of personalized air pollution- is not regarded as harmful for most people, it seems doubtful whether the general contaminants in ordinary city air have any perceptible effect on the health of urban dwellers."

2 Opinions

For reasons elaborated in more detail throughout the rest of this report, I offer the following opinions:

1. ***Prior to 1978, when a national ambient air quality standard for lead was established, the focus of air pollution control was on total suspended particulates and gases like sulfur dioxide.***

As with all modern environmental programs starting in the second half of the 20th Century, the largest, fundamental issues needed to be addressed first. For air quality, particulates and gases were the initial fundamental issues. The earliest scientific air pollution studies, c. 1920s-'50s, focused on smoke, suspended particles, total dustfall, and sulfur dioxide caused by industrial, residential, municipal, and transportation sources. Initially, these factors were viewed only as nuisances, not health issues, but by about 1950 they and smog were considered potential health problems needing to be addressed. Air problems caused by smelters during this time also were viewed in terms primarily of fundamental parameters – smoke, sulfur dioxide, and fumes.

Air emissions began to be inventoried in the 1950s, and emission factors compiled by the US Public Health Service in the 1960s are examples of our first attempts to provide systematic understanding of air pollution sources. Lead smelters were included but these early emission factors were limited to particulates and sulfur compounds. For all sources, stacks and other point sources were the focus of control efforts up through the early 1970s, even though fugitive emissions were known to exist.

The 1970 Clean Air Act (CAA) accelerated and formalized the progress along the same track as noted above, but also laid the framework for addressing more sophisticated issues, once the fundamentals were addressed. Point source control of particulates and gases, emission inventories, modeling, and measurement improvements were the initial emphasis of the CAA. By the mid to late 1970s, US EPA was ready to consider refinements in air quality issues and promulgated a national ambient air quality standard for lead, $1.5 \mu\text{g}/\text{m}^3$, for the first time. Both the date of EPA's first lead standard and the many technical issues related to attaining the standard were complicated by the widespread use of tetraethyl lead in auto gasoline.

Companies, including lead smelters like Doe Run, turned their attention to such specific parameters for the first time in the mid-1970s while continuing their control efforts with the fundamentals. For an element like lead, the 2 were related. For example, although Doe Run was measuring lead and controlling it prior to the first air lead standard, its early control programs at the smelter were focused on criteria air pollutants such as particulates and SO₂, with the ancillary benefit of lead control.

2. *Air pollution control has been one of the most difficult environmental quality issues to manage due to its unique technical character.*

Some of the factors making air pollution control a difficult technical issue to address/understand include:

- the presence of both mobile and stationary sources,
- point and fugitive (dispersed) sources,
- the vast and highly variable receiving reservoir (atmosphere), atmospheric chemistry and physics, the large engineering scales of control technologies, and
- difficulties understanding the science – *e.g.*, measurement, modeling and cause-effect relationships.

The mobile-stationary source issue was especially pertinent to lead due to the role of leaded gasoline. The fugitive emission issue, which only started being seriously addressed in the 1970s/80s, was especially significant at lead smelters. Finally, air pollution, and thus its control, could not be understood without developing accurate measurement and complicated modeling tools, both of which were very difficult to refine for air pollution.

Accurate, precise air measurement and modeling technologies took decades to develop, as discussed below. Control technologies also took time to evolve, partly due to engineering limitations on point source controls but also due to the poor understanding and unwieldiness of fugitive emissions, also discussed below. In addition, the required targets were unclear, as reflected by the slow and changing development of many air quality standards. Thus industry looked to government for guidance, and in many cases the 2 needed to collaborate on technical advances to ensure that control efforts were on the right track and effective. This was a long and arduous process.

3. *Accurate air sampling and lead measurement was technically difficult and took a long time to develop.*

Air quality measurement problems began early as engineers and scientists encountered many difficulties trying to develop instruments that could accurately collect and characterize particles. These difficulties included uncertainties about relevant particle sizes and representative sampling. With the standardization of Hi-Vol samplers in 1971 and the refinement of particle size measurement techniques in the 1980s and beyond, particulate sampling became better defined. Pertinent to lead, the need for accurate, convenient chemical speciation of particles came next, c. >1970s and was solved with the commercial laboratory establishment of atomic spectral property instruments. Not until this time period was a governmental federal reference method established for the standardized measurement of airborne lead to support its control, a date not surprisingly coinciding with establishment of the first lead air standard.

A clear understanding of where to measure air was also elusive and critical to successful development of pollution control. This location issue was extremely complex because it dovetailed with both source and transport understanding and thus, with modeling capabilities. Today's understanding of downwind vs. fenceline monitoring started with US EPA regulations in 1978 but wasn't clarified until the 1980s. US EPA's guidance on monitoring networks for lead sources was not finally refined until the late 1990s.

Doe Run experienced these monitoring network difficulties at its Herculaneum smelter. The 1980 State Implementation Plan for lead controls established the attainment monitoring station at a nearby High School, the location believed to have the highest air concentrations. It took until the mid-1980s, and many years of air dispersion model refinements with a better understanding of fugitive emissions, to determine that the fenceline was a better monitoring location, which was reflected in the 1990 State Implementation Plan. This is an example of the interactive complexities of many factors, not just monitoring.

4. *Much insight into air pollution control was gained by air modeling, but refinement of this science into a reliable tool took a long time to develop.*

As with most areas of science, effective understanding is not possible without a solid theoretical and mechanistic basis, and modeling provided that insight for air pollution control. Air modeling allowed better understanding of the relative roles of point vs. fugitive emissions because it allowed

cause-effect examinations. Air modeling allowed better monitoring network design because it predicted how concentrations would disperse downwind. And air modeling allowed effective control technology evaluation because it could simulate variations on cause-effect.

Rudimentary regulatory air quality modeling did not start until the 1970s, however, and it wasn't standardized until approximately 1980, with major model shortcomings remaining unaddressed until the 1990s. Modeling retains many uncertainties still today. Progress has been slow due to the need to develop, but more importantly to codify and provide computational power for, the basic theoretical description as represented by Gaussian mathematics as well as the need to define source and atmospheric characteristics. Atmospheric conditions and fluid dispersion factors were first systematized by Turner in 1967. The quantitation of emission factors for various kinds of sources began with the US Public Health Services "AP-42" handbook in the late 1960s, which has been updated at least 5 times by US EPA since 1972. Lead emission factors first appeared in such guidance in 1979 for point sources and in 1986 for fugitive emissions. Fluid physics and emission factor refinements resulted in a 1979 state of the art model known as the Industrial Source Complex (ISC) model, which had a major overhaul in 1992, followed by a lengthy period of standardized use, culminating in its replacement (*i.e.*, modeling still being refined) in 2005 with US EPA's new AERMOD model.

The Doe Run smelter was at the forefront of model use and development as it implemented its lead emission controls at Herculaneum but was constrained by the limitations of the technology itself. The State performed the original smelter emission/downwind modeling, using standard approaches at the time, for its 1980 State Implementation Plan and US EPA first rejected and then accepted this modeling. Agency disagreements about modeling deficiencies reflected the imperfect state of the art at the time. Both the State and Doe Run performed refined modeling for the additional controls defined by the 1990 State Implementation Plan, but the science was still rudimentary and some emission factors needed to be drawn from analogous industries rather than being lead smelter-specific. Doe Run performed additional modeling to implement further reasonably available control technologies in the 1990s. Although the air modeling helped determine control measures needed for Doe Run to attain air quality standards, the technical limitations of the science at the time allowed for only part of the solution. Even US EPA's 1995 modeling overpredicted the impacts of Doe Run's emission control efforts to attain the lead standard.

5. *In addition to the evolving nature of air pollution control technology, a sufficient understanding of fugitive emissions to allow their control at necessary levels was perhaps the most difficult element of attaining desirable air quality.*

Just as with water pollution control, initial efforts to improve air quality focused on point source control. Not only were stack emissions obvious targets for such efforts but they were believed to be the most significant sources of air pollution. Fugitive emissions were acknowledged during the advent of air pollution management but they were poorly understood, both in terms of their nature and their significance. This was especially true of smelters, which had many kinds of fugitive emissions, some with possible controls that actually could endanger human health. For example, obvious methods of lead dust emission controls from inside smelter buildings involved sealing/limiting air flow, a condition that threatened workers' lives due to potential carbon monoxide build-up. More sophisticated approaches required time for the science and technology to evolve.

Within this context of poor understanding of the significance of and controls for the many fugitive emissions of a lead smelter, Doe Run and the State systematically ratcheted down on the most obvious controls first and then, when air quality was still not attained, addressed more and more fugitive emission issues. A 1988 State regulation had Doe Run cap emissions and create a work practice manual to manage operations leading to fugitive emissions. In response, Doe Run hired consultants who determined 14 reasonably available control technologies and performed modeling to evaluate their impact on air quality, which resulted in Doe Run performing 16 distinct emission control projects in the 1990s. Doe Run was responsive and persistent as it systematically searched for the combination of controls that would lead to air quality attainment.

6. *The development of air and lead standards for smelters was but one part of the technically complex air quality issues facing the government, which has taken over 30 years to implement the Clean Air Act.*

Initially, US air regulation was local and focused on smoke and other nuisances. Federal enforcement, albeit awkward by today's standards, originated in 1963 and relied on the States to implement air quality standards that were of a general nature (e.g., total suspended particulates, not lead). The 1970 Clean Air Act revolutionized the regulatory structure of air quality management and required US EPA to develop a list of criteria air pollutants with State Implementation Plans as the mechanism for all pollution control. The first 6 of these hazardous pollutants/groups was issued by US EPA in 1971 – sulfur dioxide, carbon monoxide, photochemical oxidants, nitrogen dioxide, hydrocarbons, and particulates – whereas lead was not regulated as a criteria air pollutant until 1978. The delay of lead

regulation was partially due to the significance of leaded gasoline, which began phase-out in 1973 and was completed in 1996. While all agencies and industry struggled to learn about emissions and their best available control technologies during this time, the States were required to develop implementation plans which US EPA was required to approve. Technical and administrative difficulties caused Congress to amend the Clean Air Act in 1977 and to extend the deadline for attainment of air standards to 1987. During this time, not only were best available control technologies and emission characteristics poorly understood, but the science underlying the standards was recognized as highly uncertain and US EPA was instructed by Congress to review them every 5 years.

After 20 years of technical and regulatory learning, Congress passed the 1990 Clean Air Act Amendments, a major overhaul of all aspects of air pollution control. The Amendments focused specifically on nonattainment, as this was a fairly widespread issue, emission standards, and maximum achievable control technologies among many other elements. The job of implementation was left with the states, while US EPA issued thousands of rulemakings and guidance documents.

As noted above, the first lead air standard,² $1.5 \mu\text{g}/\text{m}^3$, was not established by US EPA until 1978. US EPA anticipated problems with attaining this standard when it was promulgated, particularly for smelters, due to an acknowledged poor understanding of fugitive emissions and their control. The agency recommended new data collection and issued guidelines on this topic over the next several years. The states, through their implementation plans, and US EPA struggled along with the smelting industry with these issues over the next decade. It was not until 1999 that US EPA understood enough to issue national emission standards for lead and other hazardous pollutants (NESHAPs) at lead smelters – 500 grams emissions/million grams of product on a plantwide basis – with 9 specific smelter point and fugitive sources listed. US EPA also required smelters to develop standardized operating procedures for fugitive dust sources at this same time, while viewing its new rules as "consistent and compatible with the current limitations and work practices" at smelters. Thus, US EPA still recognized the attainment difficulties faced by smelters as late as 1999.

² Referred to as a NAAQS, a National Ambient Air Quality Standard.

7. ***Doe Run's Herculanum smelter faced all of these difficult technical issues while it spent over \$60 million to comply with all government air control requirements to attain the lead air quality standard.***

Prior to lead regulation, Doe Run implemented many controls for conventional air pollution control with coincident benefits of lead control – its first baghouse in 1910, more particulate controls in the 1950s, major SO₂ controls in 1969, and plant process modifications also in the 1960s. In immediate response to the 1970 Clean Air Act, Doe Run reduced half of its lead emissions by 1979 through \$13 million of projects aimed at particulate controls. Working with the State on its first (1980) implementation plan for the Clean Air Act, Doe Run implemented 19 different projects to reduce fugitive lead emissions during just 1978-79, and conducted 9 additional research projects and implemented additional control projects as an immediate result of the State Implementation Plan. This 1980 State plan acknowledged Doe Run had already implemented an "extremely high degree of control."

Nevertheless, Doe Run's attainment of the lead NAAQS was difficult due to knowledge limitations of sources, controls, measurement, and modeling, by both the company and the agencies. Many of the problems originated with the fugitive emission issue. Measurement problems persisted in part because it was unclear until the mid-1980s that fugitive emissions contributed to greater lead impacts at points closer to the plant than at the High School monitoring location. Modeling, which was critical to enable prediction of control requirements, had many issues. Initially both agencies and the company recognized the limitations of defining emission factors for modeling, which correlated poorly with measurements, so the 1980 plan assumed a simple proportional reduction – a 50% reduction in emissions was assumed to result in a 50% improvement in downwind air quality. NAAQS attainment was targeted for 1984.

When the NAAQS was not attained after at least 25 pollution control projects, 99% of the projected emission reductions, and making "conscious efforts" while meeting "the terms of their consent order," the State and Doe Run both used new state of the art air modeling to examine emissions and controls more closely to help design the 1990 State Implementation Plan. Model and monitoring refinement by that time showed reasonable correlation for the High School monitoring location. Doe Run then hired a consultant (Fluor Daniel, Inc.) to comb through the plant and available technologies to develop a list of 14 additional state of the art emission controls which were then evaluated for NAAQS impact by more refined modeling. Doe Run then implemented 16 new emission control projects as well as SIP-specified contingency measures, but the NAAQS was still not attained by the mid 1990s. By this

time, Doe Run had built world-class air filtering systems, enclosed fugitive emissions, and improved materials handling to the best degree possible at the time and in compliance with all regulatory requirements. NAAQS attainment was frequent, but not constant, at the High School monitoring station and less frequent at the fenceline station by 1996.

In this final phase, Doe Run continued with model refinements and 21 further fugitive emission controls aimed at a 99% reduction of the emissions believed to be responsible for the continued nonattainment. NAAQS attainment was finally maintained at all monitoring stations from 2002 through 2004. Minor exceedances have occurred since, and Doe Run continues to examine, model, and implement additional controls to establish permanent attainment.

Doe Run implemented pollution controls over time as soon as they understood the need, consistent with the best knowledge of the time. All of their efforts were under State and US EPA review and approval. The long period to reach attainment reflects the technical difficulties related to lead pollution control from lead smelters, not any lack of intent or delay on Doe Run's part. Control of lead emissions at Doe Run has very much been an iterative process, driven by advancements in the science, evolution of technology and regulations, and collaborative efforts between Doe Run, the state of Missouri, and US EPA in developing and implementing SIPs. Throughout this period of the 1970 Clean Air Act to the present, Doe Run has been in or ahead of compliance with all regulatory requirements, despite the lack of NAAQS attainment until 2002.

3 Evolution of the Science of Air Pollution

Today's science of air pollution did not develop overnight. It is the product of a number of air pollution events, research accomplishments, and public and governmental activities. This section examines progress in our understanding of several air pollution topics over the last century to illustrate the incremental improvements in our knowledge of air pollution problems culminating in today's modern science of air pollution. Although this section demonstrates that we have made major strides in our scientific understanding of air pollution problems over the years, it also shows that each research accomplishment yielded additional topics for research as we gained further insight into the complexity of air pollution problems.

3.1 Early Understanding of Air Pollution Forms, Sources, Properties, and Transport: 1900 to 1950s

By the early 1900s, both gases and solids were recognized as forms of air pollution. The use of poison gases in World War I, acute occupational exposures such as in the "dusty trades," and early smoke-fog events in cities such as Glasgow and London (Chambers, 1968; Foulger, 1952b) are examples of this early recognition. Sources of smoke and fly ash such as chimneys, locomotives, power plants, incinerators, and heating plants were the primary focus of early air pollution inquiries and pollution abatement efforts in the United States (Lagarias, 1982). Despite this narrow focus, Green (1931) provided an exhaustive list of other recognized sources of airborne particulates in addition to chimney smoke: "Dust and dirt particles blown in the air make up some portion; iron from the working of this metal, from industrial grinding processes, and from the wearing of street car rails and brake shoes; products resulting from the wear of asphalt pavements; minute particles of rubber from the wearing of tires and even rubber heels." Green (1931) further identified "the handling and storage of crushed stone, gravel, sand, lime, cement, brick, and tile" as dust sources, which suggests early recognition of fugitive emission sources. Drinker (1939) highlighted chemical and metallurgical stacks as key air pollution sources, but also discussed dust generation from grinding, blasting, or drilling of rock. Meller (1931) discussed the effects of fuel combustion by-products including sulfuric acid and sulfurous acid, hydrogen sulfide, hydrochloric acid, ammonia, and organic acids. Wells (1917) and Swain (1939) recognized smelters to be sources of both visible smoke and other air pollutants including sulfur dioxide, sulfuric

acid, metal fumes and metal dust (Baskerville, 1910; Ebaugh, 1910; Westby, 1912; Selby Smelter Commission, 1915; Wells, 1917).

Automobile emissions were recognized soon after the advent of leaded gasoline to be sources of airborne lead, although there was controversy regarding the health effects of auto emissions (Lewis, 1985; Hernberg, 2000). In fact, shortly after the introduction of lead as an anti-knock additive in gasoline in the 1920s, the US Surgeon General held a meeting among industrial representatives and public health experts in 1925 to debate the safety of tetraethyl lead as a gasoline additive (Lippmann, 1990; Needleman, 1998; Hernberg, 2000). Although several leading scientists including Dr. Alice Hamilton of Harvard University and Dr. Yandall Henderson of Yale University were very outspoken regarding the potential for widespread health risks associated with lead in automobile emissions, the meeting ended in disarray without any conclusions (Lippmann, 1990; Hernberg, 2000). A committee convened by the Surgeon General concluded in 1926 that there was a lack of evidence to recommend a ban for tetraethyl lead. The large-scale use of tetraethyl lead in gasoline commenced.

Although scientists focused heavily on abatement of visible smoke and hence total particulate mass in the pre-World War II years, there was a growing understanding of the role of particle size, shape, and chemical composition on the nature and magnitude of air pollution problems (Combes and Warren, 2005). Drinker and Hatch (1936) summarized the state of the knowledge regarding the various forms of particulate air pollution, defining dust, fumes, smoke, and mist or fogs based on such characteristics as their sources and mechanism of formation, particle size, and behavior. Early air pollution studies such as the 1931-1933 study of 14 of the largest US cities quantified amounts of carbon, silica, iron, and sulfur compounds to characterize the nature of the smoke problem (PHS, 1936). These studies also reported particle size distributions for suspended dust samples using microscopic analyses that identified particles with diameters down to approximately 0.2 microns.

By the 1930s scientists recognized particle size as a fundamental property affecting the behavior, effects, and control of airborne particles. Drinker and Hatch (1936) recognized that particle size not only dictated the settling properties of airborne particles, but also influenced their physiological effects. Munger (1952) understood that particle size was a factor determining the method of sampling and analysis of airborne particles, the equipment for separating particles from air, and the method for disposal. Both Munger (1952) and Clayton (1949) highlighted that particle size was a key factor

influencing how long particles remain in the air and the distance they travel prior to deposition on the ground. Clayton (1949) distinguished between larger particles settling near their emission source under normal weather conditions and smaller particles (*i.e.*, less than a micron in size) remaining suspended in the atmosphere for distant transport.

The critical relationship between air pollution and meteorological conditions was also examined in the early 1900s. Wells (1917) identified 4 critical weather conditions associated with high ground-level SO₂ concentrations and plant damage at the American Smelting and Refining Co. smelter in Murray, Utah: (1) temperature above 40 degrees Fahrenheit; (2) relative humidity above 70%; (3) daylight; and (4) prevalent winds of 3 hours or more. The first 3 factors were related to stomata opening and uptake of gases by plants, while the fourth factor affected the duration of exposure. He concluded it was "essential" to have a complete installation of standard weather instruments at smelter sites.

Air transport concepts were recognized to provide rudimentary predictive theory and simple analytical techniques by the 1930s. The American Smelting and Refining Co. (ASARCO) collected comprehensive ground-level SO₂ air concentration data at various downwind distances for different sets of stack conditions (*e.g.*, stack height, stack gas temperature) at the Murray smelter (Wells, 1917). Wells (1917) also studied plume rise and atmospheric dispersion, observing that the greater the difference in temperature between the stack gases and the outside air, the greater the distance at which gases met the ground and the less the ground-level concentrations. This was the genesis of air modeling, which, in the 1930s and 1940s, was captured in simple mathematical expressions for predicting air concentrations resulting from pollutant sources (Bosanquet and Pearson, 1936; Sutton, 1947).

Some of the foundations of today's principles of air pollution were thus established by the 1940s, although technological limitations, prevailing beliefs, and a lack of validating data and quantitative theories were key barriers to the level of progress. At that time, air pollution studies were generally conducted for empirical investigation of the magnitude of smoke problems in cities through the collection of large amounts of data, rather than data collection for the development and testing of theories. Data analyses were typically simple in nature, such as ranking cities according to air pollutant levels and identifying qualitative relationships between different factors (*i.e.*, PHS (1936) reported that atmospheric pollution was less on Sundays than on weekdays, indicating the importance of industrial sources). Overall, there was a practical understanding of the relationship between air pollution and various factors,

such as particle size and weather, but a general lack of quantitative theories, confirmatory models, and validating data analyses.

3.2 Early Source Inventories and Emissions Factors: 1950s and 1960s

Following the recognition that the air pollution problem was more complex than just a smoke problem and was instead related to a variety of pollutant emissions and sources, the 1950s saw the advent of pollutant emission inventories and source characterization (Schueneman, 1963; Rupp, 1956). Prior to this, air pollution studies generally focused on development of sampling methods and measurement of contaminants (Larson *et al.*, 1953).

Some of the earliest emission inventories were performed in the Los Angeles area (Southerland, 2005). By using source contributions and relating them to air sampling data, Larson *et al.* (1953) developed emissions inventories for the base year 1951 in Los Angeles County and used adjustment factors to obtain estimates for 1940 and 1948. They used field testing data from more than 350 tests on pollution sources in the Los Angeles area. New York-New Jersey, Washington, and St. Louis inventories followed in the 1960s (NAPCA, 1969a).

Standardized emission factors for industrial air pollutant sources were developed by the US Public Health Service in the 1960s. This effort culminated in a May 1965 compilation that was expanded to cover additional sources and re-released as the "Compilation of Air Pollutant Emission Factors" in 1968 (PHS, 1968). As discussed in PHS (1968), the purpose of these early compilations was to provide source emission factors for use in conducting air pollutant emission inventories. PHS (1968) noted that emission factors may be based upon tests at a single facility or just a few facilities, and were thus intended for making estimations rather than exact calculations of emissions. Primary lead smelters were among the source types covered in PHS (1968), although these early smelter emission factors were limited to particulates and sulfur compounds from 3 types of lead furnaces (cupola, pot, and reverberatory/sweating) but no other smelting processes. Lead or fugitive emission sources were not addressed in the early emission factor compilations.³

³ Section 4 discusses in greater detail the evolution of the emission factors compilations, which became the responsibility of the US EPA in the early 1970s and are now known as the AP-42 documents. As discussed in this section, air lead emission factors for a number of industrial sources, including primary lead smelters, were provided for the first time in 1979. The 1986

3.3 Initial Insights Into Fugitive Emissions: 1970s to 1980s

Given their clear and obvious presence, stacks and other industrial point sources typically were the focus of early pollution control measures up through the preparation of the earliest state implementation plans for TSP (Total Suspended Particulates) in the early 1970s (US EPA, 1977a). Fugitive emission sources were known to exist prior to the 1970s, but due in part to difficulties in their measurement and estimation of air quality impacts, they were not emphasized (US EPA, 1977a). A renewed interest in fugitive emission sources only developed in the mid-1970s when they were identified as potential barriers affecting attainment of the TSP National Ambient Air Quality Standards (NAAQS) in some parts of the country (Lillis and Young, 1975; US EPA, 1977a; 1982).

The increased attention did not immediately translate into reliable emission factors or improved, accurate technologies for quantifying air quality impacts. Our ability to predict fugitive source impacts remained inadequate, and to the present, is limited and uncertain. Although our ability to model has vastly improved since the 1970s (see Section 4), the same limited and uncertain techniques originally identified by US EPA (1976a; 1976b; 1976c) for measurement of fugitives remain the best available options today (US EPA, 1993a). Twenty years after initiating a series of focused fugitive emission studies, US EPA (1993) concluded that it was still not possible to draw any firm quantitative conclusions about fugitive emissions measurement accuracy due to the general lack of available validating studies.

Following the recognition that fugitive sources were likely an important factor contributing to TSP nonattainment in some areas, US EPA sought to define the scope of the fugitive emissions problem by funding a number of research projects, sponsoring meetings and conferences, and developing fugitive emissions guidance in the 1970s. In their seminal article, "EPA Looks At Fugitive Emissions," Lillis and Young (1975) distinguished between 2 categories of fugitive emissions – industrial (*i.e.*, process-related) fugitives and fugitive dust. Industrial fugitive emissions were defined as "both gaseous and particulate emissions that result from industrial related operations and which escape to the atmosphere through windows, doors, vents, *etc.*, but not through a primary exhaust system, such as a stack, flue, or control system" (Lillis and Young, 1975). Fugitive dust emissions were defined as natural or anthropogenic

Supplement A to the fourth version of AP-42 provided, for the first time, lead emission factors for fugitive sources at primary lead smelters as well as particle size distribution data for fugitive sources (US EPA, 1986b).

dusts (particulates only) made airborne by wind, human activity, or both (Lillis and Young, 1975). In a later guidance document, US EPA (1977a) defined industrial process fugitive particulate emissions (IPFPE) to include fugitive emissions (industrial) and fugitive dust emissions that originated from within industrial facilities (IPFPE is hereafter used in this section to refer to any fugitive emissions arising from within the boundaries of an industrial facility).

Lillis and Young (1975) and US EPA (1977a) argued that fugitive emissions could have a greater effect on air quality in close proximity to the source than stack emissions, in part because they tend to occur at or near ground level and remain there due to a lack of plume rise. They cited a handful of studies to support this idea, including a 1975 study of fugitive lead emissions at the Silver Valley/Bunker Hill primary lead smelter in Idaho, where preliminary results indicated that fugitive lead emissions were approximately 2 to 3 times the magnitude of process (stack) emissions (Lillis and Young, 1975). The air quality significance of IPFPEs was a subject of debate at the US EPA-sponsored "First Symposium on Fugitive Emissions," held May 17-19, 1976, in Hartford, CT. For example, Yocum (1976) argued that fugitive emissions were site-specific (and thus defied unified prediction) but could have significant fence line effects. On the other hand, McCutchen (1976) argued that iron and steel mill fugitive emissions were largely "cosmetic" in nature.

Uncertainty and debate surrounded the potential air quality impacts of IPFPEs in the 1970s, mainly due to difficulties associated with their measurement. Conventional techniques were generally not appropriate for measurement of IPFPEs since they are not emitted from a definable point source such as a stack (Lillis and Young, 1975; US EPA, 1977a). Few reliable emissions data on IPFPEs were available to characterize even the relative magnitude of emissions (Lillis and Young, 1975; US EPA, 1977a; 1979a). Lillis and Young (1975) and US EPA (1977a) concluded that the lack of reliable data contributed to the general lack of inclusion of fugitive emission sources in source emission inventories prepared by states and local air pollution control agencies in support of the first SIPs for TSP.

To promote necessary research on fugitive emissions, US EPA funded efforts to identify and assess the state of the practice for measurement of IPFPEs. An ultimate product of this effort was the 1976 US EPA *Technical Manual for Measurement of Fugitive Emissions: Volumes 1 through 3* (US EPA 1976a; 1976b; 1976c) that outlined 3 basic approaches to the measurement of atmospheric fugitive

emissions that had been developed by this time: (1) quasi-stack,⁴ (2) roof monitor,⁵ and (3) upwind-downwind.⁶ None of these techniques was widely accepted as an accurate measurement method (McCutchen, 1976) since each was burdened with technical limitations and uncertainties (US EPA, 1976a; 1976b; 1976c). The technical manual provided criteria for the selection of the most applicable of the 3 measurement methods for a given set of conditions, as well as detailed sampling procedures (US EPA, 1976a; 1976b; 1976c). However, the 1976 technical manual provided little quantitative information for assessing the measurement accuracy or emission factor reliability of these methods, as did a 1980 updated guideline protocol document (TRC, 1980).

Modeling was an alternative approach to measurement of air quality impacts from IPFPEs, but modeling was limited by the lack of reliable emission factors. The 1977 US EPA *Technical Guidance for Control of Industrial Process Fugitive Emissions* (US EPA, 1977a) noted the flaws of fugitive emission modeling due to several complicating factors, such as variable emission rates and the lack of detailed particle sizing data needed to model deposition.

Primary lead smelters were a particular focus of US EPA's IPFPE programs in the late 1970s, with studies conducted to measure fugitive emissions and to develop fugitive source emission factors for primary lead smelters. These studies identified a number of possible fugitive emission sources at primary lead smelters, including: (1) unloading, material handling, and concentrate storage; (2) material handling, sinter crushing, particulate escaping sintering machine hoods; (3) fugitive emissions from blast furnaces; (4) fumes from molten metal handling during the refining process; (5) material handling operations; and (6) windblown dust resuspended from ground, storage piles, or open areas around smelter (US EPA, 1979a). Most notable was the 1977 US EPA study, *Sample Fugitive Lead Emissions from 2 Primary Lead Smelters* (US EPA, 1977b), which summarized measurements made at 2 primary lead smelters and provided a number of fugitive lead emission factors.

⁴ The quasi-stack sampling method refers to the temporary installation of a hood or enclosure over the source, with venting to an exhaust duct or stack of regular cross-sectional area. This method allows for the use of standard stack sampling techniques. The major limitations of this technique include its use for only those sources amenable to the installation of a hood or enclosure, and the possibility that the hood or enclosure may alter emissions.

⁵ The roof-top sampling method involves the operation of samplers at building or other enclosure openings such as roof-top vents, doors, windows, *etc.* Limitations of this technique include having to sample very large openings and dealing with large variations in flow-through openings.

⁶ The upwind-downwind sampling method involves the use of upwind and downwind ambient monitors to determine the differential air quality impact associated with IPFPEs. This technique is generally considered the least reliable of the three methods due to a variety of complicating factors, including background sources of the pollutant of interest, issues associated with monitor siting, *etc.* (US EPA, 1993a).

US EPA (1977b) summarized a limited set of tests conducted at the ASARCO smelters in Glover, Missouri and East Helena, Montana, in July 1976. As described in their report, testing was not exhaustive in nature, as it was conducted over weekly timescales and no process data were recorded for these periods. Fugitive emissions were characterized using roof-top samplers, and specifically High-Volume (Hi-Vol) samplers, as well as 5-stage Sierra cascade impactors for collection of particle sizing data. Fugitive emissions were reported for entire processes, such as the sinter building, thus grouping emissions from individual sources. US EPA (1977b) observed the dross/reverberatory building to be the dominant source of lead fugitives at the East Helena smelter (contributing over 80% of total estimated fugitives), while the sinter building and the combined blast furnace/dross-kettle areas were both found to be major fugitives sources at the Glover smelter. Particle sizing data demonstrated that a large portion of fugitive emissions are of sub-micron particles, particularly from the blast furnace area. Data collected in this study, although very limited in nature, were used as the basis for US EPA AP-42 emission factors for fugitive lead at primary lead smelters up through the September 1990 supplement (US EPA, 1990a).

US EPA (1977a) also focused on IPFPEs from primary lead smelters, producing an extensive compilation of total particulate fugitive source emission factors.⁷ This compilation of fugitive source emission factors covered 25 emission points, but did not address either emissions from plant upset conditions, nor from plant haul roads. US EPA (1977a) reported major IPFPE sources to include sintering operations, lead ore concentrate handling and transfer operations, and zinc fuming furnace vents. The majority of the emission factors were based on estimates from just one primary lead smelter, the Bunker Hill Smelter in Idaho's Silver Valley, and all factors were rated "D" to reflect the limited quantity of data used in their derivation as well as the generally poor data quality. Several other emission factors were based on data from facilities other than primary lead smelters, including Taconite and coal unloading operations and steel facilities.

Despite US EPA efforts to improve fugitive emission descriptions, accurate and validated emission factors remained elusive in this time period. As discussed in Section 4, air lead emission factors for fugitive sources at primary lead smelters finally appeared in the US EPA AP-42 emissions factor documents in the mid-1980s, but these emissions factors were assigned the second lowest emission

⁷ US EPA (1977a) reported fugitive source emission factors for only total particulate and not lead for primary lead smelters. However, US EPA (1979a) converted these particulate emission factors into lead emission factors using data on the lead content of fugitive particulate emissions from various primary lead smelting operations that were also provided in US EPA (1977a).

factor rating of "D," indicating their low reliability for specific sources within the source category population.

3.4 Improved Particle Characterization: 1980s to Present

Coinciding with improved analytical capabilities for lead and other trace metals (see Section 3), studies began to appear in the literature around 1980 on the chemical characterization of lead smelter and other industrial emissions (Eatough *et al.*, 1979; Foster and Lott, 1980; Harrison *et al.*, 1981; Harrison and Williams, 1983). In addition, better particle size distribution data were also collected, including for primary lead smelter emissions.⁸ At this time it was recognized that these data were not only important for characterizing pollutant sources, but also for assessing potential health effects (*e.g.*, by providing data on mobility and bioavailability) and for refining predictive air quality models (*e.g.*, by providing improved emission factors and inputs for deposition modeling). Although these data have provided some valuable insight on the importance of various smelter processes as sources of lead emissions, they have also shown the complexity of the smelter emissions problem and revealed large data gaps and uncertainties requiring further study.

Foster and Lott (1980) was among the earliest studies reporting chemical speciation for particulate emissions from primary lead smelters. Working with Hi-Vol TSP samples collected at the Glover (MO) and Herculaneum (MO) smelters in the early to mid-1970s, Foster and Lott (1980) applied X-ray diffractometry to these samples for chemical speciation, to "identify fugitive industrial air particulate pollutants." Foster and Lott (1980) identified galena (PbS) to be an indicator species for the impacts of ore handling operations on airborne particles, and lead oxide species to reflect the impacts of actual smelting operations such as the blast furnace and dross plant on airborne particles. Strikingly different chemical speciation results were observed at the 2 smelters. For the Glover smelter samples, high levels of galena and other compounds associated with lead ore concentrate were observed, indicating that lead ore concentrate was a significant contributor to fugitive emissions at that plant. For the Herculaneum smelter samples, only low levels of galena were observed. Although Foster and Lott (1980) hypothesized that these disparate findings reflected reduced fugitive PbS emissions at

⁸ As discussed in Section 2.3, US EPA (1977c) is one of the few early studies reporting particle size distribution data for primary smelter emissions. In addition to this study, Dorn *et al.* (1976) reported particle sizing data for 1972 ambient air sampling conducted at a Missouri farm approximately 800 meters from the base of a lead smelter smokestack (smelter not named). For over 70 sampling days, Dorn *et al.* (1976) reported that approximately 66% of the collected Pb was associated with particles with diameters of less than 4.7 μm .

Herculaneum due to a different ore handling process and/or a more efficient sintering operation, they also cited several complicating factors affecting interpretation of the Herculaneum data. Specifically, they hypothesized that the elevated location of the Herculaneum monitor atop a school building may have limited the measurement of ground-level fugitive emissions, and that the small number of samples available for the Herculaneum monitor were predominantly collected during a wet period when surface dampness may have limited fugitive emissions. These observations on data collection emphasize the technical complexity of precise air quality characterization of smelter emissions.

At a large U.K. zinc-lead smelter (Harrison *et al.*, 1981), Harrison and Williams (1983) reported both chemical speciation data and particle sizing data for ambient air samples collected at 3 locations in the smelter vicinity. For the closest monitoring station to the smelter (situated on industrial land approximately 500 meters from the smelter stacks and 30 meters from the overhead conveyor system for transporting ore concentrates from the dock to the smelter), elevated concentrations of coarse-sized (mass median aerodynamic diameter greater than 11 μm) lead and zinc sulfide ore minerals were measured for 5 days of sampling. These data provided evidence of fugitive dust impacts at this sampling location, with possible sources being losses of ore concentrate from the overhead conveyor and resuspension of dust. In contrast, further stations 700 and 1,200 meters downwind showed mostly fine fume impacts from stack emissions. These results were similar to those of Dorn *et al.* (1976) for a US primary lead smelter, where relatively fine particle sizes were measured downwind although there was some evidence of coarser particles during one sampling period.

More recently, at an Australian primary lead smelter, Ohmsen (2001) provided chemical speciation data and particle size distributions for a variety of different smelter processes. Ohmsen (2001) reported that blast furnace emissions were the smallest-sized lead emissions (*i.e.*, micron to submicron fume), dusts associated with raw materials were typically in the size range of 10 to 400 μm , copper dross particles ranged from 10 to 300 μm , and refinery dusts were typically between 1 and 30 μm . This finding that blast furnace emissions are associated with finer particles than emissions from other areas, such as sintering and storage areas, is consistent with findings from the earlier US EPA (1977b) and Spear *et al.* (1998) studies of US primary lead smelters. With respect to chemical speciation, Ohmsen (2001) observed that primary Pb species followed a progression of PbS through PbSO₄ and PbO to Pb⁰ (metal), moving from raw materials, smelting in the blast furnace, slag fuming, to the refinery. Ohmsen (2001) also identified a larger number of Pb-bearing species, indicating a more complex chemistry than

previously reported. In particular, blast furnace fugitive emissions were found to be of more complex chemistry than fugitive material from other source areas, including a number of phases characteristic of sinter dusts as well as a range of Cl-bearing minerals.

The collection of detailed particle characterization data for primary lead smelter emissions represents a significant advancement since these data provided insight on the identity of specific smelter processes that were significant sources of airborne lead, in particular for fugitive emission sources. In addition, the general paucity of particle size distribution data and lead content data for fugitive emissions was a key factor slowing the development of AP-42 emission factors for lead fugitive sources at primary lead smelters in the 1970s and 1980s. Although still limited, the detailed characterization data noted above have pinpointed some sources of fugitive emissions at primary lead smelters for application of pollution control measures. However, they have also raised additional questions regarding the mineralogy of smelter emissions and identified the need to better understand the chemistry underlying fume formation in smelting processes for more effective emissions control.

4 Sampling and Analysis of Ambient Airborne Lead

The development of air sampling was critical to air pollution control because, if it cannot be measured, it cannot be defined and controlled. Compared to other media (*e.g.*, soil, water), air sampling engineering has proven to be more difficult to develop. The main problem has been sample representativeness of particles and gases with precise characterization of their physical properties and chemical composition. The proper location of samplers and chemical analysis of collected samples has been a strong factor in this development.

Lead is primarily emitted into the atmosphere in particulate form⁹ so the historical development and regulatory adoption of sampling techniques for suspended particulate matter (SPM) is the foundation of its measurement. SPM consists of a complex mixture of airborne solid and low vapor pressure liquid particles having aerodynamic particle sizes ranging from below 0.01 μm to 100 μm and larger. The complexity of SPM and the measurement of individual analytes associated with SPM have presented major sampling and analytical challenges through the years.

4.1 History of Particulate Sampling Methodology

Air particulate sampling remains imperfect today, but has evolved from sampling all particles by deposition (settling), to impingement of moderate air flows, to filtering of large volumes of air, to selective sampling of different-sized particles, to highly sensitive direct-reading instrumentation. Table 4-1 documents the development of various samplers for airborne particulates.

⁹ Note that lead can also be emitted as an organic gas from some sources (*e.g.*, leaded gasoline), although these amounts are small compared to particulate Pb emissions (US EPA, 1977c).

Table 4-1
Key Dates in the Development and Application of Direct Sampling Methods
Used to Collect Suspended Particulate Matter

Year	Sampling Method
1900s	• Dustfall collectors gained usage in early air pollution investigations
1920s	• Owens Jet Dust Counter developed • Greenburg-Smith Impinger developed
1930s	• Midget Impinger developed
1940s	• Precursor to modern Hi-Vol Sampler developed • First cascade impactor developed • American Iron and Steel Institute (AISI) Spot Tape Sampler developed
1950s	• Hi-Vol sampler selected for usage in Public Health Service's NASN
1960s	• Modified Andersen Cascade Impactor developed and applied to ambient suspended particulate matter
1970s	• Hi-Vol promulgated as federal reference method for TSP and Pb • Modified Andersen Cascade Impactor selected by US EPA for usage in NASN cascade impactor network • Dichotomous sampler gained usage as size-selective sampler
1980s	• PM₁₀ replaced TSP as NAAQS, and PM₁₀ federal reference methods first developed
1990s	• PM_{2.5} NAAQS promulgated and PM_{2.5} federal reference methods first developed

Dustfall collectors, consisting of a large conical funnel connected by tubing to a glass bottle, were among the rudimentary samplers used to collect dust and rain in a number of early air pollution studies conducted in US cities (PHS, 1936). Variations of the dustfall collector later evolved into a dustfall method codified in the 1950s and 1960s by the National Air Pollution Control Association (NAPCA) and the American Society for Testing and Materials (Chow, 1995; Hendrickson, 1968). These samplers collected large particles ($>5 \mu\text{m}$) by gravitational settling into open containers over several weeks. They suffered many interferences from insects, fungi, bird droppings, and plant materials, and accuracy was affected by wind speed and direction. The uncertainty of the method was confirmed by highly variable results from nearby samplers (Chow, 1995). Smaller particles were poorly sampled due to their low settling velocities and wind effects.

Wet impingers, such as the Greenburg-Smith impinger and later the more portable midget impinger, were developed in the 1920s and soon thereafter gained widespread usage (Greenburg and Smith, 1922; Hendrickson, 1968; Marple, 2004). Impingers had a glass tube with a small orifice through which air was drawn at high velocity and sprayed onto a flat surface submerged in water or some other liquid. Good collection efficiencies were reported for particles with diameters down to about 1 μm for the Greenburg-Smith impinger (Giever, 1968). Impingers were used in 1920s and 1930s studies for sampling lead dust and fume (Bloomfield and Isbell, 1933; Littlefield *et al.*, 1938; Case, 1941).

The Owens Jet Dust Counter was an early version of modern day impactor samplers (PHS, 1936; Marple, 2004). A pump plunger was used to draw a jet of air through a slit where water condensed on particles and the wetted particles impinged/adhered to a cover glass. Moisture was then evaporated and the cover glass was analyzed microscopically for counting and sizing of particles. This device was used in several prominent 1920s and 1930s air pollution studies, including the Kimball and Hand (1924; 1931) studies of the dust content of the atmosphere in Washington, D.C. and Chicago and the PHS (1936) atmospheric pollution study of 14 of the largest US cities. PHS (1936) reported that they were able to count and size particles down to a diameter of about 0.2 microns with the Owens Jet Dust Counter.

The method of collecting particles by drawing large volumes of air through a filter was first used in approximately 1885; however, the technique was not very accurate because of the lack of electrically operated pumps, timing mechanisms, and flow measurement devices (Chow, 1995). It was not until the late 1940s that this method was refined for measurement of airborne radioactivity from nuclear weapons testing (Chow, 1995). It was soon applied to a variety of particle types, including textile dusts, silica dust, lead fume, and tobacco smoke (Silverman and Viles, 1948). This early sampler, which relied on high volume air sampling and filter weighing, was the predecessor to today's Hi-Vol sampler.

Following its use in the 1953 Public Health Service's National Air Sampling Network (NASN, later renamed the National Air Surveillance Network), the Hi-Vol sampler quickly became the workhorse sampler for airborne particulates. The Hi-Vol became the Federal reference method in 1971 for the TSP National Ambient Air Quality Standard (NAAQS) (PHS, 1958; US EPA, 1971a), and up through the 1980s, thousands of TSP Hi-Vol monitors were operated throughout the United States. Although ambient particulate matter is no longer regulated as TSP and the Hi-Vol sampler is no longer commonly

used to measure ambient particle mass concentrations,¹⁰ the Hi-Vol sampler has remained part of the federal reference method for determination of lead in suspended particulate matter for compliance with the lead NAAQS since its promulgation in 1978 (US EPA, 1978a).

Although widely used over the years, the Hi-Vol sampler's measurement flaws have been extensively noted. Initially, lack of filter standardization (glass felt and polystyrene were often used) was a problem (NAPCA, 1969a), but the system was eventually standardized with flat glass fiber filters contained in a box with a peaked roof to prevent passive dust settling onto the filter (Chow, 1995). NAPCA's 1969 *Air Quality Criteria for Particulate Matter* study noted "... the filter material may contaminate the sample; different substances in the sample may react with each other; and losses may occur through volatilization of material." Greater use and study of the Hi-Vol revealed that collection efficiencies declined above particle sizes of 20 μm , while sampler orientation and wind direction/velocity also affected results (US EPA, 1986a; 1999a). Incidental dust settling was found to create positive biases of 10-15% despite the sloped roof of the units (Chow, 1995). Also, the glass fiber filters were shown to absorb sulfur dioxide and nitrogen oxides, potentially adding several $\mu\text{g}/\text{m}^3$ to the samples (Chow, 1995). US EPA (1977c) identified many issues associated with filter selection and sample preparation, including variable lead content of glass fiber filters. Scott *et al.* (1976) found no lead interference problems, however, thus leaving doubt. Lastly, carbon and copper from the pump were also identified as a source of contamination (Chow, 1995).

Despite heavy reliance on the Hi-Vol for total mass sampling, other particulate samplers also gained usage for providing other types of information not available from the Hi-Vol, such as near-continuous measures of airborne particle levels and particle size distributions. First developed in the late 1940s with widespread usage in the 1950s and 1960s (Longhurst, 2005; US EPA, 1977c), the AISI spot tape sampler was used for near-continuous particulate sampling over 2 to 4 hr periods. Although

¹⁰ A re-evaluation of the TSP NAAQS beginning in 1978 resulted in the 1987 replacement of the TSP standards with standards for PM_{10} , defined to include those particles collected by a sampler with a specified penetration curve yielding an upper 50% cut-point of 10 μm aerodynamic diameter (US EPA, 1987a). This change in the NAAQS was motivated by the desire to regulate the inhalable fraction of airborne particles that can be deposited in the lower regions of the human respiratory tract. Although the first reference method for PM_{10} was essentially an updated version of the Hi-Vol sampler with size-selective inlets, a number of other sampler types were eventually designated as reference or equivalent methods for sampling PM_{10} and determining NAAQS compliance (Chow, 1995). In 1997, US EPA again changed the nature of the particulate matter NAAQS, retaining the PM_{10} standard but also adding new $\text{PM}_{2.5}$ standards to address fine particles. Although a variety of PM_{10} and $\text{PM}_{2.5}$ samplers are currently used to collect samples for lead determination, these samplers are not discussed in any detail in this section since the lead NAAQS continues to be for total suspended particulate (TSP), as collected by a Hi-Vol sampler. Later in this section, we discuss the development and use of size-selective samplers since, although they may not be required for regulatory lead sampling, they have provided important information characterizing lead emission sources and the fate and transport of lead particulates.

typically used as an indirect measure of particulate matter, commonly referred to as the soiling index or coefficient of haze, the AISI sampler was used for lead determination in some studies including a 1960s survey of airborne lead in Cincinnati, Philadelphia, and Los Angeles (Diggs *et al.*, 1963; Ludwig *et al.*, 1965). The AISI sampler was also used in the early 1970s to determine diurnal airborne lead concentrations in Chicago and Washington, although the study authors reported tape filter contamination with metals and low collection efficiencies for the paper tape filters relative to the glass fiber filters used in NASN Hi-Vol samplers (MacLeod and Lee, 1973). Near-continuous methods have continued to evolve, with several gaining federal equivalent status for PM₁₀ in the early 1990s, including the Rupprecht & Patashnick Tapered Element Oscillating Microbalance (TEOM) PM₁₀ Monitor, the Andersen Instruments PM₁₀ Beta Attenuation Monitor, and the Wedding & Associates PM₁₀ Beta Gauge (US EPA, 2005a).¹¹

Size-selective samplers have been used since the 1970s to provide particle size distribution information for ambient particles, including by studies characterizing lead emission sources at primary lead smelters and the fate and transport of lead particulates. Modern size-selective samplers were developed in the 1940s with the earliest cascade impactor, but they did not gain widespread usage in ambient particulate matter studies until the 1960s and 1970s following the commercialization of the Andersen cascade impactor (Marple, 2004). Through its use in the NASN cascade impactor network in the early 1970s, the Andersen cascade impactor provided some of the earliest size distribution measurements (in 6 size ranges) for trace metal components including lead (Lee *et al.*, 1972). Early in this program, Lee and Goranson (1972) reported sample losses related to fitting the filter properly in the filter holder, flow rate variability, and system leaks. Although these sample loss problems were largely addressed as operators gained experience (Lee and Goranson, 1972), particle bounce and re-entrainment has been a persistent source of sample loss for these samplers since their development (US EPA, 1986a; Chow, 1995). In addition, some studies have shown a bias towards small particles due to fracturing of larger particles at impaction (US EPA, 1982). Despite its limitations, the cascade impactor is still used today for collection of particle size distribution data.

The dichotomous sampler also gained usage as a size-selective sampler in the 1970s for collection of particles in 2 size ranges, with a typical particle diameter demarcation between 2.0 and 3.5

¹¹ Federal equivalent methods for criteria pollutants such as lead, PM₁₀, and PM_{2.5} are established in accordance with Title 40, Part 53 of the Code of Federal Regulations (40 CFR Part 53). Federal equivalent methods must meet rigorous requirements for adequacy. US EPA maintains a listing of designated reference and equivalent methods (US EPA, 2005a).

microns (US EPA, 1977c). Following research indicating that atmospheric particles commonly occur in 2 distinct modes, often referred to as "fine" and "coarse," the dichotomous sampler was developed in the 1970s using a "virtual" impaction technique that eliminated the particle bounce issue commonly experienced with cascade impactors (US EPA, 1977c; US EPA, 1986a). Dzubay and Stevens (1975) published one of the earliest studies where the dichotomous sampler was used to collect samples for lead determination, showing that at least 75% of the lead for ambient samples collected in St. Louis was contained within particles less than 2 μm in diameter.

Currently, state-of-the-art near-continuous instruments are available for measurement of particle size distributions (US EPA, 2004).

4.2 Analytical Methods Used for Determination of Inorganic Lead Associated with Particulate Matter

For air lead measurement, chemical analysis is required after particle collection. Initially this was achieved with "wet chemistry," while electronic instrument chemistry techniques have evolved since the 1950s (Table 4-2). Today, AAS (Atomic Absorption Spectrophotometry) and ICP (Inductively Coupled Argon Plasma emission spectrometry) are accurate methods of choice (US EPA, 1998a).

Colorimetric analysis for lead using the reagent dithizone was a standard method for lead determination from the 1940s until the 1970s (Skogerboe *et al.*, 1977). This method was sensitive and accurate but was complex, costly, and required a skilled analyst (US EPA, 1977c; Skogerboe *et al.*, 1977). NRC (1972) recommended the ASTM Dithizone Method (*i.e.*, Tentative Method of Test for Lead in the Atmosphere) ASTM Designation D 2681-68T) for sampling and analysis of both particulate and nonparticulate (organic) lead, reporting a method detection limit of approximately 0.2 $\mu\text{g}/\text{m}^3$. The dithizone method was used for lead analysis of AISI spot tape samples collected during the Ludwig *et al.* (1965) study of airborne lead in Cincinnati, Los Angeles, and Philadelphia. Results from an interlaboratory comparison were unsatisfactory and the authors hypothesized it was due to "a lack of discrimination of the method in analyzing the complex particulate sample as compared to a soluble, essentially pure lead compound in the synthetic sample" (Ludwig *et al.*, 1965).

Optical emission spectroscopy (OES) was popular in the 1950s, most notably for lead determination of suspended particulate matter samples collected from the Public Health Service's National Air Sampling Network (NASN) from the mid-1950s into the 1970s (PHS, 1958; US EPA, 1976d; 1977c). It was also used in the NASN cascade impactor network (Lee *et al.*, 1972), as well as other contemporaneous air pollution studies (e.g., Morrow and Brief, 1971; Scott *et al.*, 1976). OES was a precursor to today's ICP spectroscopy,¹² relying on an electric arc or high-voltage flame as an emission source rather than a plasma flame. Prior to 1960, emission spectrometers were commonly found in specialized trace-detection laboratories since they could be used for simultaneous analysis of a large number of elements (US EPA, 1977c).

Although OES was considered a rapid and practical technique for particulate lead determination, it had some key shortcomings, including lower precision and sensitivity than alternative techniques (US EPA, 1976d; Skogerboe *et al.*, 1977). Scott *et al.* (1976) reported a method detection limit of 0.15 µg/m³ for OES analysis of particulate lead samples, while US EPA (1976d) reported lower analytical discrimination values of approximately 0.02 µg/m³ for OES analysis of NASN samples. US EPA (1976d) reported that the OES analysis of the 1970-1974 NASN samples was not "considered to be as sensitive or precise a method as a specific determination method for a single element, such as in the case of determination of lead by atomic absorption," useful for relative order but not accurate concentrations. In addition, OES required that samples be in solution, and prior to 1966, this was done using a high-temperature muffle furnace for NASN samples. Potential losses of the more volatile metals, including lead, as a result of the high-temperature ashing were later reported to be a problem for the analysis of NASN samples prior to 1966 (US EPA, 1976d; 1977c).

Atomic absorption spectroscopy (AAS) eventually replaced OES and colorimetric dithizone for rapid, accurate, and sensitive particulate lead determination.¹³ Although AAS originated in academic labs in 1955 (Skogerboe *et al.*, 1977), it was not used for routine lead analysis until the late 1960s and early 1970s. Chakrabarti *et al.* (1966) is among the earliest studies employing AAS for lead determination in atmospheric particulate samples. Following this study, a growing number of air pollution studies employed AAS for lead determination, including Burnham *et al.* (1969), Kneip *et al.*

¹² Robinson (1978) noted that the earliest uses of a plasma as the excitation source in atomic emission spectroscopy date back to the early 1960s, although detection limits at this time were extremely high.

¹³ Traditional AAS employs a flame to vaporize lead atoms in a sample. Nonflame (graphite furnace) AAS employs a graphite furnace rather than a flame to vaporize trace metal atoms. Nonflame AAS gained commercial usage in the 1970s (Skogerboe *et al.*, 1977), and as discussed later in this section, is currently a federal equivalent method for lead determination in suspended particulate matter samples in support of the lead NAAQS.

(1970), Ranweiler and Moyers (1974), and Scott *et al.* (1976). This method was recommended as a reliable, sensitive, and interference-free method for airborne lead measurement in the National Academy of Sciences report on lead in 1972 (NRC, 1972), and in 1975 it was named a tentative ASTM method for testing of particulate lead in the atmosphere (US EPA, 1977c).

Although commonly used, AAS has inherent uncertainties including background absorption, chemical interferences, background light losses, and matrix effects (Skogerboe, 1974; US EPA, 1977c). In addition, some early studies showed that acid digests of filters, followed by AAS, yielded low results due to incomplete digestion of particles (Skogerboe, 1974). Refinements to the AAS method were made in the 1970s to address some of these issues, and in a large mid-1970s study where approximately 1,000 NASN samples were analyzed using both AAS and OES, Scott *et al.* (1976) demonstrated the superior performance of AAS, including no discernible interference problems, a low method detection limit ($0.1 \mu\text{g}/\text{m}^3$), and low lead contamination of glass fiber filters. In the 1970s and 1980s, commercial AAS instruments became available and more widely used for rapid particulate lead determination, although US EPA (1986b) reported that there remained a persistent problem of sampling and laboratory contamination.

In 1978, AAS was promulgated as the federal reference method for lead determination in suspended particulate samples in support of the lead NAAQS (US EPA, 1978a). Detection limits for AAS are currently on the order of $0.002 \mu\text{g}/\text{m}^3$ (US EPA, 1999a). AAS currently remains the federal reference method for particulate lead determination, although a number of other methods have achieved federal equivalent status. Federal equivalent methods for particulate lead determination currently include: nonflame GFAA spectrometry, X-ray fluorescence spectrometry (XRF), inductively coupled argon plasma-optical emission spectrometry (ICP-OES), inductively coupled argon plasma-atomic emission spectrometry (ICP-AES), and inductively coupled argon plasma-mass spectrometry (ICP/MS) (US EPA, 2005a).

Table 4-2

Timeline of Analytical Methods Used to Determine Particulate Lead

Table	Analytical Method
1920s	Chromate method (<i>i.e.</i>, modified Fairhall method) gains usage for lead determination, in particular for PHS investigations of tetraethyl lead
1940s	Colorimetric dithizone gains acceptance as standard method for lead determination
1950s	- PHS first employs optical emission spectroscopy (OES) for trace metal analysis of NASN samples - Birth of modern AAS
1960s	- First applications of AAS for particulate lead determination - Commercial AAS instruments become available - Early applications of graphite furnace atomic absorption (GFAA) and ICP-AES for elemental analysis
1970s	- AAS promulgated as federal reference method for lead determination in suspended particulate matter - GFAA and ICP-AES become commercially available
1980s-present	- ICP-MS becomes commercially available - Methods such as GFAA, X-Ray Fluorescence Spectrometry (XRF), ICP-OES, ICP-AES, ICP/MS attain federal equivalent method status for particulate lead determination

These newer methods offer some unique advantages compared to AAS, but also some notable disadvantages (US EPA, 1999a). Some of these methods such as GFAA and ICP/MS have increased sensitivity for lead compared to AAS (detection limits for lead are approximately 0.00005 and 0.00001 $\mu\text{g}/\text{m}^3$ for GFAA and ICP/MS, respectively), but they both require greater operator skill (US EPA, 1999a). The ICP-based methods are the most expensive, and can be affected by interferences. XRF offers the advantage of being non-destructive and requiring minimal sample preparation compared to AAS; however, it is not very sensitive for single elements, and it can have problems with matrix offsets and background impurities. Overall, AAS remains a well-proven method for rapid analysis of particulate lead, but there are a number of additional methods currently available for rapid, accurate, and precise measurement of particulate lead.

4.3 US EPA Guidelines on Air Monitoring Around Lead Sources

Following the 1978 promulgation of the $1.5 \mu\text{g}/\text{m}^3$ lead NAAQS and the commencement of the SIP process for lead, US EPA required the States to establish and operate monitoring networks for ambient lead. Despite this requirement, little guidance was available at the time regarding site selection criteria for monitors and how to set up a monitoring network. As noted in the 1977 *Air Quality Criteria for Lead* (US EPA, 1977c), "Much remains to be done toward establishing criteria for location of samplers." As discussed below, guidance and regulations regarding ambient air surveillance of lead were slow to develop, resulting in uncertainty regarding where to site monitors and what types of data to collect.

In the 1978 Federal Register notice promulgating the lead NAAQS, US EPA called for at least 2 permanent lead ambient air quality monitoring stations to be established in each urbanized area that: (1) had a 1970 population greater than 500,000; or that (2) had a lead air quality exceeding the $1.5 \mu\text{g}/\text{m}^3$ quarterly average since 1974 (US EPA, 1978a). Further, it specified that at least one of the monitors be a roadway type monitor (located adjacent to a major roadway) and that at least one be a 'neighborhood site' monitor, in accordance with US EPA's *Supplemental Guidelines for Lead Implementation Plans* (US EPA, 1978b). This ruling did not specify specific sampling requirements in the vicinity of major lead point sources; instead it required SIPs to contain a "demonstration" that the standard would be met and maintained in areas in the vicinity of several specific point sources including primary lead smelters.

On May 10, 1979, a final ruling was published in the Federal Register that provided a more detailed set of requirements for air quality monitoring for all criteria pollutants, except for lead (US EPA, 1979b), which was still under development. This was defined as the State and Local Air Monitoring Stations (SLAMS) network. A National Air Monitoring Stations (NAMS) network was also defined in this ruling as a subset of the SLAMS network for US EPA's determination of national trends in air pollution.¹⁴ The number of SLAMS in any Region was determined by the meteorology, population density, and emission density on a case-by-case basis, depending on SIP needs, while a minimum number of NAMS was defined.

¹⁴ Other types of stations were also defined. These stations included Special Purpose Monitors (SPMs), which the State could use to monitor around point sources or for special projects (without following the requirements set forth for SLAMS stations, unless they were used for support of SIPs); and the Prevention of Significant Deterioration stations or PSDs, generally operated for short periods of time by a source owner or operator (a SLAMS could also serve as a PSD).

US EPA's May 1979 ruling indicated that the agency had "reevaluated the need for specific regulations for lead monitoring around point sources" and concluded that the SLAMS network would satisfy the requirements (US EPA, 1979b). Furthermore, until lead monitoring regulations, siting criteria, and quality assurance requirements were issued, the ruling specified that States follow the draft guidelines for lead monitoring in the vicinity of point sources, which were later finalized until 1981 (US EPA, 1981a). States could also require point sources to conduct specific/targeted monitoring following the long-term monitoring guidelines (US EPA, 1979b).

On September 3, 1981, US EPA promulgated specific requirements for lead monitoring (US EPA, 1981b). The largest distinction between the lead guidelines and earlier guidelines for other criteria pollutants was the emphasis on mobile source monitoring for lead. Thus, 1 of the 2 stations required as a minimum in a NAMS lead network was to target roadway emissions. The second station was to aim at a larger geographical area or "neighborhood scale," typically located in a residential area with a high population and high traffic density.¹⁵ This latter monitor would represent neighborhood scale impacts of point sources if they existed (US EPA, 1981b).

In a related action, US EPA finalized its "Guideline for Lead Monitoring in the Vicinity of Point Sources" in 1981 (US EPA, 1981a). This guideline required operator or State monitoring near point sources such as lead smelters, independent from NAMS or SLAMS urban site monitoring. Requirements included a minimum of one year of lead monitoring data to determine compliance with NAAQS, and as a secondary objective, to determine the contributions from fugitive emissions (US EPA, 1981a). One year of coincident meteorological data to provide information on the adequate placement of monitors was also required (US EPA, 1981a). The number of monitors would be determined by site-specific factors, *e.g.*, meteorological conditions, terrain, and other nearby sources; dispersion modeling was allowed to help design a network based on emissions, wind speed, and wind direction (US EPA, 1981a). US EPA's minimum recommended network included 1 upwind background station, 2 monitors sited to capture the

¹⁵ Spatial scales for monitors were defined in this ruling and included a Microscale monitor, for street canyons and traffic corridors, where point sources may impact under "fumigation conditions"; a Middle scale monitor for areas several blocks in size, which was the typical scale for measuring point source impacts; a Neighborhood scale, an area with uniform land use patterns (*e.g.* residential area) from 0.5 to 4 km, often used for measuring impacts on children; an Urban scale monitor for areas 4 to 50 km to address city-wide air quality; and a Regional Scale monitor for areas greater than 50 km, typically used to measure background levels. A spatial scale representativeness was typically assigned to each monitoring station.

maximum concentration impacts of stack emissions, and 2 fugitive monitors (one close to the fenceline and 1 < 1 mile downwind).

Lead monitoring requirements were revised in November 1997 to account for the decline in leaded gasoline usage (US EPA, 1997a), but US EPA withdrew these revisions in December 1997 (US EPA, 1997b) due to technical criticisms. US EPA further revised and finalized the requirements in January 1999 (US EPA, 1999b), allowing the discontinuation of many lead SLAMS stations in urban areas along major roadways while maintaining a focus on stationary point sources.

With US EPA's 1999 revisions, a minimum of 2 SLAMS stations (more in complex areas) was now required in areas exceeding the lead NAAQS in any of the most recent 8 quarters (US EPA, 1999b). With the discontinuation of many SLAMS lead monitoring stations, NAMS requirements were modified to require only 1 NAMS station at the maximum concentration site in 1 of the 2 most populated cities within each US EPA region, and 1 station in any city/county with NAAQS violations over the last 8 quarters (US EPA, 1999b). The focus of the revised NAMS network was on area-wide lead emissions rather than on stationary sources.

US EPA (1997c) established guidelines for States to establish monitoring networks around point sources to maximize the probability of capturing maximum lead concentrations, with the minimum number of monitors and at a minimum cost. The guidelines addressed source data collection, topography, land use, meteorology, and air modeling considerations. Requirements included a minimum of 2 monitors near the locations of maximum impact of point sources based on modeling and/or previous monitoring data (US EPA, 1997c). Furthermore, if both stack emissions and fugitive emission impacts were anticipated, 1 monitor was to be used for stack impacts and the other for fugitive emission impacts (US EPA, 1997c). A primary lead smelter case study was included in the guidance, as was emphasis on the use of site-specific information to determine both the number and the location of monitoring sites around any given stationary source to capture the maximum lead concentrations (US EPA, 1997c).

5 Evolution of Air Modeling Capabilities

Air quality simulation modeling predicts the geographic distribution of air concentrations caused by a specific emission source or combination of sources. Usually, the process of air modeling requires 2 major steps: (1) the estimation of the emission rate of a pollutant from a specific source (normally expressed in units of mass/time, *e.g.*, g/sec); and (2) the prediction of a time-averaged air concentration of a pollutant (normally expressed in units of mass/volume, *e.g.*, $\mu\text{g}/\text{m}^3$) resulting from the transport and dispersion of the pollutant emissions from the source to a given location.

There are many different types of air quality simulation models applicable for different distance scales and pollutants. For example, long-range transport models can track pollutants traveling for thousands of kilometers from a single source. Urban and regional scale photochemical models are used for ozone and other secondary pollutants (*e.g.*, sulfates and nitrates), and they incorporate hundreds of chemical reactions.

This review will focus on short-range air models typically used to predict air concentrations of primary (*i.e.*, emitted) pollutants within 50 km of a specific emission source or an industrial source complex. The primary pollutants (*e.g.*, lead, sulfur dioxide) are generally considered non-reactive in short-range air modeling; however, some air models can include simple exponential decay of pollutants as a function of travel time. This section will cover the important historical air modeling events concerning short-range (less than 50 km), non-reactive air models, and the subsequent evolution of US EPA regulatory dispersion models. Figure 5-1 presents a timeline of important air modeling events since the 1940s that are discussed in this section.

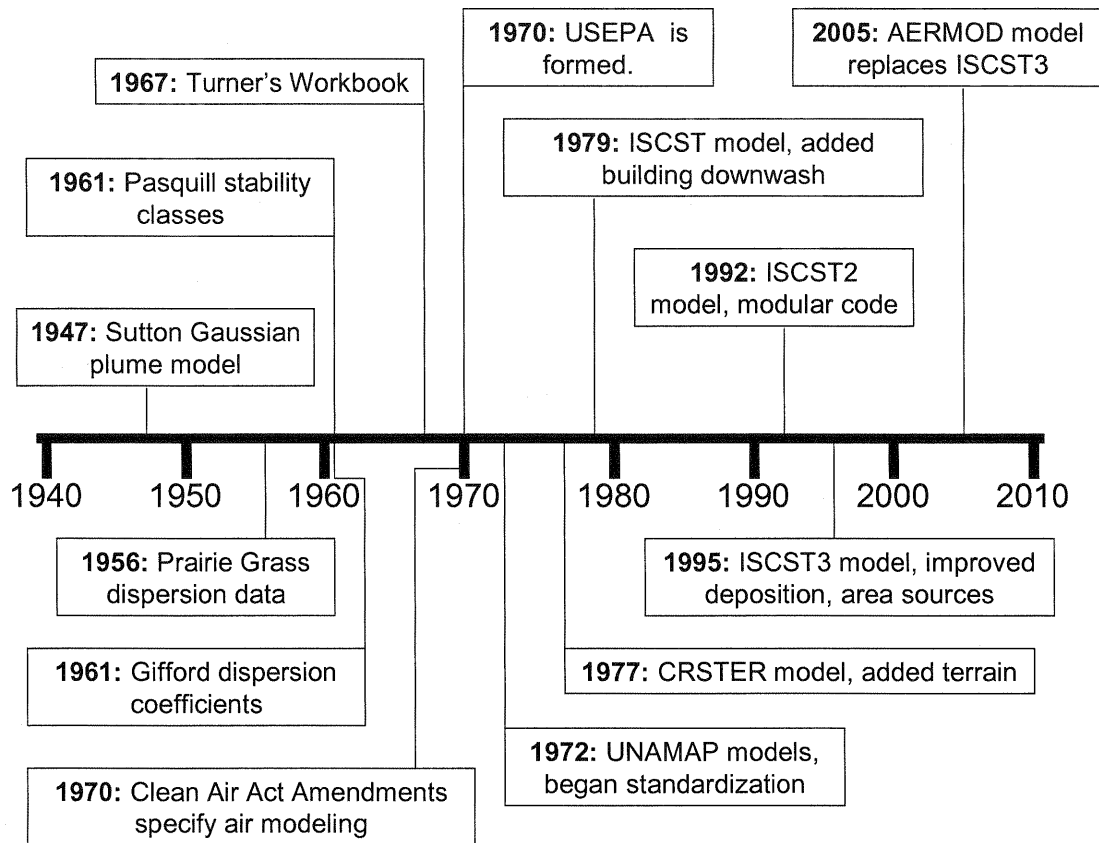


Figure 5-1
Timeline of Important Events in Air Dispersion Modeling

5.1 The Gaussian Plume Model

Atmospheric turbulence is difficult to simulate by a simple mathematical formulation because of the randomness of turbulent fluctuations in the atmosphere and the wide size range of turbulent eddies affecting dispersion. Nonetheless, driven partly by the use of mustard gas in World War I and the fear of further use of chemical warfare, a simple formulation, easily calculable by hand, was developed in the 1930s and 1940s to predict the air concentrations resulting from pollutant sources (Bosanquet and Pearson, 1936; Sutton, 1947). This mathematical technique is a relatively simple equation known as the Gaussian plume dispersion model, because the spread of a plume from a point source is approximated as a Gaussian (*i.e.*, bell-shaped) distribution in both the horizontal and vertical directions. Sutton (1947)

described this equation almost exactly as used by current US EPA air dispersion models. Interestingly, even in the 1940s, a "factor of two" accuracy was claimed when comparing Gaussian plume predictions with limited experimental data (Sutton, 1947).

In the 1950s and 1960s, air modeling using a Gaussian plume formulation became more standardized through the use of dispersion coefficients based on experimental data. An important experimental program to study atmospheric dispersion was performed in 1956 over relatively flat terrain in Nebraska. This comprehensive program of over 70 tracer experiments (using SO₂ as a tracer gas) with detailed meteorological measurements became known as Project Prairie Grass, and the data from this program resulted in the first useful set of dispersion coefficients for air modeling purposes.

Although it was obvious from the Prairie Grass data that greater dispersion occurred during times of greater atmospheric turbulence, the problem was how to account for differences in turbulence or atmospheric stability in a practical manner that could be used in an air dispersion model. The key breakthrough has been credited to Pasquill (1961), who developed a set of discrete atmospheric stability classes based on 2 easily observable meteorological parameters: insolation and wind speed. The development of these discrete atmospheric stability classes, normally designated as a set of 6 classes (A through F, from very unstable to very stable), was a key factor in the practical and widespread use of Gaussian plume dispersion models.

Pasquill (1961) expressed dispersion coefficients based on the Prairie Grass data in the form of plume angular spread, as a function of discrete atmospheric stability class. Gifford (1961) converted Pasquill's angular spreads into a set of plume standard deviations in the horizontal and vertical directions (σ_y , σ_z) that could be directly input into the Gaussian plume equations. Turner (1961) expressed Pasquill's stability classes in terms of standard hourly airport observations, and published a classic document in 1967 called "Workbook of Atmospheric Dispersion Estimates" (Turner, 1967), which presented practical Gaussian plume equations and a set of dispersion coefficient graphs of σ_y and σ_z as a function of downwind distance for Pasquill's 6 atmospheric stability classes. These dispersion coefficient graphs have become known collectively either as the Pasquill-Gifford (PG) or the Pasquill, Gifford, Turner (PGT) dispersion curves, and other experimental dispersion programs conducted since the 1960s have verified the accuracy of these dispersion curves. The PG or PGT dispersion coefficients,

based on the 1956 Prairie Grass experiments, have been used with only minor changes by most Gaussian plume models developed and recommended for use by US EPA from the 1970s to the present.¹⁶

5.2 US EPA Regulatory Air Models

The history of US EPA regulatory air modeling began in 1970, and Irwin (2002) recently published an excellent reference document presenting a detailed evolution of US EPA air modeling. In 1970, 2 milestone regulatory developments occurred: (1) the US EPA was formed from parts of several other Federal agencies, and (2) the 1970 amendments to the Clean Air Act were passed, which specified the use of air dispersion modeling to predict the impact of new sources, and to verify that existing sources were not causing violations of the newly promulgated air pollution standards, known as the NAAQS, for criteria pollutants including total suspended particulates (TSP) and sulfur dioxide (SO₂).

The regulatory driving force of the 1970 Clean Air Act amendments created a new business enterprise – air pollution consulting. During the 1970s, a number of small environmental consulting firms were formed to satisfy the new need for regulatory air modeling. The consultants were primarily meteorologists, who realized that their knowledge of atmospheric turbulence and dispersion theory could be put to practical use. Since US EPA funded a reasonable amount of academic research in atmospheric dispersion starting in the early 1970s, the first college courses devoted specifically to air pollution problems began in the mid-1970s, leading to the evolution of entire college programs in atmospheric science.

Since there were no standardized computer air models available in the early 1970s, air modeling at that time was usually done by hand calculations of Gaussian plume equations, which were generally based on the *Workbook of Atmospheric Dispersion Estimates* (Turner, 1967). A number of consultants developed proprietary dispersion models, which ran on the large mainframe computers of the time. Because there were no standard air models, and different consultants developed their own proprietary air models, US EPA and state regulatory agencies found it difficult to judge the accuracy and consistency of air modeling studies submitted to satisfy air regulations.

¹⁶ In November 2005, US EPA recommended the AERMOD model to replace ISCST3 as a preferred short-range dispersion model (US EPA, 2005b). AERMOD does not use the discrete Pasquill stability classes, but calculates dispersion coefficients based on a continuous atmospheric stability formulation.

To partially alleviate this lack of standardization, US EPA developed a number of simple computer models in the early 1970s, based on the Gaussian plume model equations and the dispersion curves presented in Turner (1967). The equations for calculating the plume rise caused by the buoyancy and momentum of a hot point source (e.g., a power plant stack) were based on the classic review of plume rise equations by Briggs (1969). These early models were designated as the UNAMAP (User's Network for Applied Modeling of Air Pollution) set of models, and were originally only available in an interactive mode through a teletype connection to US EPA in North Carolina. For more widespread use, the National Technical Information Service (NTIS) distributed the UNAMAP models on computer tapes to interested users in the 1970s and 1980s. With the advent of the Internet c. 1990, the US EPA established an air modeling web site, www.epa.gov/ttn/scram, which provides free downloads of recommended air models and meteorological data.

The earliest US EPA models in the UNAMAP series in the early 1970s were simple FORTRAN computer programs that provided an alternative to hand calculations of Gaussian plume equations for a point source, and were called PTMAX (Point Source: Maximum), PTDIS (Point Source: Dispersion), and PTMTP (Point Source: Multiple Point Sources). Although relatively simple, these programs began a trend toward air model standardization. In 1977, US EPA developed a more sophisticated point source model called CRSTER¹⁷ that included, for the first time, the effect of complex terrain interactions on an elevated point source.

To provide greater model standardization and to assure consistent application of air models, US EPA in 1978 published the first edition of "Guideline on Air Quality Models" (US EPA, 1978c), which specified "preferred" air models, like CRSTER, and provided guidance on meteorological and model input parameters. The "Guideline on Air Quality Models" has been updated frequently since 1978, and has resulted in widespread acceptance and standard use of US EPA's "preferred" air models, as well as the use of consistent meteorological and model input parameters, to provide a large measure of standardization in regulatory air modeling.

¹⁷ Because US EPA wanted to quickly develop a sophisticated point source model, the model development effort became known as the "crash (CRS)" program for its tight deadlines (Irwin, 2002). When the model was adapted to include terrain, the model name was coined, CRSTER. Irwin (2002) provides a number of similar insights into how air models were named in his historical review.

5.3 The Industrial Source Complex (ISC) Model

In 1979, US EPA added the simulation of aerodynamic building wake effects or "building downwash," based on experimental wind tunnel studies, to the CRSTER model, which became the first version of the ISC model (US EPA, 1979c). The ISC model quickly became popular because of its ability to handle terrain, building downwash, and any combination of multiple point, area, and volume sources. Because of computer limitations at the time, 2 ISC models were developed by US EPA: the detailed ISCST (Industrial Source Complex, Short Term) version, which used hourly meteorology to calculate short-term (1-hour, 3-hour, 8-hour, and 24-hour) averages of air concentrations; and the simpler ISCLT (Industrial Source Complex, Long Term) version, which used long-term averaged meteorology to calculate annual and quarterly averages.¹⁸ These ISC models have been designated as "preferred" models in the various releases of US EPA's "Guideline on Air Quality Models" since 1979, and they have become the air models used for almost all regulatory air modeling of industrial sources over the last 25 years.

The original ISCST model in 1979 calculated deposition of particles by a simple gravitational settling velocity as a function of particle size, and used an empirical "reflection coefficient," which ranged from 0 to 1 depending on particle size, to estimate what fraction of the particles deposited when they contacted ground surface. This model formulation was designed for relatively large particles (greater than about 20 μm), which are affected primarily by gravitational settling. The area source algorithm used in ISCST was based on a finite line source technique, which was shown in a later study to predict unrealistic concentrations for receptors located within or near the area source (US EPA, 1989).

Because of inefficiencies in the FORTRAN programming of ISCST, a major overhaul of the programming in ISCST occurred in 1992, when the FORTRAN code was modified significantly to make the code more modular. The re-coded model was designated as ISCST2 (US EPA, 1992a). However, the basic deposition and area source algorithms were unchanged from the original ISCST model.

¹⁸ Although the ISCST model can also calculate annual averages, the long computer run times in the 1980s necessary to calculate hourly concentrations over an entire year (*i.e.*, 8760 hours) favored the use of the simpler and faster ISCLT model, which used an annual or quarterly frequency of wind speeds, directions, and stability classes (known as STAR data). With the advent of faster computers, the ISCLT model has become obsolete, and the ISCST model (as the ISCST3 version) has been used almost exclusively for all air modeling since 1996.

Because of the known deficiencies in the ISCST and ISCST2 area source calculations, an improved integrated area source algorithm was implemented into ISCST2, and released to the public in draft form as the AREA-ST model. Concurrently, development progressed on improved dry deposition algorithms that could more accurately model small particles (less than 10 μm), a new wet deposition technique, and an improved plume depletion technique that accounted for all particles that had deposited on surfaces. These techniques were independently implemented into ISCST2 and were released to the public in draft form as the DEPST model. The AREA-ST model and the DEPST model were then combined into a single draft model called ISC-COMPDEP, which in 1995 was released as the ISCST3 model (US EPA, 1995a).

Thus, it was not until 1995 that the ISC model was sufficiently improved to accurately predict air concentrations and surface deposition of fugitive area sources that release relatively small particles. Since 1995, only minor changes to the ISCST3 model have been made, including the addition of gas-phase deposition on surfaces in 1999. In November 2005, US EPA replaced the ISCST3 model with the AERMOD model as the preferred short-range air dispersion model, but allowed use of the ISCST3 model for regulatory air modeling until November 2006 (US EPA, 2005b).

Because of its widespread usage, a number of validation studies of the ISC model have been performed, in both rural and urban locations, over the last 25 years (*e.g.*, Bowers and Anderson, 1981; Schulman and Hanna, 1986; Riswadkar and Kumar, 1994; Kumar *et al.*, 1999). The Kumar *et al.* (1999) study compared the ISCST3 model with air monitoring data for long-term predictions of SO_2 from 123 industrial stacks in Lucas County, Ohio. The results depended somewhat on the statistical measures used for comparison, but in general, the ISCST3 model consistently predicted within a "factor of two" of the observed values. Since Sutton (1947) claimed the same accuracy for the basic Gaussian plume model, it appears that a "factor of two" may be the limit of accuracy expected from the simplification of complex atmospheric turbulent processes by a Gaussian plume equation.

5.4 Emission Estimation Techniques for Primary Lead Smelters

The overall accuracy of air concentrations predicted by a dispersion model is dependent on the accuracy of the emission rates input to that model. Since the air concentrations predicted by a Gaussian plume model are linearly proportional to the emission rate of a specific source, any errors in the source

emission rate are linearly propagated to the predicted air concentrations. Similar to the evolution of air dispersion modeling techniques, source emission estimation techniques have improved with time. As a specific example, the evolution of lead emissions to the air from primary lead smelters is discussed in this section.

Like air quality dispersion models, emission estimation techniques for a large number of industrial sources have become standardized by US EPA over the years. The equivalent US EPA document to "Guideline on Air Quality Models" that describes standardized emission estimation techniques is entitled "Compilation of Air Pollutant Emission Factors," which has been published and continually updated by US EPA since 1972 (US EPA, 1972a). This document began in 2 earlier Public Health Service emission documents (PHS, 1965; PHS, 1968) published before the US EPA was formed in 1970. Because of its widespread use for recommended emission factors for a wide variety of industrial sources, this document has become known simply by its original Public Health Service document number, "AP-42."

The AP-42 document has evolved through 5 editions since 1972, with many improvements added to a specific edition either by replacement pages or new appendices. Figure 5-2 tracks the changes through the years of the AP-42 document specifically for particulate lead emissions to the air from primary lead smelters.

Since the NAAQS air lead standard of $1.5 \mu\text{g}/\text{m}^3$ for a quarterly average was not promulgated until 1978, the first two editions of AP-42 (US EPA, 1972a; 1973a) and the original third edition (US EPA, 1977d) did not include particulate lead emission rates to the air for any industrial sources. For primary lead smelters, only total particulates (TSP) and SO_2 emissions for point sources were provided in the first 2 editions and the original third edition of the AP-42 document.

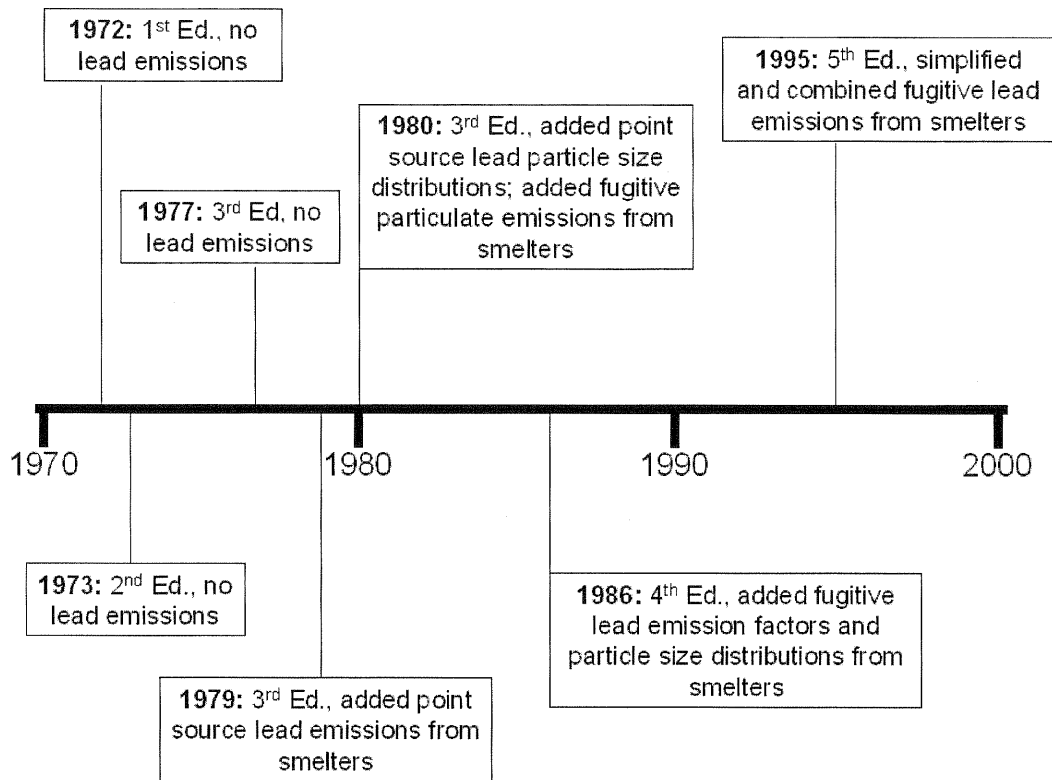


Figure 5-2
Timeline of AP-42 Changes for Lead Emissions from Primary Lead Smelters

In 1979, Supplement No. 9 of the third edition of AP-42 provided, for the first time, air lead emission factors for a number of industrial sources, including primary lead smelters (US EPA, 1979d). Emission factors were presented, in terms of lb lead emitted to the air per ton of lead produced, for 4 process-related point sources at primary lead smelters, but no fugitive sources were mentioned. In 1980, Supplement No. 10 of the third edition of AP-42 provided 2 major additions relating to primary lead smelters: (1) limited particle size information was provided for point sources only; and (2) for the first time, particulate emission factors for 15 different types of fugitive sources at primary lead smelters were included (US EPA, 1980a). No air lead emission factors were provided for these fugitive sources, and the particulate emission factors were assigned the lowest certainty rating of E to reflect the poor quality and limited amount of underlying data used to derive the emission factor.

In 1986, Supplement A to the fourth version of AP-42 provided, for the first time, air lead emission factors for 5 fugitive emission sources as well as particle size distribution data for these fugitive sources (US EPA, 1986b). These air lead emission factors for fugitive sources were assigned the second lowest certainty rating of D, indicating their low reliability for specific sources within the source category population. Finally, the fifth version of AP-42 in 1995 combined and simplified many of the fugitive emission sources at primary lead smelters (US EPA, 1995b). In addition, their emission factor ratings were reduced to the lowest certainty rating of E. There have been no changes to the primary lead smelting emission section of AP-42 since 1995.

6 Development of Particulate Air Emissions Control Technologies

Control technologies evolved concurrently with measurement and modeling developments. Early control efforts were motivated not only by pollution concerns but also by desires to improve byproduct recovery of useful byproducts (*e.g.*, rare metals, arsenic, sulfur dioxide) (Swain, 1939). Although the general principles underlying many of the primary particulate control technologies have been known for a century or more, technological advances and experience were required to improve the engineering of control efficiencies and to apply them to a larger variety of industrial processes.

6.1 History of Particulate Emission Control Technologies

The 4 primary particulate control devices developed in the 20th century (Table 6-1) are cyclones (centrifugal separators), electrostatic precipitators (ESPs), wet scrubbers, and baghouses (fabric filters) (NAPCA, 1969b; US EPA, 1977e; Cooper and Alley, 1994; EC/R, 1998). Each of these control technologies has been widely used at primary lead smelters, except for cyclones (US EPA, 1977e; 1980b), with ESPs and baghouses being the most prevalent (Stern, 1962; NAPCA, 1969b; US EPA, 1977e; 1980b; 1995c; Schupp, 2000).

Cyclones were used in industry for gas particulate cleaning by at least the 1890s, gaining commonplace usage during the 20th century (Zimmerman, 1933; Falk, 1955; Hardison, 1966; Cooper and Alley, 1994). In 1939, C.B. Shepherd and C.E. Lapple observed: "Centrifugal or cyclone collectors are widely used for the separation and recovery of industrial dusts from air or process gases. The usual type of cyclone is simple to construct and is very low in first costs compared with other types of dust collecting equipment" (Cooper and Alley, 1994). Falk (1955) described the use of multiple cyclones in series, while Hardison (1966) noted the use of cyclones as pre-cleaners ahead of other equipment. Although cyclones have not been common at primary lead smelters, US EPA (1980) reported the use of cyclones for dust control during milling and concentrating of lead ores prior to primary lead smelting.

Table 6-1
Key Events in the Development and Application of
Major Particulate Air Pollution Control Technologies at Smelters

Year	Event
<u>Baghouses (Fabric Filters)</u>	
1900s-1910	First used at lead, copper, and zinc smelters in California, Colorado, Missouri, and Utah for roaster and blast furnace gases
1930s	Common industrial use (cotton or wool bags)
1955	Efficiency >99%; use limited to gas temperatures <250° F
1950s	Development of synthetic fiber filter bags
1965	Efficiency = 99.7% overall (99.5% for 0-5 µm particles)
late 1960s	First use of synthetic fiber (fiberglass) filter bags at a smelter
1969	Baghouses and ESPs - principal particulate control technologies used at primary lead smelters
1980	Efficiency between 95-99.9% at primary lead smelters
c. 1990	Development of ceramic fabric bags that withstand temperatures up to 900° F
1990s	Continued development of specialty fabric bags with greater chemical resistance and thermal resistance up to 1,000° F
1999	Baghouses (or equivalent) required as part of EPA's final NESHAP rule for primary lead smelting
<u>Cyclones (Centrifugal Separators)</u>	
c. 1890s	First used for industrial gas particulate cleaning
1955	Efficiency of 50-90% for 5-10 µm particles; cyclones used in series called multi-cyclones
1962	Usage noted at primary lead smelters
1966	Used as pre-cleaners ahead of ESPs
1969	Efficiency >95% for >40 µm particles; very low efficiency for <5 µm particles
1977, 1980	Cyclones were not noted by EPA to be used at any primary lead smelter
<u>Electrostatic Precipitators (ESPs)</u>	
1906	Dr. Frederick Cottrell first successfully electrostatically-precipitated sulfuric acid fumes
1907	First commercial ESP demonstration; first ESP installed at a gold smelter for collection of sulfuric acid fumes
1910	First large ESP used for particulate collection at the Anaconda, MT copper smelter
1930s	Common industrial use; efficiencies near 95%
1939	By this time, ESPs had revolutionized recovery of acid mists, lead and arsenic fumes, and precious metals at smelters
early 1950s	Efficiency up to 98-99%
1969	Baghouses and ESPs - principal particulate control technologies used at primary lead smelters
1969	Efficiencies of 90-98+% (dry applications) and up to 99+% (wet applications)
mid-1970s	Efficiency >99.5%
<u>Wet Collectors (Wet Scrubbers)</u>	
early 1930s	Common industrial use
1940s	Development of venturi scrubber (most efficient of wet collectors) for particulate removal
1962	Use of various wet collectors (including scrubbing and spray towers and venturi scrubbers) noted at primary lead smelters
1965	Efficiency = 99.5% overall (99.0% for 0-5 µm particles) for venturi scrubbers
1960s	Wide variety of wet collectors in industrial use, including: spray chambers, wetted filters, mist eliminators, and scrubbers (centrifugal, impingement plate, packed bed, venturi, etc.)

In 1906, Dr. Frederick Cottrell invented ESPs for collection of sulfuric acid mists/fumes. Shortly following this invention, a large ESP for solids collection was installed in 1910 at the Anaconda, Montana copper smelter (Swain, 1949). ESPs gained widespread usage at industrial facilities by the 1930s (Green, 1931; Zimmerman, 1933; Swain, 1939), and revolutionized recovery of acid mists and metals at nonferrous smelters (Swain, 1939). NAPCA (1969b) stated: "The high-voltage electrostatic precipitator (ESP) is used at more large installations than any other type of high-efficiency particulate matter collector...High-voltage single-stage precipitators have been used successfully to collect both solid and liquid particulate matter from smelters, steel furnaces, petroleum refineries, cement kilns, acid plants, and many other operations" (NAPCA, 1969b, p. 81).

ESP improvements over the years have allowed increased collection efficiencies and wider application in a variety of industries, including primary lead smelting, particularly for treatment of sinter machine off-gases (Stern, 1962; NAPCA, 1969b; US EPA, 1977e; 1980b; 1995c; Schupp, 2000). ESP efficiencies approached 95% by the 1930s and 1940s (Cooper and Alley, 1994), 98% by the early 1950s (Anon., 1953), 99.5+% by the mid-1970s, and 99.9+% by the 1990s (Cooper and Alley, 1994). Although the ESP has been eclipsed by the baghouse as the dominant particulate control device at US primary lead smelters, it remained a widely used control technology at US primary lead smelters.

Wet scrubbers (wet collectors) in various forms have included simple spray chambers, centrifugal spray scrubbers, venturi scrubbers, impingement plate scrubbers, packed bed scrubbers, and mist eliminators (for removal of mists). Common use of wet scrubbers in industry was noted by the early 1930s (Zimmerman, 1933), and by the late 1940s, the development of the venturi scrubber was a key advance for efficient removal of fine dusts, mists, and fumes (Jones, 1949; Munger, 1951). With efficiencies of 98 to 99.8% reported for sulfuric acid mists in 1949 (Jones, 1949), 99.5% overall and 99.0% efficiency for 0-5 μm particles (Bond and Straub, 1972), venturi scrubbers are among the most efficient devices. Use of wet scrubbers at primary lead smelters was commonplace by the 1960s (Stern, 1962) in sulfuric acid "plants" for conversion of SO_2 to sulfuric acid (McKee, 1969; US EPA, 1980b; Wixson, 1982).

Baghouses (fabric filter bags) were used by industry since 1900.¹⁹ Austin (1907) noted that "[a]t the American Zinc Works, near Canyon City, Colorado, the company has for years filtered all the gases from their roasters [sintering machines] and blast-furnaces...[after] having been filtered at the bag-house, there is no smoke visible. This is also true of the bag-house installed in connection with lead-smelting plants." Austin further noted that wool bags, not cotton, were required for filtering corrosive, sulfuric acid-containing roaster gases. Ebaugh (1910) observed that "gases coming from lead blast furnaces and from zinc plants had been filtered successfully for many years," and that a Utah lead smelter began baghouse treatment of roaster and blast furnace gases in 1908 in response to a 1906 court injunction. The US Bureau of Mines (1954) highlighted the successful use of a wool baghouse for blast furnace solids collection at the Selby lead smelter in California in 1908, while the Selby Smelter Commission (1915) observed that a baghouse was in use at the Selby lead smelter in 1914 for elimination of visible smoke from the roaster stack. Schupp (2000) noted the installation of baghouses at the Herculaneum, Missouri primary lead smelter in 1910. Stern (1962) stated that "filtration is the oldest and generally the most reliable of the many methods by which dusts, mists, and fumes may be removed from gases."

Although baghouses were already widely used in industry by the early 1930s (Green, 1931; Zimmerman, 1933), technological improvements such as the use of synthetic fiber bags with greater chemical and thermal resistance (Falk, 1955; NAPCA, 1969b) led to greatly expanded baghouse use in the 1950s and 1960s. Advances such as this were important to lead smelters because Wells (1917) noted that higher stack gas temperatures resulted in greater gas travel distances and lower ground-level gas concentrations. Despite these improvements, electrical precipitators competed with baghouses because they could withstand greater gas temperatures (Wells, 1917).

Through at least 1960, baghouses primarily used woven or felted natural fiber bags of cotton or wool, which required gas temperatures of below 250°F (Zimmerman, 1933; Falk, 1955; NAPCA, 1960) and offered only fair overall chemical resistance (NAPCA, 1969b). Bags constructed of synthetic fibers (*e.g.*, polypropylene, Nylon®, Dacron®, Teflon®), asbestos, or fiberglass first appeared at a secondary lead smelter by the late 1960s (Falk, 1955; Diamond Power International, Inc., 2001; NAPCA, 1969b). These materials offered greater chemical resistance (US EPA, 1991a) and allowed baghouse use at gas

¹⁹ Bags are by far the most common type of fabric filter; hence, the term "baghouse" is widely applied to fabric filtration (EC/R, 1998).

temperatures up to 550°F (NAPCA, 1969b; US EPA, 1977e). Fabrics developed by the 1990s, such as Gore-Tex®, Chem-Pro®, and ceramics, offer even greater chemical and/or thermal resistance (up to 1,000°F for ceramics) (US EPA, 1991a; EC/R, 1998). Slight increases in collection efficiencies, up to >99%, were also realized as a result of incremental improvements in baghouse technologies (Falk, 1955; NAPCA, 1960): 99.7% (including 99.5% of 0-5 µm particles) by 1965 (Bond and Straub, 1972), between 95-99.99% by the mid-1970s (US EPA, 1977e), and 99-99.9+% in the 1990s (EC/R, 1998).

From the 1960s to the present, ESPs and baghouses have been the primary particulate control devices used at primary lead smelters (Stern, 1962; NAPCA, 1969b; US EPA, 1977e; US EPA, 1980b; US EPA, 1995c; Schupp, 2000), with baghouses becoming the more widely used technology (US EPA, 1998b). US EPA (1980b) noted that all 6 of the primary lead smelters in operation at the time used baghouses for particulates from blast and dross reverberatory furnace off-gases, and 3 of the 6 smelters used baghouses to collect particulates from the weak gas stream of sinter machines. Baghouses (or equivalents) were also required at primary lead smelters by federal regulation in 1999 as part of the final National Emission Standards for Hazardous Air Pollutants (NESHAP) rule (Section 9).

6.2 Fugitive Emission Control Technologies

By the mid-1970s it became apparent that point source controls alone would not achieve the NAAQS for particulates. As discussed in Section 2.3, US EPA then turned its attention to fugitive (non-point source) emission control (Lillis and Young, 1975; US EPA, 1977a). In 1977, US EPA published *Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions* (IPFPE), where IPFPE was defined as: "Particulate matter which escapes from a defined process flow stream due to leakage, materials charging/handling, inadequate operational control, lack of reasonably available control technology (RACT), transfer, or storage" (US EPA, 1977a). US EPA (1977a), as well as other concurrent US EPA reports (US EPA, 1977e; 1979a; 1979e), summarized the state of the knowledge on available control technologies for fugitive particulate emissions (both industrial process and open source). These documents addressed fugitive emissions at lead smelters, indicating that there was much to be learned about fugitive emissions and their control.

US EPA (1977a) discussed the following options for IPFPE control at smelters: building enclosures or hoods for the sintering and refining processes; proper operation and maintenance practices (*i.e.*, sealing of furnaces and ducts, prompt clean-up of spills); hoods for smelting and drossing processes; and enclosures, hoods, or wet suppression with water, foam, or chemicals for material storage, loading, and transfer areas. Building enclosures (typically ventilated to baghouses), however, presented worker health and safety challenges and were thus not immediately used at primary lead smelters (US EPA, 1979a). US EPA (1982) stated that use of localized hoods as opposed to building enclosures was "desirable from an economic and occupational exposure standpoint," but that building enclosures (though requiring large air flows) were being increasingly considered due to their ability to capture up to 95+% of fugitive emissions, as well as space constraints associated with the use of a number of localized hoods.

Retrofitting existing plants with fugitive emissions control systems was considered difficult due to space and operational limitations (US EPA, 1982), and there have been few major advancements in other types of techniques available for control of fugitive emissions. As noted by EC/R (1998): "The most widely used methods of controlling process fugitives are local ventilation [*i.e.*, hoods] and building enclosure/evacuation...paving of unpaved roads; eliminating, reducing, or managing truck transportation; and street cleaning are the most effective techniques to reduce fugitive dust emissions from roads" (EC/R, 1998)." These techniques are in essence the same as those identified by US EPA in its 1977 reports (US EPA, 1977a; 1977e). As discussed in Section 9, control of fugitive emission sources was addressed in US EPA's 1999 NESHAP regulations for primary lead smelters.

7 Development of Air Pollution Regulations and Standards

Air pollution management efforts in the United States began in the late 19th century with simple technical approaches to readily apparent and straightforward problems. Early attempts were made to control visible smoke and airborne soot from emerging fossil fuel burning industrial facilities through municipal ordinances prohibiting emission of visible pollution and limiting the locations in which such smoke-producing activities could be conducted. In contrast, air pollution management today has one of the most complex regulatory structures in the United States, tying together air pollution control agencies at the local, regional, state, multi-state and federal levels of government (often within the shadow of international treaties). This apparatus seeks to manage air quality problems, which often present the following characteristics:

- Air quality problems are often difficult to define and measure;
- Many air quality problems present complex technological challenges to develop effective control strategies;
- Measurement of the effectiveness of the available control strategies in achieving stated objectives is often uncertain and imprecise;
- The premises, goals, and strategies underlying various aspects of air quality management are subject to broadly divergent degrees of acknowledgement and commitment; and
- The degree of control appropriate to address air quality problems deemed appropriate for management engenders intense scientifically- and policy-based debates.

Because of these characteristics, the process of developing, promulgating, complying with and enforcing air quality standards and regulations is quite complex, as are the air quality controls themselves. An examination of the development of the modern air quality control apparatus reveals how difficult it has been to develop consensus goals and policies, to translate them into laws and a coherent body of regulations governing polluting activities, and to have these goals and regulations translate into effective control of pollutants. This section provides an overview of the major stages of developing the current air quality control system in the United States and conveys some of the complexities underlying the current system for controlling pollution.

7.1 Background of Air Quality Regulation Prior to Federal Legislation

The origins of early American efforts to control air quality are found in the smoky conditions of late 19th and early 20th century industrial cities. In cities such as Pittsburgh, St. Louis, Cincinnati and Chicago, it was commonplace for visible pollution resulting from fuel-burning industries to combine with fog and, during thermal inversions, to create conditions referred to as "Londoners" in which darkness during daylight hours caused work stoppages, school dismissals and accidents (Grinder, 1980, p. 84). Along with the visual impairment came dirt and filth and, ultimately, impaired health for the residents of these cities and a noticeably degraded urban ecology (Grinder, 1980, pp. 85-88).

These conditions gave rise to air quality control regulations in the form of local ordinances imposing emissions controls and land use controls, both growing out of legal bases in common law. Ultimately, these local ordinances were ineffective in the face of widespread industrialization and economic growth spurred on by the needs of 2 World Wars and by increasing complexities in the nature and reach of the causes of air pollution. The local programs were largely supplanted, beginning in the mid-1950s, by the current federal-state system of air pollution control.

Initial regulatory controls were carried out primarily at the municipal level (Grinder, 1980, p. 91; Reitze, 1991)²⁰ in response to these localized, though often citywide, conditions. These controls initially took the form of ordinances prohibiting or ordering the abatement of the smoke nuisance, *i.e.*, emission controls, as in Cincinnati, Cleveland, Pittsburgh, St. Louis and St. Paul (Reitze, 2001, p. 10). Many of these measures were the product of grass-roots organizations such as "Anti-Smoke Leagues" and, particularly, the efforts of women's clubs and organizations (Grinder, 1980, p. 88), typical of other Progressive Era social reform movements focused on the problems of industrialization. Development of these early ordinances was also the result of the failure of traditional common law legal principles such as nuisance, negligence and trespass to address air pollution problems effectively (Reitze, 1991, pp. 1555 – 1569; Kennedy and Porter, 1955).²¹

²⁰ Municipal ordinances of this type sometimes ran afoul of state constitutions' allocations of authority, as in Missouri where an early smoke nuisance ordinance in St. Louis was held to be an unconstitutional exercise of the police power reserved to the state, leading to a petition drive for permission to enact the ordinance (Anon., 1897).

²¹ For example, control of smoke pollution using nuisance law was frustrated by the fact that smoke was not considered to be a nuisance under the common law and that specific harm resulting from the smoke needed to be demonstrated for smoke to be established as a nuisance in a particular instance. The enactment of municipal ordinances overcame this limitation because municipalities or states were empowered to declare activities creating smoke pollution to be "public nuisances" or to regulate the activities under the police powers of the state, which authorize protection of the public health, safety, and welfare.

Many municipalities adopted smoke abatement programs beginning with the earliest in Chicago in 1881 and continuing through the turn of the century (Reitze, 2001, p. 10). There are few examples from this period of air quality programs addressing air pollutants other than "smoke" (Reitze, 2001, p. 10). By 1912, most major United States cities had enacted smoke abatement programs.²²

Early pollution control efforts acquired a technocratic aspect, as associations of engineers also became driving forces behind early municipal smoke nuisance ordinances (Reitze, 2001, p. 10). Engineers working on smoke abatement methods focused on optimizing combustion techniques as the "solution" to the smoke problem, which they viewed as an unnecessary waste of resources ancillary to the economic progress brought about by industrialization (Grinder, 1980, p. 89). However, along with this view that technology could be the solution to the smoke problem grew the contrary view that limitations to the technological ability to control or prevent smoke nuisance should be, and was adopted as, a defense to the enforcement of smoke abatement ordinances. In other words, in the interest of not inhibiting economic prosperity, there was the belief that required abatement measures should be limited to currently available technologies (Reitze, 1991, p. 1577).

Land use ordinances and regulations through the first half of the 20th century were generally limited in scope and jurisdiction and of questionable effectiveness at the citywide level, let alone against regional and trans-boundary impacts of air pollution. Zoning laws, the most common local land use control, were used initially to impose separation between industrial or commercial land uses and residential or recreational uses (Hadacheck, 1915, as cited in Reitze, 1991, p. 12). However, zoning laws and other land use laws and policies advancing this segregation have been blamed by many²³ for creating the conditions for one of the largest current air quality challenges: the land use patterns that necessitate widespread dependence upon automobiles for access to employment opportunities and affordable housing (Reitze, 2001, p. 12). At the risk of understatement, land use controls did not play a significant role in the control of air pollution during the first half of the 20th century.

Post-WWII, many cities established nuisance-based air regulations (Reitze, 2001, p. 11). These efforts often expanded the types of air pollution sought to be controlled beyond the usual smoke control

²² "By 1912, 23 of the 28 United States cities with populations in excess of 200,000 had smoke abatement programs" (Reitze, 1991, p. 1576).

²³ See Reitze, 2001, p. 12 and sources cited therein (describing high environmental costs of zoning-driven urban sprawl).

provisions to address diverse local conditions. For example, Los Angeles initiated the regulation of smudge pots used to heat citrus groves at this time (Martineau and Novello, 2004, p. 5). Some programs also strived to address air pollution problems throughout an entire air quality basin, such as the Los Angeles County Air Pollution Control District (Martineau and Novello, 2004, p. 5).²⁴ However, these programs were usually limited by minimal budgets (Reitze, 2001, p. 11; Schueneman, 1963).²⁵ State involvement was limited by the prevailing practice at the time of assigning authority to local governments for land use controls. Thus, with only a few exceptions, prior to the 1960s, air quality controls were largely limited to municipalities and local governments and had little regional or state-level presence (Reitze, 1991, p. 1580). The role of states in air quality control became much more pronounced due to the series of federal legislation that has led to the current system of air pollution control.

7.2 The Origins of the Current Federal-State Regulatory Framework

The first federal legislation that addressed air pollution specifically was enacted in 1955 (US Congress, 1959). This law authorized the expenditure of funds over a five-year period to conduct scientific and technical research on the causes of air pollution and to assist state efforts at research and training (US Congress, 1959). Although this act was reauthorized and extended for 4 years in 1959, the funding appropriated was always less than Congress authorized because "unlike water pollution, air pollution ... is essentially a local problem" (Eisenhower administration Bureau of the Budget commentary on the air pollution legislation, as cited in Reitze, 2001, p. 14). Responsibility for administering these funds was vested with the Public Health Service in the Department of Health, Education and Welfare (DHEW), and, after its creation in 1960, in the Division of Air Pollution.

Congress passed the Clean Air Act of 1963, which was signed into law on December 17, 1963 (US Congress, 1963). This Act contained the first provision authorizing a federal agency to take enforcement action to abate air pollution. This provision established a mechanism by which a State, a State air pollution control agency or, with the permission of the State, a governing body of a municipality could request DHEW to convene a series of conferences and hearings to determine whether it was necessary to abate air pollution if alleged to endanger the health or welfare of persons outside the state or

²⁴ In 1947, the California Air Pollution Control Law authorized counties to establish air pollution control districts with the authority to issue permits, promulgate rules and regulations, and take steps to penalize violators (Kennedy and Porter, 1955, pp. 854,869-76).

²⁵ 17 states had air pollution programs expending \$5,000 or more annually; total expenditures for 1961 were \$2,000,000, 57 percent of which was by California.

within the state (US Congress, 1963). The Secretary of DHEW was also authorized to take enforcement action and to invite the respective state and municipal authorities to participate (US Congress, 1963). Ultimately, if DHEW determined from these conferences and hearings that the alleged pollution was occurring and that effective progress toward abatement was not being made, the matter could be referred to the Attorney General to bring suit on behalf of the United States to secure abatement of the pollution (US Congress, 1963). This model of federal enforcement of air pollution provisions at the request of the states, in concert with the states or in place of state enforcement action, laid a cornerstone that has carried through to the present federal-state air pollution enforcement programs.

The 1963 Act also established a joint government-industry committee to evaluate progress in the development of automotive exhaust control devices and fuels and commissioned a report to Congress to recommend whether the discharge of pollutants from automotive exhausts should be subject to regulations (US Congress, 1963). This authority was expanded in amendments to the Act passed in 1965, namely the Motor Vehicle Air Pollution Control Act which authorized the Secretary of DHEW to issue emissions standards for new motor vehicles or motor vehicle engines (US Congress, 1965).

More key building blocks of the current air pollution control program were added in 1967 with enactment of the Air Quality Act of 1967 (US Congress, 1967). This Act directed the Secretary of DHEW to make grants to air pollution control agencies for a major portion (one-half or more) of the cost of planning, developing, improving, and maintaining programs for the prevention and control of air pollution and for the implementation of air quality standards to be developed under the Act (US Congress, 1967). The Act directed the Secretary to designate AQCRs, based on jurisdictional boundaries both interstate and intrastate, in which air quality control programs would be established to facilitate adequate implementation of air quality standards. The AQCRs would be defined on the basis of those aspects of climate, meteorology and topography which affect the interchange and diffusion of pollutants in the atmosphere (US Congress, 1967). The Secretary was further directed to develop and issue AQC's, consisting of summaries of the latest scientific information on the adverse effects of air pollution agents on man and the environment and the variable factors that may alter the effects on public health and welfare (US Congress, 1967).

Designation of the AQCRs and the AQC's was the centerpiece²⁶ of the Act, namely Section 108, which provided for development of air quality standards to protect the public health and welfare and outlined a programmatic means for the abatement of air pollution in any state or states which endangers the health or welfare of any persons (US Congress, 1967). Section 108(c) of the Act authorized states to adopt ambient air quality standards (AAQS) for any AQCRs within their respective state and to adopt a plan for the implementation, maintenance and enforcement of the AAQS. Under Section 108(c), if the Secretary determined that a state's AAQS were consistent with the federal AQC's, that the plan would assure the achievement of the AAQS within a reasonable time, and that the state had adequate means of enforcement of the standards and the plan, then the state's standards and plan would serve as the air quality standards applicable to that state (US Congress, 1967). In the absence of state-enacted AAQS or implementation plans with respect to any AQCR or portion thereof, the Secretary was authorized to promulgate standards consistent with the purposes of the Act for that AQCR, after providing ample opportunity for the state to cure its nonperformance (US Congress, 1967). Once AAQS were developed for a state of an AQCR, Section 108 provided for enforcement of the AAQS either by the state or by the Secretary under some fairly arduous procedural limitations.²⁷

These early measures to establish a coordinated federal and state government effort to control air pollution set the foundation for all subsequent air regulation. These measures established a federal-state relationship in which states were encouraged to take a leadership, hands-on role in establishing the front-line regulatory programs to deal with individual sources of pollution, while federal authorities could be exercised if states inadequately regulated the local pollution sources. Nevertheless, the federal government established the broad policies and criteria upon which the actual standards for air quality were to be based. In addition, it was largely the federal responsibility to provide funding, conduct research, set policies, and oversee state programs. Within this policy framework, the states were to develop implementation plans, which became the SIPs of today, detailing how the federal precepts were

²⁶ The Act also had provisions addressing motor vehicle emissions, including a provision directing the Secretary to prescribe standards applicable to the emission of any substance from any new motor vehicle or new motor vehicle engine which contributed to air pollution endangering the health or welfare of any persons and to prohibit the sale or importation of any new motor vehicle or motor vehicle engine unless it is in conformity with these emission standards (US Congress, 1967).

²⁷ Section 2, subsection 108(c)(4) provides that, if the Secretary finds that the ambient air quality does not meet the AAQS in an AQCR or state because the state has failed to take reasonable action to enforce the standards, the Secretary may notify the relevant state of the failure and, if the failure does not cease within 180 days of notification, the Secretary may request the Attorney General to bring suit (in the case of interstate air quality standards violations) or, for intrastate violations, at the request of the Governor, may provide resources for the state to bring enforcement action or, again at the request of the Governor, request the Attorney General to bring suit to abate the air pollution (US Congress, 1967).

to be translated into regulations tailored to actual sources, and the states were to take the initiative in enforcing these state regulations, usually under state law.

As a result of this complex structure, the actual abatement of air pollution was attenuated under the 1967 Act and the earlier measures. It required the adoption of AQCRs and AQC's by DHEW, followed by the adoption of AAQS and an SIP by each state (or by the Secretary in the event of state default), promulgation of the necessary state laws and regulations to effectuate the SIP (often not until after federal approval of the plan²⁸) then, finally, either enforcement action brought by the state under state law to enforce the implementation plan or the AAQS, or a tortuous enforcement proceeding brought by the Attorney General on behalf of the state, in the event that the state had failed to take reasonable enforcement action on its own. Little air pollution control was achieved because the states proved to be less than enthusiastic in their embrace of these new authorities. Only 21 implementation plans were filed by the states between 1967 and 1970, none of which were approved by DHEW (Reitze, 1991, p. 1590). This problem of great delays between setting policy goals and actually controlling emissions is a product of the complex federal-state relationship built into the foundation by these early measures, which remains a central feature of air pollution control programs today.

7.3 The Modern Era of Air Pollution Control

In 1970, frustration with the slow progress of air pollution abatement and the generally heightened public environmental concerns combined to provide the necessary political support for the Clean Air Act Amendments of 1970, which asserted a major federal regulatory role²⁹ and strengthened enforcement authorities at the federal level. Authority to administer the federal role under the Clean Air Act and to conduct all of the federal air quality management responsibilities was given by the 1970 Amendments to the newly established US EPA (US Congress, 1970).

The 1970 Amendments significantly reconfigured the federal and state roles in the cornerstone programs in several significant ways. The Amendments required US EPA to develop a list of priority air

²⁸ Following the 1994 decision in *Natural Resources Defense Council, Inc. v. EPA*, US EPA has taken the position that SIPs must be comprised of controls which are already in regulatory force, and presumably enforceable under state law at the time of submission of the SIP (Martineau and Novello, 2004, p. 45).

²⁹ The 1970 Amendments expanded the federal regulation of mobile sources by imposing technology-based emission standards on motor vehicles and other mobile sources and authorizing land use and transportation controls in urban areas if necessary to achieve NAAQS (Reitze, 2001, p. 16).

pollutants (the "criteria pollutants") and to develop AQC's for these pollutants (US Congress, 1970). The Amendments removed the states' authority to establish AAQS and required US EPA to propose national standards, NAAQS, for each criteria pollutant. NAAQS were defined as levels of air quality of criteria pollutants, allowing an adequate margin of safety, that are requisite to protect public health (primary NAAQS) and to protect the public welfare from known or anticipated adverse effects of ambient air pollution by criteria pollutants (secondary NAAQS) (US Congress, 1970). Although states were assigned primary responsibility for assuring air quality in AQCRs, US EPA was authorized to establish any intrastate or interstate region as an air quality control region if necessary for the attainment of NAAQS (US Congress, 1970). States were required to submit for US EPA review an implementation plan that provided for the implementation, maintenance and enforcement of each primary and secondary NAAQS in each AQCR within the state in such a manner as to attain the NAAQS within stringent time limits (US Congress, 1970). If a state failed to submit an implementation plan that US EPA deemed approvable under standards set forth in the Act, US EPA was authorized to publish a regulation promulgating an implementation plan in place of the deficient state submission (US Congress, 1970). Moreover, if US EPA determined that a state was failing to enforce its implementation plan effectively, US EPA was authorized to notify the state and to enforce any requirements of the state's plan following the notification until the state satisfied US EPA that it would enforce its plan ("period of federally assumed enforcement") (US Congress, 1970).

The 1970 Amendments also directed US EPA to develop standards of performance for new stationary sources of air pollution (New Source Performance Standards or NSPS) under which new sources would be assigned to categories and regulations would be developed for each new source category to establish federal standards of performance (US Congress, 1970). A standard of performance was defined as "a standard of emissions which reflected the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated" (US Congress, 1970). The NSPS program was also to be implemented through a federal-state partnership involving state submission of new source implementation plans, US EPA review and approval of the plans, and delegation of the authority to implement and enforce the NSPS program (US Congress, 1970).

The 1970 Amendments also required US EPA to develop a list of Hazardous Air Pollutants for which no AAQS is applicable which, in the judgment of the Administrator, may cause or contribute to an

increase in mortality or an increase in serious, irreversible or incapacitating reversible illness (Hazardous Air Pollutants or HAPs) and publish emission standards for the listed pollutants (National Emission Standards for Hazardous Air Pollutants or NESHAPs) (US Congress, 1970). The states were again authorized to develop a plan for implementing and enforcing emission standards for HAPs acceptable to US EPA and thereby achieve delegation of the HAPs program (US Congress, 1970).

Thus, the 1970 Amendments established a federal-state partnership in which US EPA made basic regulatory and scientific judgments about the degree of control of criteria pollutants in ambient air necessary to protect public health and welfare, designated as NAAQS, and the states were required to develop a SIP under which the specific sources of criteria pollutants within their borders were to be abated to the extent necessary to achieve the NAAQS. If the state defaulted on its responsibility to develop and implement an effective SIP, US EPA was authorized to develop and implement a surrogate federal implementation plan (FIP) in order that air quality within the deficient state would attain NAAQS notwithstanding the state's default. Similarly, US EPA was directed to develop NSPS and emissions standards for HAPs, which could then be incorporated into a state's implementation plan, subject to US EPA's determination that the plan was adequate to achieve the goals of the Act.

Implementation of the 1970 Amendments at the federal level began briskly with the 1971 promulgation by US EPA of NAAQS for 6 criteria pollutants: sulfur dioxide, particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons and nitrogen dioxide (US EPA, 1971b). Lead was not among these original pollutants. Among several significant policy judgments made by US EPA in promulgating these standards, US EPA determined that the development of NAAQS for criteria pollutants should not be limited by the feasibility of implementation of the standards. This determination was made based on the interpretation that the Clean Air Act does not permit any factors other than health to be taken into account in setting the primary NAAQS (US EPA, 1971b). No further criteria pollutants were named until 1976, when US EPA added lead to the list of criteria pollutants (US EPA, 1976e) in compliance with a federal court order in a lawsuit against US EPA brought by the Natural Resources Defense Council (NRDC) (US District Court, Southern District of New York, 1976). To date, no further pollutants have been listed and the initially listed hydrocarbon pollutants were dropped in 1983 (US EPA, 1983a).

Through the early 1970s, the states assembled the elements of their air quality control program envisioned in the 1970 Amendments. States upgraded their implementation plans to conform to the Amendments, enacted statutes and regulations which authorized the states to promulgate the specific emission controls necessary to seek attainment with NAAQS, and put in place the technical and bureaucratic infrastructure to pursue the goals of the Amendments (Martineau and Novello, 2004, p. 6). Despite, or perhaps because of, the fact that the states also responded briskly to the 1970 Amendments with SIPs, SIPs of uneven quality were submitted, which led US EPA to conclude that many were inadequate, resulting in FIPs and other US EPA requirements in response (Martineau and Novello, 2004, p. 6). Even the original 1970s SIPs approved by US EPA often failed to achieve attainment of the NAAQS within the statutory periods. This fact led directly to revisions of the Act in 1977 (US EPA, 1987b).

In 1977, a comprehensive package of amendments to the Clean Air Act was passed by Congress in response to frustration that the developing programs, and the submittal and review of SIPs had not met the goals of the 1970 Act. In particular, a disappointing number of the AQCRs across the country were meeting or making significant progress toward attaining the NAAQS (Martineau and Novello, 2004, p. 6).³⁰ As a result, the 1977 Amendments extended the deadlines to 1987 (US Congress, 1977) for reaching attainment with the primary NAAQS while imposing more stringent emissions standards on areas in nonattainment status (US Congress, 1977). A nonattainment area was defined to be "for any air pollutant an area which is shown by monitored data or which is calculated by air quality modeling (or other methods determined by the Administrator to be reliable) to exceed any national ambient air quality standard for such pollutant" (US Congress, 1977).

States were required to submit revised implementation plans for nonattainment areas to demonstrate how they would meet the revised deadlines and to obtain US EPA approval for the revised SIP by July 1979 (US Congress, 1977). In nonattainment areas, the revised SIPs were required to impose a higher technological standard of controls, RACT on existing major stationary sources, and to require permits for the construction and operation of major new stationary sources or major modifications to existing major stationary sources (the nonattainment area "New Source Review" program) (US Congress, 1977). These permits were required to impose emission controls to meet the lowest achievable emission

³⁰ "When the [statutorily mandated] time for compliance [with primary NAAQS] arrived in 1975, many AQCRs failed to meet the NAAQS" (Reitze, 2001, p. 55).

rate (LAER) for any nonattainment criteria pollutant (US Congress, 1977). LAER was defined to be "the most stringent emission limitation which is contained in the implementation plan of any State for such class or category of source, unless the owner or operator of the proposed source demonstrates that such limitations are not achievable, or the most stringent emission limitation which is achieved in practice by such class or category of source, whichever is more stringent" (US Congress, 1977). Moreover, the Amendments required that new sources in nonattainment areas must compensate for their proposed increase in emissions of criteria pollutants in the area by obtaining a corresponding reduction in emissions of the criteria pollutant from their own sources or from other sources in the nonattainment area (US Congress, 1977).

Similar provisions applicable to new or significantly modified major stationary sources were imposed by the 1977 Amendments on AQCRs which were in compliance with the NAAQS ("attainment areas") in order to ensure that the nominally clean air in attainment areas was not degraded by increases in emissions. These provisions enacted into statute the "Prevention of Significant Deterioration" (PSD) program regulations which had been imposed upon US EPA as the result of litigation over the provisions of the 1970 amendments (US Court of Appeals, District of Columbia Circuit, 1972). This program required the issuance of permits for construction in attainment areas of new or modified "major emitting facilities" and required preconstruction review of the facility in order to determine that the facility would be consistent with the emissions limitations and implementation plan applicable to the attainment area (US Congress, 1977). These permits were required to impose the best available control technology (BACT), a stringent technology based standard, to prevent air quality deterioration.³¹ The BACT standard was also imposed by the 1977 Amendments on new sources in attainment areas under the NSPS program (US Congress, 1977).

The 1977 Amendments established an ambitious agenda and added considerable substantive law and complexity to the Clean Air Act. However, the heart of the amended Act remained the establishment, implementation and achievement of the NAAQS for criteria pollutants (Reitze, 2001, p. 19). The complexities of the NAAQS process and the attendant federal-state interactions in turn, resulted in the continuance of the slow speed of progress in developing and enforcing meaningful air quality

³¹ BACT was defined to be "an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from or which results from any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such facility through application of production process and available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of each such pollutant" (US Congress, 1977).

standards nationwide. For example, to assure that the NAAQS were based on up-to-date technical data, the 1977 Amendments imposed the requirement that US EPA must, beginning in 1980 and every 5 years thereafter, conduct a thorough review of the AQCs and the air quality standards supporting and comprising the NAAQS and recommend any changes (US Congress, 1977). Whether because of the political climate of the 1980s or the inherent inertia of the Clean Air Act regulatory process, these periodic reviews proved to be time consuming and controversial (Belden, 2001, p. 19). The initial five-year review of the ozone standard commenced in the early 1980s and was not completed until 1993, based not on contemporaneous data but on 1986 data updated in 1989 (Belden, 2001, p. 19). The initial review of the lead criteria and NAAQS did not commence until 1984 and was not concluded until 1991 (Martineau and Novello, 2004, p. 35). Some commentators have observed that "litigation, chaos and uncertainty" in implementation of the 1977 Amendments resulted from the standoff between Congress and the White House beginning with the 1980 election, "even as the deadlines of the 1977 Amendments approached in the late 1980s and passed" (Martineau and Novello, 2004, p. 6).³²

7.4 The 1990 Amendments and Current Air Pollution Control

The 1990 Amendments to the Clean Air Act (US Congress, 1990) built upon the programs and federal-state approach of the 1977 Amendments to refine most of the existing federal air programs, and enacted a number of significant new air pollution control programs.

Title I of the Amendments refined the provisions for attainment and maintenance of the NAAQS. This title defined more clearly the federal and state roles in designating AQCRs as being in attainment status or nonattainment status. Specific designations of nonattainment AQCRs were required for ozone, carbon monoxide and particulate matter criteria pollutants (US Congress, 1990). The designation of attainment or nonattainment carried with it increasing significance under the 1990 amendments as the respective designations resulted in varying degrees of control over existing and new sources within the designated AQCRs. In addition, nonattainment AQCRs for ozone and carbon monoxide were further classified based on the severity of their respective nonattainment conditions. The severity classifications for ozone and carbon monoxide (marginal, moderate, serious, severe and extreme) were then translated

³² These commentators note that, despite the chaos, air quality management programs matured at the state and local air quality regulatory level during the 1980s and undertook their own initiatives to deal with local issues (see also Reitze, 2001, pp. 19-21).

into the time periods within which an AQCR must come into compliance with the respective NAAQS and the rate of progress that must be demonstrated toward compliance.

Title I of the Amendments revised the manner in which nonattainment AQCRs are regulated, generally lengthening the periods allowed for coming into compliance with the NAAQS. Areas designated in nonattainment were required to submit revised SIPs that will "provide for the implementation of all reasonably available control measures as expeditiously as practicable (including such reductions in emissions from existing sources in the area as may be obtained through the adoption, at a minimum, of reasonably available control technology)" (US Congress, 1990), "require permits for the construction and operation of new or modified major stationary sources anywhere in the nonattainment area" (US Congress, 1990), and include enforceable emissions limitations, and such other control measures, means or techniques (including economic incentives such as fees, marketable permits, and auctions of emissions rights), as well as schedules and timetables for compliance, as may . . . provide for attainment of such standard in such area by the applicable attainment date" (US Congress, 1990). Title I also detailed specific programs for areas in nonattainment with the ozone, carbon monoxide and particulate matter NAAQS, with escalating requirements corresponding to increasing severity of the nonattainment (US Congress, 1990). The Amendments did not make significant changes to the nonattainment programs for sulfur oxides, nitrogen dioxide or lead, other than to modify the deadlines for coming into attainment (US Congress, 1990).

Title III significantly altered the Hazardous Air Pollutants program. Between 1970 and 1990, US EPA succeeded in listing only 8 Hazardous Air Pollutants under the initial Hazardous Air Pollutants program which was focused solely on the determination of adverse health effects of potential HAPs (Belden, 2001, p. 8). Rather than allowing US EPA to continue to develop a list of HAPs through a demonstrably slow regulatory process, the 1990 Amendments contained an initial list of 189 HAPs that would be subject to technology-based and health-based emissions standards and specified the procedures to modify or revise the list (US Congress, 1990). Title III also required US EPA to develop within 12 months a list of categories and subcategories of major sources³³ and area sources³⁴ of Hazardous Air Pollutants and to revise the list periodically thereafter, no less frequently than every 8 years.³⁵

³³ A "major source" is defined to be "any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants" (US Congress, 1990).

US EPA was directed to establish initial technology-based (Belden, 2001, p. 68) emission standards for each category and subcategory of major sources and area sources of listed Hazardous Air Pollutants (US Congress, 1990). A second phase of emission standards was to be developed if it was determined that the further regulation beyond the technology-based standards was necessary to achieve adequate protection of public health.³⁶ The promulgated emission standards³⁷ must require the maximum degree of reduction in emissions that the US EPA determines is achievable for new or existing sources in the category or subcategory of sources to which the standard is to apply, taking into consideration the cost of achieving such reduction and the health, environmental and energy impacts of doing so (the Maximum Achievable Control Technology, or MACT, standard) (US Congress, 1990). Title III retained a distinction between new and existing sources, requiring new sources to implement the emission control that is achieved in practice by the best controlled similar source, where existing sources could be regulated somewhat less stringently, but would still be bound to emission controls equivalent to those used by the top tier in emissions reduction effectiveness of similar sources (US Congress, 1990).³⁸

Title III also established a program for prevention of accidental releases of Hazardous Air Pollutants (US Congress, 1990).³⁹

Other significant changes enacted in the 1990 Amendments include: Title II of the 1990 Amendments made widespread refinements and additions to the mobile source emissions control programs, including significantly strengthened emission standards for conventional motor vehicles and a

³⁴ An "area source" is defined to be "any stationary source of hazardous air pollutants that is not a major source," not including motor vehicles (US Congress, 1990).

³⁵ US EPA was directed to make the list of categories of sources of hazardous air pollutants consistent with the list of categories of sources to be compiled for implementation of the new source performance standards pursuant to § 111 (US Congress, 1990).

³⁶ The health risk-based HAPs controls commenced with a requirement that US EPA investigate and report on, within six years of the 1990 Amendments, methods of calculating the risk to public health remaining or likely to remain from sources after application of the MACT emission standards, the public health significance of such remaining risk, the actual health effects experienced by neighbors in the vicinity of sources or experienced in response to background concentrations of HAPs, and recommendations concerning such remaining risk (US Congress, 1990). US EPA was required to promulgate second phase standards if the MACT standards do not reduce lifetime excess cancer risks to the individual most exposed to emissions of a source in the category or subcategory to less than one in a million (US Congress, 1990).

³⁷ US EPA was directed to establish emission standards for categories and subcategories of sources according to an aggressive schedule which required that emissions standards be promulgated for all categories and subcategories no later than 10 years after the date of enactment of the 1990 Amendments (US Congress, 1990).

³⁸ The top tier of similar sources was defined to be the average emission limitation achieved by the best performing 12 percent of the existing source in the category or subcategory for categories and subcategories with 30 or more sources or the best performing 5 sources for categories or subcategories with fewer than 5 sources (US Congress, 1990).

³⁹ This provision was a further legislative response to the Bhopal, India industrial disaster, which had previously been addressed in Emergency Planning and Community Right to Know provisions of the Superfund Amendments and Response Act of 1986 (US EPA, undated).

program for regulation of mobile source-related air toxics (US Congress, 1990).⁴⁰ Title IV (Acid Deposition Control) established an emissions trading program to reduce emissions causing acid rain (US Congress, 1990). Title V (Permits) (US Congress, 1990) extended the Clean Air Act permit program to apply to existing sources and created a permitting process similar to those of other major federal environmental programs, *e.g.*, the National Pollutant Discharge Elimination System permitting program, whereby all requirements applicable to a permittee are captured by the permit, which is required to be renewed every 5 years (Reitze, 1991, p. 1611). Title VI (Stratospheric Ozone Protection) imposed stringent limitations on certain stratospheric ozone pollutants consistent with the provisions of the Montreal Protocol on Substances That Deplete the Ozone Layer (US Congress, 1990). Title VII (Provisions Relating to Enforcement) included more severe criminal enforcement consequences, including new authority for US EPA to undertake enforcement through administrative rather than judicial actions and to issue field citations for violations observed during inspections (US Congress, 1990).

Overall, the 1990 Amendments established an ambitious agenda for US EPA, the states, and the regulated community. It has been estimated that thousands of rulemakings by US EPA have been necessary to implement the 1990 Amendments, accompanied by thousands of guidance documents and even more interpretations (Martineau and Novello, 2004, p. 8). The states' responsibilities are multiples of US EPA's responsibilities, in that the states must apply the policies, regulations and guidance to individual sources of air emissions within their boundaries. And, of course, the regulated community must find a way to comprehend this complex body of regulations and laws, determine its impact on the affected businesses and organizations, and implement the required controls in a manner that is viable and effective.

The respective federal and state responsibilities were comprehensively set forth in US EPA's "General Preamble for the Implementation of Title I of the Clean Air Act Amendments of 1990" (US EPA, 1992b). This document focused primarily on the SIP submissions required for nonattainment areas by the Act. It also laid out US EPA's interpretation of the New Source Review provisions of the Act, which required that the states submit SIP revisions in 1992 and 1993 conforming their NSR programs for nonattainment areas to US EPA's interpretations. The Preamble identified 31 major deliverables pertaining only to the ozone classification and CO classification portions of the Act which were due from

⁴⁰ US EPA was instructed to conduct a study of the emission of then-unregulated toxic air pollutants from mobile sources and to develop regulations "containing reasonable requirements to control hazardous air pollutants from motor vehicles and motor vehicle fuels" (US Congress, 1990).

the states within 4 years of enactment (US Congress, 1990). The Preamble sought to provide an overall picture of the activities necessary to complete the obligation that all necessary SIP revisions be made and approved by US EPA within 6 years of enactment (US Congress, 1990). The 6-year deadline was also the milestone by which ozone nonattainment areas in moderate or worse condition must achieve a 15 percent reduction in volatile organic compound (VOC) emissions. This timeframe illustrates the optimistic end of the range of expectations for the length of time it takes under the existing federal-state regulatory apparatus to determine specific air quality control policies and to actually see implementation of resultant improvements in air quality.

8 Lead in the United States: Overview of Historical Uses and Trends in Atmospheric Concentrations

Lead has been used since antiquity. Leaded gasoline, leaded paints, and batteries are among the widespread current and historical uses of lead that make it a ubiquitous constituent in our environment.

8.1 History of Lead Use

High density, low melting point, ease of casting and fabrication, corrosion resistance, chemical stability, sound attenuation, and vibration-damping are among the advantageous properties of lead that have contributed to its widespread use by human civilizations (Grayson and Eckroth, 1981). The discovery of lead dates back to at least 3500 B.C. (Lin-Fu, 1985). The Romans made aqueducts of lead, and reportedly produced an average of 60,000 tons of lead per year for 400 years (Lin-Fu, 1985).

In the US, leaded gasoline and lead-based paint were dominant uses for much of the 20th century. The commercial use of tetraethyl lead as an anti-knock agent in automotive gasoline started in 1923 (Needleman, 2000). At its peak in 1970, approximately 250,000 tons per year of tetraethyl lead were added to gasoline (ATSDR, 1999). The phase-out of lead in most gasoline began in the 1970s and was completed in 1996, but lead is still used in aircraft and racecars fuels (ATSDR, 1999). Lead-based paints were first produced in the late 1800s, were considered high quality materials, and were widely used for both interior and exterior applications through the 1950s (Markowitz and Rosner, 2000). Beginning in the 1940s, lead was increasingly replaced by other pigments in interior paints (Markowitz and Rosner, 2000). In 1977, the Consumer Product Safety Commission banned the use of paint (both interior and exterior) containing more than 0.06% lead (CPSC, 1977).

The largest use of lead in the US today is for lead-acid storage batteries in automotive and industrial applications (as cited in ATSDR, 1999). Lead is also used in ammunition, radiation shielding, solders, pigments, electronic equipment, cable sheathing, and building construction materials (Smith, 1998a).

8.2 General Trends of Lead in Air

In 1961, the US Public Health Service, Division of Air Pollution, conducted a study of air lead concentrations in 3 major cities, as part of an evaluation of the public health aspects of a proposed increase in the allowable tetraethyl lead content of gasoline from 3 to 4 milliliters per gallon (Ludwig, *et al.*, 1965). The annual average air lead concentrations ranged from 1-2 $\mu\text{g}/\text{m}^3$ in Cincinnati, 1-3 $\mu\text{g}/\text{m}^3$ in Philadelphia, and 2-3 $\mu\text{g}/\text{m}^3$ in Los Angeles, with overall averages of 1.4, 1.6, and 2.5 $\mu\text{g}/\text{m}^3$, respectively. Averages in heavy traffic areas ranged from 14 to 44 $\mu\text{g}/\text{m}^3$. In a 1969 follow-up study, average (geometric mean) air lead concentrations in the urban portions of Philadelphia, Chicago, and New York were reported as 1.7 $\mu\text{g}/\text{m}^3$, 1.8 $\mu\text{g}/\text{m}^3$, and 2.1 $\mu\text{g}/\text{m}^3$, respectively (US EPA, 1972b). Air lead levels had declined slightly by 1979 with average concentrations of 1.1, 0.8, 0.9, 0.8, and 1.4 $\mu\text{g}/\text{m}^3$ reported for New York, Boston, Houston, Chicago, and Los Angeles, respectively (US EPA, 1986a).

Airborne lead concentrations decreased dramatically from about 1970 onward, largely due to the phase-out of leaded gasoline additives (US EPA, 2006a). From 1971 to 1980, the percent of urban stations reporting air lead concentrations of 1-1.9 $\mu\text{g}/\text{m}^3$ decreased from about 60% to less than 1% (US EPA, 1986a). Based on maximum quarterly average lead concentrations from 36 sites, the composite average concentrations decreased from about 1.3 $\mu\text{g}/\text{m}^3$ in 1977 to about 0.4 $\mu\text{g}/\text{m}^3$ in 1984 (US EPA, 1986a). Ambient air lead concentrations in the US decreased 94% from 1983 to 2002 (US EPA, 2003). Average air lead concentrations nationwide decreased from about 0.3 $\mu\text{g}/\text{m}^3$ in 1985 to about 0.04 $\mu\text{g}/\text{m}^3$ in 2000 (US EPA, 2006a).

9 Overview of US Primary Lead Production

9.1 Introduction

Primary lead production refers to the processes by which pure metallic lead, Pb, is recovered from mined lead ore concentrates.⁴¹ Lead is found in the environment in lead-bearing ores, the most common of which is galena, lead sulfide (PbS) (US EPA, 1980b), which contains 86.6% lead by weight. Lead is most often found in a variable mixture of metals, typically copper, zinc, silver, cadmium, iron, *etc.* (Wixson, 1982). Over 80% of the lead currently mined in the US originates in the "New Lead Belt" area of southeastern Missouri. Mining in this area, portions of which consist of nearly pure galena, began in 1967 (US EPA, 1980b).

At lead mines, the following processes occur (US EPA, 1980b):

- Lead-containing ores are mined and transported to the surface;
- Mined ores are progressively screened and crushed into smaller fragments (milling);
- Lead-containing components are separated from the remaining rock either by gravity methods (based on particle density, with heavier, lead-containing particles sinking to the bottom) and/or flotation (based on use of compressed air and chemicals to create a froth in which mineral particles are separated out by flotation to the surface); and
- If flotation is used, the separated lead-containing froth must be concentrated *via* dewatering, which includes thickening, flocculation, settling, and vacuum filtration.

After mining, milling, and concentrating, the lead ore concentrates, containing 45-75% lead, are transported by rail, truck, or barge to primary lead smelting and refining facilities for lead metal production (US EPA, 1979a).

All primary lead smelters in the US have generally employed the same basic processes, although there are some differences in operational details (McKee, 1969). As described in more detail below and depicted in Figure 9-1, primary lead production consists of 4 principal processes: sintering (oxidation of lead sulfide to lead oxide), blast furnace smelting (reduction of lead oxide to metallic lead), drossing

⁴¹ Distinct from primary lead production, secondary lead production refers to the processes by which lead-containing scrap (mostly from lead-acid batteries, but also sheet metal, pipes, cable coverings, *etc.*) is recycled for metallic lead recovery (US EPA, 1995b). Secondary lead production is conducted at different facilities (*i.e.*, secondary lead smelters) from primary lead production.

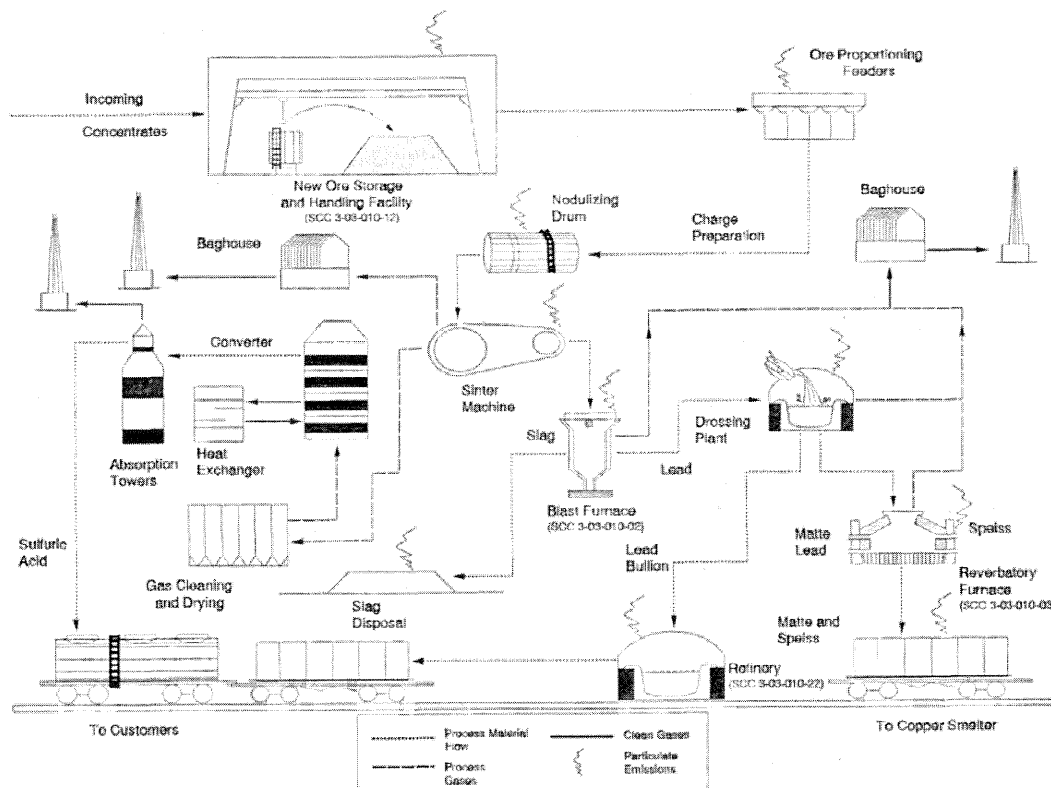


Figure 9-1
Process Flow for a Typical Primary Lead Smelting and Refining Operation
(from US EPA, 1995b; with Source Classification Codes in parentheses)

9.2 History of US Primary Lead Production

Lead was first mined and forged in the US in Virginia in 1621 (US EPA, 1985a; Smith, 1998b), and primary lead production was first recorded in 1825 in the US (Smith, 1998b). Large-scale smelting operations began by the late 1800s in El Paso, Texas (1887), East Helena, Montana (1888), and Herculaneum, Missouri (1892) (White *et al.*, 2006; US EPA, 2005c; Schupp, 2000). In 1969, there were 8 primary lead smelters in the US (McKee, 1969). Since then, no primary lead smelters were built, but many were closed. By 1999, only 3 primary lead smelters remained in operation – Glover and

Herculaneum, Missouri and East Helena, Montana (Smith, 1999). With the closure of East Helena in 2001 (US EPA, 2005c) and the placement of the Glover facility on standby care and maintenance status in December 2003 (Smith, 2003), the only remaining operating primary lead smelter is The Doe Run Company's Herculaneum facility (US EPA, 2005d).

Annual US production of primary refined lead was 145,000 tons in 1887 (Smith, 1998b) and increased to a high of 818,000 tons in 1926, which was 75% of total US refined lead production (DiFrancesco and Smith, 2003). Primary lead production has gradually decreased over the last century due to increased secondary lead production (DiFrancesco and Smith, 2003) and reduction in demand (Smith, 2003). US primary refined lead production fell to 473,000 tons by 1960. After a brief resurgence in the late 1960s and 1970s (high of 696,000 tons in 1973), production declined to 603,000 tons in 1980, 444,000 tons in 1990, and 375,000 tons by 2000, which was only 24% of total US refined lead production (DiFrancesco and Smith, 2003). During the first 3 quarters of 2005, only 113,000 tons of primary refined lead were produced, all at the Herculaneum facility (US EPA, 2005d).

9.3 Sintering

Sintering removes sulfur from the lead ore concentrates by oxidation of lead sulfide to lead oxide and produces a dense, permeable clinker (sinter) suitable for blast furnace smelting. Lead ore concentrates are mixed with various fluxing agents (*e.g.*, limestone, silica sand, iron, particulates collected from dust collection devices) and recycled sinter in order to produce a feed material (charge) suitable for sintering with a sulfur content of 6-12%. For higher sulfur-content ores, sintering may be performed in 2 stages. Prior to mixing, the fluxing agents and recycled sinter are crushed and appropriately sized.

By 1980, all primary lead smelters utilized updraft sintering machines (US EPA, 1980b), also known as Dwight-Lloyd machines, which are essentially large conveyor belts (ranging from 22 to 103 ft in length and 3.5 to 10 ft in width) consisting of connected grate-bar pallets, upon which sinter feed travels. They have 2 feeders in series: the first feeder places a thin layer of sinter feed that is ignited before the pallet reaches the second feeder, which then places a 12 to 18 inch layer of feed. In this way, feed is heated from bottom to top. This is aided by the vacuum pulled (updraft) on an upper wind box,

into which off-gases and particulates are collected and transported through ducts to air pollution control equipment. The sinter charge is roasted in the presence of oxygen at temperatures less than 1,400° F in order to minimize volatilization of metals, fusion of the sinter, and damage to the sintering machine. The resulting sinter is subsequently crushed and screened to size the material for blast furnace reduction; additionally, a portion is recycled to the sintering process (McKee, 1969; US EPA, 1982).

Within updraft sinter machines, nearly 85% of the sulfur content of the sinter feed is removed, mostly as sulfur dioxide (SO₂) (US EPA, 1995c; US EPA, 1980b). Formerly, primary lead smelters utilized downdraft sinter machines, which were more difficult to control and less efficient in removing sulfur. As a result, their SO₂ emissions were at concentrations too low for economical recovery as sulfuric acid (McKee, 1969). With the conversion to updraft sinter machines in the 1960s and 1970s, sulfur removal was more efficient, and plants began constructing acid plants to recover SO₂ as sulfuric acid for commercial sale. In 1980, 3 of the 6 primary lead smelters in operation had acid plants, and a fourth was in the process of planning to install one (McKee, 1969; US EPA, 1980b).

In updraft sintering machines, the gases are usually split into 2 streams: the stream at the front end of the process (strong gas stream) contains most of the SO₂ (approximately 5.7%) and the stream at the back end (weak gas stream) contains approximately 0.5% SO₂ (US EPA, 1980b). Additionally, up to 20% of the sinter feed material can be emitted as dust and fumes, which primarily contain lead and zinc compounds and are recycled (US EPA, 1982). The typical particle size distribution for sinter machine flue dust is (by weight): 15-45% between 20-40 µm, 9-30% between 10-20 µm, 4-19% between 5-10 µm, and 1-10% <5 µm (US EPA, 1977a). The strong gas stream, containing most of the SO₂ and particulates, is treated typically using ESPs and wet scrubbers, with the particulates being recycled to the sinter feed preparation process and the SO₂ gases being directed to a sulfuric acid plant (where SO₂ is catalytically oxidized to sulfur trioxide and then absorbed by water to form sulfuric acid for commercial re-sale). The weak gas stream is combined with other gas streams for treatment, or is discharged after particulate removal (US EPA, 1995c; 1980b).

9.4 Blast Furnace Smelting

Blast furnace smelting (blast furnace reduction) is performed to reduce lead oxide in the sinter to metallic lead. Three principal chemical reactions take place within the blast furnace:

- (1) $\text{PbO} + \text{CO} + \text{heat} = \text{Pb} + \text{CO}_2$ (reduction of lead oxide to metallic lead, called lead bullion)
- (2) $\text{C} + \text{O}_2 = \text{CO}_2 + \text{heat}$ (combustion of coke which produces the heat for the furnace)
- (3) $\text{C} + \text{CO}_2 + \text{heat} = 2 \text{CO}$ (remaining coke reacts with carbon dioxide to produce carbon monoxide, the reducing agent for the smelting reaction)

Sinter is mixed with coke (about 9 to 12% of the charge) and fluxing agents (similar to sintering) and fed into the blast furnace, where reduction of the lead oxide to metallic lead occurs at temperatures that range from 1,800° F to 2,200° F (McKee, 1969; US EPA, 1980b). The products of the blast furnace typically include 4 liquids and flue gas. The 4 liquids, which are separated by gravity due to density differences, include (from heaviest to lightest): rough lead bullion (94-98% metallic lead by weight with various impurities), slag (primarily silicates, but may contain up to 20% zinc, 2% lead, and 3% sulfur), matte (typically includes 44-62% copper, 10-20% lead, up to 13% sulfur, and small amounts of zinc, iron, and silica), and speiss (according to US EPA (1980b), containing mostly arsenic, antimony, and iron, although McKee (1969) reports a composition of 55-64% copper, 8-18% lead, and small amounts of arsenic, antimony, sulfur, zinc, iron, and silica). Matte and speiss from the blast furnace are either directly sold to copper smelters for recovery of copper and other precious metals or are transported with the molten rough lead bullion to the dressing process. Blast furnace slag is either directly discarded or partially recycled in a slag (zinc) fuming furnace, if present, for zinc recovery (US EPA, 1995c; McKee, 1969).

Nearly all of the remaining 15% of the sulfur from the lead ore concentrate is removed in the blast furnace, with about half removed as SO_2 gas and the other half removed in the blast furnace slag and particulate emissions (US EPA, 1995c). Particulates emitted from blast furnace reduction also may contain up to 65% lead (often as lead oxides), as well as lesser amounts of cadmium, arsenic, and other metals. The flue gas containing these particulates is diluted with ambient air both to convert the CO to CO_2 and to reduce the gas temperature to below 250° F prior to entering a baghouse for particulate collection. Fugitive emissions from blast furnace reduction are primarily lead oxides, of which 92% are less than 4 μm in diameter (US EPA, 1982).

9.5 Drossing

Drossing prepares the rough lead bullion for pyrometallurgical refining by removing copper as well as other impurities.⁴² The term "dross" refers to any solid material that floats on top of a molten metal bath. During drossing, the molten lead bullion (with or without matte or speiss from the blast furnace reduction) is transported to large kettles where it is agitated and cooled in a controlled manner to just above the freezing point of lead (between 700° F and 800° F). To enhance copper recovery, the molten lead bullion may be treated with sulfur-containing materials to remove remaining copper as cuprous sulfide. This process results in the flotation and solidification of a dross on the surface of the lead bullion, which is subsequently skimmed off. This dross is usually further processed to recover non-lead minerals in a dross reverberatory furnace (with the addition of iron, silica, and limestone fluxes) to produce copper-rich matte and speiss (US EPA, 1980b), which are then sold to copper smelters. The decopperized lead bullion, with a remaining copper content of about 0.01%, is then pumped to the refinery (US EPA, 1995c; McKee, 1969; Wixson, 1982).

Particulates and fumes (typically containing <0.05% SO₂) from the dross reverberatory furnace are generally combined with blast furnace emissions for particulate removal in baghouses (US EPA, 1980b).

9.6 Pyrometallurgical Refining

Decopperized lead bullion is refined to remove remaining impurities (*e.g.*, gold, silver, zinc, bismuth, oxides of antimony, arsenic, tin, and copper) by pyrometallurgical methods, which involves the addition of selective reagents, agitation, and controlled heating/cooling in one or a series of cast iron kettles to form drosses, which are subsequently removed and usually sold to other refineries (US EPA, 1995c; Wixson, 1982). Up to 5 separate refining processes are described in the primary lead smelting literature, depending on the source of the lead ore and impurities remaining in the lead bullion (US EPA, 1995c; 1985b; 1982; 1980b; McKee, 1969; Wixson, 1982).⁴³

⁴² Dross may contain about 90% lead oxides, 2% copper, 2% antimony, and small amounts of sulfur, arsenic, and nickel (US EPA, 1985b; 1980b)

⁴³ At Doe Run's Herculanum facility, only three refining processes (desilverizing, dezincing, and final refining) are employed due to the high quality of lead ore concentrates used (Schupp, 2000).

First, if present, antimony, tin, and arsenic are removed in a process known as kettle softening, which involves the addition of sodium hydroxide and sodium nitrate and heating to nearly 1,300° F to produce a dross of sodium-metal salts. Second, gold and silver, as well as any remaining copper, are removed in a desilverizing process, which involves the addition of zinc (silver and gold have a greater affinity for zinc than lead) at a temperature near 1,000° F followed by controlled cooling to form insoluble zinc alloys that rise to the surface as a dross. These silver-rich drosses are typically sold to silver refineries. Third, zinc is removed in a vacuum distillation process, which involves the heating of desilverized lead to nearly 1,100° F and the insertion of an inverted bell that extends into the molten lead to form a seal. A vacuum is drawn on the bell and the kettle is agitated, resulting in the vaporization of zinc and subsequent condensation on the inside of the water-cooled bell. Recovered zinc may be recycled to the desilverizing process. Fourth, bismuth, if present, is removed in a debismuthizing process, which involves the addition of calcium and magnesium at a temperature near 1,000° F to form a compound of all 3 elements that has a higher melting point and lower density than lead. Therefore, once this bismuth-rich compound is cooled to just above the freezing point of lead (near 700° F), it solidifies as a dross on the lead surface. The fifth and final refining process involves the addition of oxidizing agents (e.g., sodium hydroxide, sodium nitrate) to remove any remaining trace quantities of metal impurities. Once refining is complete, the refined lead bullion, which consists of 99.99% or greater pure lead, is directly cast as 1 ton ingots or as 60 or 100 lb pigs, or it may be blended with other materials to create specialized alloys. The casted lead or alloyed materials are then ready for sale (US EPA, 1995c; 1980b).

Particulate and fume emissions from the pyrometallurgical refining processes are typically directed to baghouses for dust collection prior to atmospheric discharge (Wixson, 1982).

9.7 Liquid and Solid Wastes Generated From Primary Lead Production

Several processes involved with primary lead production produce wastewaters and slurries. These waste streams include: sulfuric acid plant blowdown, slag granulation wastewater (produced when hot slag from various processes is cooled with water prior to transport to a slag stockpile), and wash waters from various plant housekeeping processes (US EPA, 1995c; 1980b). Often, these waste streams are transported to lined surface impoundments where solids accumulate prior to off-site removal and disposal. Once these wastes, which often contain high concentrations of lead and other metals, are

removed from the surface impoundment(s), they are regulated as a listed Resource Conservation and Recovery Act (RCRA) hazardous waste with an industry-specific waste code K065 (US EPA, 1995c). Additionally, molten slag is produced in the blast furnace, dross kettle, and certain other refining processes, and is subsequently cooled into a solid material, granulated, and either recycled or stockpiled on-site. Slag waste from primary lead production is exempt from RCRA hazardous waste regulations under the Bevill exemption (US EPA, 1995c).

10 Development of Ambient Airborne Lead and Primary Lead Smelter Standards and Regulations

Section 6 provided an overview of the development and key provisions of the Clean Air Act Amendments of 1970 and 1990 that serve as the framework of today's modern air pollution control programs. Within this framework, several key standards and regulations pertaining to ambient airborne lead and primary lead smelters have been promulgated in the last 30 years, albeit in a piecemeal fashion and often lagging behind legislation by a number of years (Table 10-1). From readily available information, it is clear that at the time of rulemaking, it was well-recognized that the technical and economic feasibility of complying with these standards and regulations was not a foregone conclusion at primary lead smelters. Due to gaps in our scientific understanding, as well as many uncertainties in the available information, it was not well known at the time of promulgation of standards and regulations how difficult their compliance would be at primary lead smelters, or whether they were even technically or economically feasible.

10.1 National Ambient Air Quality Standards (NAAQS) for Lead

As discussed in Section 6, lead was not among the original set of criteria pollutants for which the first NAAQS were adopted in the 1971.⁴⁴ As discussed in USBM (1986), US EPA relied upon the 1972 National Academy of Sciences publication "Lead: Airborne Lead in Perspective" in making a judgment that there was insufficient evidence at the time to identify an appropriate ambient air lead standard. In the early 1970s, US EPA's initial approach for control of airborne lead instead involved limiting lead emissions from automobiles, which were considered to be the principal source of lead in air (US EPA, 1978a).

Following a 1976 NRDC suit, US EPA was ordered to designate lead as a criteria pollutant and to develop a NAAQS for lead. US EPA added lead to the list of criteria pollutants in 1976 and established the first NAAQS for lead in October 1978.⁴⁵ Both primary and secondary NAAQS were set at $1.5 \mu\text{g}/\text{m}^3$, averaged over a calendar quarter. These NAAQS of $1.5 \mu\text{g}/\text{m}^3$ were retained in 1991

⁴⁴ The first set of criteria pollutants included sulfur dioxide, particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons, and nitrogen dioxide.

⁴⁵ The Lead Industries Association, Inc. brought a challenge against the lead NAAQS in 1979 in the federal Court of Appeals for the District of Columbia in which St. Joe Minerals Corp. intervened. This challenge was denied by the DC Circuit in 1980 and the US Supreme Court declined to review the denial of the challenge.

following an extensive review initiated in 1984. As discussed in US EPA (2007a), US EPA considered the latest lead health effects evidence, as reflected in such documents as the 1986 Air Quality Criteria for Lead (US EPA, 1986a), the 1990 Supplement to the criteria document (US EPA, 1990b), and the 1990 Staff Paper (US EPA, 1990c), in reaching its decision not to propose a revision to the lead NAAQS in 1991. The NAAQS are once again currently under review, with US EPA yet to propose revisions to the standards.⁴⁶

The NAAQS for lead were established following a comprehensive scientific and technical policy assessment process that included the preparation of an "air quality criteria" document for lead. Following an extensive peer review process where opportunity for public comment was provided, the Air Quality Criteria for Lead was published by US EPA in December 1977 (US EPA, 1977c). US EPA (1977c) summarized the state of the science regarding what was known about lead in the environment and its potential for adverse health effects.

Despite much progress in the understanding of the relationship between airborne lead and human health effects since publication of the 1972 NAS report, the Air Quality Criteria for Lead (US EPA, 1977c) and the final rulemaking for the Pb NAAQS (US EPA, 1978a) both acknowledged many remaining uncertainties. Among the key data gaps highlighted by US EPA (1977c; 1978a) were a variety of monitoring uncertainties including the lack of site selection criteria for locating airborne lead samplers, outstanding questions regarding interferences and collection efficiencies of various filter media, and uncertainties related to the extent to which a monitoring network is able to represent the actual exposure situations for young children. Significant data gaps also limited our understanding of airborne lead exposures and toxicity, as US EPA (1977c) highlighted the lack of quantitative data on the relative contributions of various sources of airborne lead to blood lead levels, the lack of information on the contribution of food to human exposure, and gaps in the knowledge of the effects of lead on the hepatic, cardiovascular, immunologic, and endocrine systems. Despite these and other key data gaps and

⁴⁶ As discussed in the December 17, 2007, Advance Notice of Proposed Rulemaking (ANPR) for the lead NAAQS (US EPA, 2007a), US EPA recently solicited comments on a range of alternative standard levels for the lead NAAQS, up to and including the current level of 1.5 $\mu\text{g}/\text{m}^3$. Staff within the US EPA Office of Air Quality Planning and Standards (OAQPS) previously made recommendations regarding ranges of alternative standard levels. As stated in the final Staff Paper for lead (US EPA, 2007b), OAQPS staff recommended that consideration be given to a range of alternative standard levels from as high as 0.1 to 0.2 $\mu\text{g}/\text{m}^3$, which represent current levels in many U.S. urban areas, down to the lowest levels of 0.02 to 0.05 $\mu\text{g}/\text{m}^3$ evaluated in the final Human Exposure and Health Risk Assessment for lead (US EPA, 2007c). OAQPS staff based their recommendations on a growing body of evidence on lead health effects, as well as on findings from the lead risk assessment of "estimated decrements in IQ for policy-relevant exposures associated with the current NAAQS that are clearly of a magnitude that might be reasonably be judged to be highly significant from a public health perspective." (US EPA, 2007b, p. 5-22)

uncertainties, the 1977 Air Quality Criteria served as the primary scientific reference underlying the first Pb NAAQS.

Table 10-1
Timeline of Ambient Lead and Primary Lead Smelter Regulatory Activity

Year	Regulatory Activity
1970	Clean Air Act
1973	Leaded gasoline phasedown promulgated
1975	NRDC suit to make lead a criteria air pollutant
1976	Standards of performance promulgated for new and modified primary lead smelters
1976	Court order requiring designation of lead as criteria air pollutant
1977	First US EPA Air Quality Criteria document for lead issued
1978	Lead Primary and Secondary NAAQS promulgated
1986	US EPA issued revised Air Quality Criteria document for lead
1990	Clean Air Act Amendments
1990	US EPA issued supplement to 1986 Air Quality Criteria document for lead
1991	US EPA retained lead NAAQS of 1.5 $\mu\text{g}/\text{m}^3$ following completion of review process
1996	Leaded gasoline phasedown completed
1999	National Emission Standards for Hazardous Air Pollutants (NESHAP) adopted for primary lead smelters
2004	US EPA initiated review process for lead NAAQS
2006	US EPA issued final lead Air Quality Criteria document
2007	US EPA issued final lead Risk Assessment Report and final lead Staff Paper; US EPA issued Advance Notice of Proposed Rulemaking (ANPR) for lead NAAQS

A variety of key issues associated with the technical and economic feasibility of the lead NAAQS was recognized by US EPA and others prior to its promulgation in October 1978. For example, US EPA had initially proposed NAAQS of 1.5 $\mu\text{g}/\text{m}^3$, averaged over 1 month, but changed to a less stringent quarterly averaging period following industry comments concerning the scientific and technical difficulties presented by the selection of the calendar month averaging period (US EPA, 1978a). US EPA also recognized that attainment of the standard may be problematic in areas with high background concentrations of airborne lead due to contributions from a variety of different sources (US EPA, 1978a). In fact, in promulgating the lead NAAQS, US EPA (1978a) noted that its own "economic analysis does indicate that there may be significant problems in attainment of the standard in the vicinity of nonferrous smelters and other large industrial sources of lead emissions." Previously, this idea that smelters may

have great difficulties complying with the NAAQS was reflected in a September 29, 1978 press release on the lead NAAQS where Administrator Douglas M. Costle is quoted as stating that (US EPA, 1978d):

Most primary smelters have their greatest impact in more sparsely populated areas. Our preliminary assessments indicate that some non-ferrous smelters may not be able to technically or economically achieve the standard. But our information on how bad the environmental problem is and how much it will cost to control these sources adequately is not good enough... During the next 6 to 9 months, we will work closely with the states and the affected industry to develop a plant-by-plant analysis of how serious the problems are, and what would be a reasonable compliance program for each smelter. We want to formulate a control strategy which will avoid significant disruption in the lead and smelting industries without compromising our goal of protecting public health. If our study of these impacts over the next 18 months indicates economic effects unwarranted by the health protection involved, we will consider a wide range of remedial action, including the possibility of seeking revisions to the Clean Air Act.

Because only generic emission factors and plant configurations were typically available to assess the nature of air quality problems and the potential impact of the standard around pollutant sources such as smelters, US EPA (1978a) encouraged state regulators and regulated entities to gather plant-specific air quality data, technical information and plant configurations in order to develop and "better consider approval of alternative approaches to emission control in the State plans." With respect to smelters, US EPA (1978a) specifically acknowledged that attaining the standard may require control of fugitive emissions, which were difficult to estimate, measure, and control. Recognizing the large uncertainties associated with the air quality impacts of fugitive emission sources, US EPA (1978a) concluded that "nonferrous smelters may have great difficulty in achieving lead air quality levels consistent with the proposed standard in areas immediately adjacent to the smelter complex."

It was thus well-recognized that few lead air quality data had been gathered around sources of fugitive emissions such as smelters, in part because there had never been any specific requirements in SIP regulations calling for the collection of such data around specific sources (US EPA, 1978a). To address this glaring data gap, as part of its promulgation of the NAAQS, US EPA (1978a) announced its intention to require installation of ambient air quality monitors in the vicinity of primary lead smelters (as well as at other lead point sources, including primary copper smelters and secondary lead smelters). This proposed rulemaking was generally intended to initiate a process for the collection of facility-specific data needed to assess the nature and magnitude of the lead problem at these major point sources, and to base further revisions of the SIPs consistent with the nature of the problem. It was specifically aimed at gathering information for characterizing the nature, extent, and impact of fugitive lead emissions from

smelters. The final rulemaking for these proposed ambient air quality monitoring requirements at smelters, as well as the final version of the US EPA document "Guideline for Lead Monitoring in the Vicinity of Point Sources," was not published until nearly 3 years later in 1981 (US EPA, 1981a; 1981b).

As part of the October 1978 proposal involving ambient air quality monitoring in the vicinity of major point sources such as primary lead smelters, US EPA (1978a) announced its intention "to develop more accurate emission factors that relate the operation of a source to the amount of fugitive emissions the source generates." Although US EPA (1978a) acknowledged that there would be delays in the development of these factors such that they would not be available until some time after lead SIPs had been prepared and submitted by states, air lead emission factors for fugitive sources were not provided in the US EPA AP-42 emissions factor documents until 1986 and these emission factors were assigned the second lowest emission factor rating to D to indicate their low reliability (see Section 4.4).

Time has shown US EPA to be omniscient regarding the difficulties associated with attainment of the NAAQS in areas with primary lead smelting operations. For example, the East Helena area in Montana's Lewis and Clark County remains a lead nonattainment area despite closure of the smelter in 2001. In addition, constant attainment has proven difficult for the Doe Run Herculaneum smelter, as the Herculaneum area monitored attainment for 10 consecutive calendar quarters from the August 2002 attainment date but exceedances of the standard at the Broad Street monitor returned in 2005 despite compliance with all control measures contained in the 2002 SIP revision (US EPA, 2005d). In addition, although they have achieved attainment with the standard, a number of counties where primary lead smelters and/or refineries were formerly active are among the small list of lead maintenance areas, *i.e.*, areas that were at one time in non-attainment but have more recently been re-designated as attainment areas. These include Collin County in Texas, Iron County in Missouri, and Douglas County in Nebraska.

10.2 Leaded Gasoline Phasedown

As discussed in Section 9.1, US EPA's rationale for not including lead among the original set of 6 criteria pollutants involved its belief that airborne lead could be controlled through its programs at the time for phasing out lead in gasoline (US EPA, 1978a). US EPA (1977c) cited data indicating that mobile-source emissions were responsible for an estimated 88 percent of total lead emissions in the United States. US EPA began its phasedown program for leaded gasoline in 1973, with its first reduction standards calling for a gradual phasedown of lead to 0.6 grams per total gallon by July 1, 1978 (US EPA,

1973b).⁴⁷ Implementation of this program was delayed by litigation until 1976. This program was tightened in 1982 and 1985, with the 1985 standard reducing the limit for lead content of gasoline down to 0.1 grams per gallon, effective January 1, 1986 (US EPA, 1985c). US EPA's 25-year program phasing out lead additives in gasoline was completed in 1996 when a direct final rule was published that banned the use of any lead additive in the production of unleaded gasoline (US EPA, 1996; ATSDR, 1999).

10.3 New Source Performance Standards for Primary Lead Smelters

Pursuant to Section 111 of the Clean Air Act, US EPA proposed standards of performance for new and modified sources for primary lead smelters and 2 other categories of stationary smelters (primary copper smelters and primary zinc smelters) on October 16, 1974. These standards of performance were then promulgated in final form on January 15, 1976, nearly one and a half years later (US EPA, 1976f).

The promulgated standards of performance for new and modified primary lead smelters addressed particulate matter emissions in gases discharged to the atmosphere from blast furnaces, dross reverberatory furnaces, and sintering matching discharge ends, limiting them to 50 mg/dscm. In addition, opacity of these gases was limited to 20 percent, and continuous monitoring systems were required to monitor and record the opacity of emissions. Additional emission limits were also imposed for sulfur dioxide.

10.4 National Emission Standards for Hazardous Air Pollutants (NESHAP) for Primary Lead Smelting

Over 9 years following the Clean Air Act Amendments of 1990 which required US EPA to adopt regulations for Hazardous Air Pollutants (HAPs), US EPA issued its final rule setting national emission standards for Hazardous Air Pollutants (NESHAP) for new and existing primary lead smelters (US EPA, 1999c; 1999d). The NESHAP for primary lead smelters required that all primary lead smelters meet emission standards consistent with the application of MACT. More specifically, the final rule set a "plant wide" emission limit of 500 grams of lead per megagram of lead produced from the combined emissions from 9 identified process and process fugitive emission sources:

⁴⁷ US EPA (1996) states that the average lead content in gasoline in 1973 was 2-3 grams per gallon, or about 200,000 tons of lead per year.

- (1) Sinter machine;
- (2) Blast furnace;
- (3) Dross furnace;
- (4) Dross furnace charging location;
- (5) Blast and dross furnace tapping locations;
- (6) Sinter machine charging location;
- (7) Sinter machine discharge end;
- (8) Sinter crushing and sizing equipment; and
- (9) Sinter machine area.

In addition to emission limits, US EPA (1999c) also required work practice and operating standards for the above-listed fugitive sources (sources 4 through 9). Smelters were required to develop a Standard Operating Procedures (SOP) manual for fugitive dust sources that outlined detailed procedures for limiting fugitive dust emissions. Provided that it addressed the identified fugitive dust sources, such an SOP manual could be an existing manual developed as part of a facility's SIP. Work practice standards included the installation of hoods ventilated to an air pollution control device for the charging, tapping, and sinter handling sources identified above (sources 4 through 8). In addition, for sinter machine and sinter crushing and sizing equipment, requirements included location in a building ventilated to a baghouse or equivalent device at a rate capable of maintaining an in-draft.

US EPA (1999d) acknowledged that regulation of lead as a criteria pollutant already imposed federally enforceable emission limitations and work practice requirements on the 3 operating primary lead smelters, and that US EPA had concluded that these existing emission limitations and requirements were representative of Clean Air Act requirements of MACT for the industry. In other words, by promulgating a NESHAP requiring application of MACT, US EPA (1999c) promulgated requirements that were "consistent and compatible with the current limitations and work practices" rather than additional and more stringent emission controls (US EPA, 1999d). US EPA (1999d) confirmed that no quantifiable emission reductions or other environmental impacts were anticipated from this rulemaking, but that it was intended to improve emission control device operation and maintenance procedures and to achieve significant but unquantifiable reductions in lead emissions. Importantly, by establishing a "plant wide" emission limit, US EPA (1999c) provided smelters with the flexibility to determine whether and how much control of specific sources was needed to meet the limit.

11 Chronology of Herculaneum Plant Regulation and Compliance

The 1970 Clean Air Act (CAA) was the impetus for a continuous series of pollution control enhancements at the Doe Run lead smelter at Herculaneum, Missouri (Doe Run).⁴⁸ Doe Run's efforts were iterative, as would be expected during this period of technology and regulatory evolution in the field of air pollution control. Over the years, Doe Run's efforts have gone beyond SIP-related and other regulatory requirements, including both additional control projects and a number of engineering and research studies to identify process changes and opportunities for emissions reductions. Air pollution enhancements have cost the company over \$60 million in capital expenditures over the past 40 years.

11.1 Pre-SIP Air Pollution Control Measures

Doe Run led advances in air pollution control even many years prior to state or federal control of air quality. In these pre-regulatory years, Doe Run's air pollution control measures were targeted at reduction of SO₂ and particulate matter, but had the ancillary benefit of simultaneously reducing lead emissions. For example, Doe Run voluntarily installed its first baghouse, one of the first industrial baghouses in the world, to capture smelter smoke in 1910. On its own initiative, Doe Run installed additional major air pollution control equipment in the 1950s (wet scrubbers and a second baghouse) and the early-mid 1960s (a third baghouse, several enhancements to reduce slag handling emissions, a new blast furnace to reduce emissions during charging, and a new updraft sintering machine) (Schupp, 2000; Sherman, 1970. DR4700732).

Following the formation of the Missouri Air Conservation Commission (MACC) in 1965 (MDNR, 2006) and the promulgation of air quality standards for the St. Louis Metropolitan Area for SO₂ and particulate matter (Fuller, 1967. DR991841), Doe Run voluntarily implemented several additional air pollution control enhancements in the late 1960s. These included additional ventilation and water cooling systems to reduce blast furnace emissions and construction of an Acid Plant in 1969 (Sherman, 1970. DR4700732). While the primary purpose of the Acid Plant was to reduce SO₂ emissions by converting these waste gases into a useful product, sulfuric acid, for resale, it also provided some benefit to lead emission control because sinter gases had to be pre-treated (at Doe Run, using wet scrubbers and

⁴⁸ In this report section, the Doe Run lead smelter at Herculaneum, Missouri, represents the Doe Run Company and all predecessor companies (including St. Joe Minerals Company/Corporation) that owned and operated the Herculaneum, Missouri primary lead smelter.

a baghouse) to remove particulates before acid manufacture. Doe Run's Acid Plant was recognized as state-of-the-art for removal of SO₂ (Anon., 1979. DR2600589), while other smelters, such as ASARCO's Glover, Missouri primary lead smelter, lagged behind such technology (Beilstein, 1973. DR4700302). Overall, during the decade of the 1960s (before the 1970 CAA), Doe Run spent \$7.8 million in capital expenditures for air pollution control enhancements (Sherman, 1970. DR4700732).

Following promulgation of the 1970 CAA and the 1971 implementation of NAAQS for SO₂ and particulate matter, but prior to the lead SIP process, Doe Run escalated its investment in air pollution control equipment and enhancements, spending over \$13 million in capital expenditures during the 1970s (Sherman, 1970. DR4700732; Anon., undated. DR1000613; Anon., 1973. DR5200201; St. Joe Minerals Corporation, 1976. DR2600287; St. Joe Minerals Corporation, 1976-1989. DR1103028). Included among these projects were 2 additional baghouses (#4 and #5) that more than doubled the smelter's filtration capacity, many modifications and additional air pollution control equipment for the sinter and acid plants, and construction of a new smelter stack (DeClue, undated. DR2600397; Anon, undated. DR1000613). In fact, Doe Run's major new baghouse, installed cooperatively with the State in 1972 (#5), reduced lead air emissions by half as of 1979 (Doe Run Company, 1990).

Well before the promulgation of the US EPA lead NAAQS in 1978 and SIP-related sampling requirements, Doe Run measured airborne lead levels at its network of monitoring stations. As early as the mid-1960s and through the 1970s, Doe Run routinely had portions of its high-volume filters that were collected during TSP monitoring also analyzed for lead (Fuller, 1967. DR991841; DeClue, 1976. DR3201459). Although these lead data are not comparable to later lead data or the lead NAAQS that are based on the federal reference method for lead determination due to differences in analytical measures and quality assurance/quality control measures, they demonstrate Doe Run's early commitment to understanding and reducing lead air impacts, in addition to air impacts from regulated pollutants such as SO₂ and TSP, from smelter emissions.

As discussed in the first Missouri lead SIP, Doe Run had actively pursued fugitive emissions control projects, as well as numerous engineering and research studies, even prior to the first Consent Order. During the period from January 1978 to mid-1979 alone, Doe Run undertook 19 different projects to reduce fugitive lead emissions, with estimated reductions in the uncontrolled inventory of lead emissions at the plant of 162 tons per year. The first SIP acknowledged 9 additional engineering and research studies that Doe Run had underway at the time of the SIP submission, including process,

fugitive emissions, and traffic control studies, and authorized but did not require the company to implement the results. Based on its review of emissions inventories for the 3 Missouri primary lead smelters including Doe Run at the time of the first SIP, the state made the conclusion that "These inventories show the extremely high degree of control already existing at all point process, process fugitive and open fugitive emission sources in steady-state operation."

Coincident with its increased investment in air pollution control enhancements during the 1970s, Doe Run developed a corporate environmental program in 1974 with dedicated corporate environmental staff to coordinate its environmental activities. As part of this program, Doe Run began preparing annual environmental planning reports in 1975. Doe Run's environmental program primarily focused on issues of air and water pollution and occupational health. The purpose of Doe Run's environmental planning reports was to propose environmental projects to address identified environmental problems. These reports typically included summaries of pertinent regulatory developments, environmental and occupational health projects, and spending on environmental projects to date, as well as corporate environmental budgets for the upcoming 5-year period (Welch, 1975. DR5004009; Welch, 1979. DR5003547).

11.2 Overview of Doe Run's SIP-Related Efforts

Doe Run's iterative efforts to control lead emissions proceeded in accordance with a series of CAA-defined State Implementation Plans (SIPs), which gave rise to advances in emissions monitoring, key emissions identification, emission control technology, and air quality modeling, all under the auspices and approval of the MDNR and the US EPA. The process of developing and implementing the SIPs to control lead emissions at Doe Run involved: 1) preparation of a lead emissions inventory and gathering of historical emissions data by industry and the State; 2) consultations between Doe Run and the State, with periodic US EPA involvement, to develop emissions control technologies, emissions limits, and emissions control management practices for each emissions source to be enacted into state regulations; 3) negotiation between the State and Doe Run of Consent Orders with emitters to provide an enforceable agreement by Doe Run to implement emission controls on a specified timeline; 4) development by the State of a draft SIP containing the outcomes of the consultations and negotiations; 5) US EPA review and approval of the SIP; 6) implementation of the emissions controls and management practices provisions of the Consent Orders; and, 7) performance of confirmatory monitoring and modeling to demonstrate attainment of air quality standards at the Doe Run facility.

The state has developed, and US EPA approved, a series of 4 distinct SIPs for Doe Run since US EPA first promulgated the NAAQS for lead in 1978. Each of the SIPs was developed in response either to the regulatory program imposing more stringent requirements, or to data indicating that the then-applicable SIP was inadequate to attain the NAAQS for lead at Doe Run. The initial SIP, prepared in response to the newly promulgated lead NAAQS, was submitted in 1980 and received final approval in 1984 (the "1980 SIP"). In 1986, US EPA determined that the 1980 SIP was inadequate to attain the lead NAAQS at DR and called for submission of a revised SIP. The second SIP was submitted in 1990 and approved in 1992 (the "1990 SIP"). In 1991, US EPA required development of another SIP that would demonstrate compliance with the more stringent requirements of Part D of the 1990 Amendments to the Clean Air Act. The third SIP was submitted in 1993 and approved in 1995 (the "1993 SIP" or "Part D SIP"). In 1997, US EPA determined that the 1993 SIP was inadequate to attain the lead NAAQS and called for submission of a revised SIP. The fourth SIP was submitted by the State in 2001 and approved by US EPA in 2002 (the "2002 SIP"). Most recently, in April 2007, the Missouri Air Conservation Commission unanimously approved the 2007 revised MDNR SIP for Herculaneum, which was developed following the April 2006 determination by US EPA that the 2002 SIP was inadequate to attain the lead NAAQS (Doe Run Company, 2007a).

Each SIP was developed by the State, in consultation with US EPA and Doe Run, made available for public review and comment, submitted to US EPA for review, and approved by US EPA. Each SIP imposed specific emission controls, management practices, and monitoring and reporting requirements, memorialized in an enforceable Consent Order signed by Doe Run and the State and subject to implementation by Doe Run according to a specific schedule for compliance. According to available documentation, Doe Run consistently implemented all requirements of each of the 4 SIPs on or before the applicable deadlines, and was not alleged to have failed to implement required emissions controls. Notwithstanding the iteratively more stringent requirements imposed by this rigorous SIP process, and despite Doe Run's record of aggressive and steadfast implementation of the emissions controls imposed by this series of 4 SIPs, it has proven much more difficult than Doe Run, US EPA or the State expected to attain the lead NAAQS at Doe Run.

Doe Run implemented pollution control as soon as they knew of the need, consistent with the best knowledge at the time. All of Doe Run's efforts were conducted under State and US EPA review and approval. The public also has had the opportunity to provide input as part of the SIP process.

Despite being in compliance with agency emissions control requirements throughout the nearly 30-year era of the lead SIP regulatory program, and despite promptly implementing all actions required by the successive SIPs, attainment of the lead NAAQS has proven elusive, requiring great technological effort by Doe Run, US EPA, and the State and great expenditure of resources by Doe Run. Below is a summary of this iterative process.

11.3 1980 SIP

The promulgation of the lead NAAQS in October 1978 set in motion an intensive 18-month effort in Missouri to develop its first SIP for lead. As a major center of the US lead industry, Missouri faced a particularly challenging endeavor in developing a SIP for lead. The state's lead facilities included at least one type of each source of lead listed at the time in the federal regulations. In particular, 3 of the operational primary lead smelters existing in the United States were located in Missouri, and nonferrous metal smelters were acknowledged by US EPA to present great difficulty in achieving the lead NAAQS. These 3 facilities produced about 90 percent of the newly refined lead in the United States in the early 1980s (MDNR, undated. DR5501396).

This intensive effort involved development of state-wide lead emissions inventories, implementation of a short-term monitoring program in the vicinity of the 3 primary lead smelters to collect facility-specific data in support of emissions controls design,⁴⁹ development of facility-specific emission control equipment and control measures for the respective emissions sources, and negotiation of enforceable agreements (in the form of Consent Orders signed by the facility and the State) to require implementation of the facility-specific controls according to a specified schedule. In the case of Doe Run, the State worked with the company in a lengthy series of meetings and exchanges of technical information to develop a set of emissions controls and management practices for the facility that were incorporated in a consent order between the State and the facility that was, in turn, incorporated as part of the SIP.

The Missouri Air Conservation Commission prepared and submitted the state's initial SIP for lead in September 1980.⁵⁰ Key elements of the SIP included: a summary of measured air quality from

⁴⁹ State of Missouri, Air Pollution Control Program, Short-Term Lead Monitoring Plan in the Vicinity of Significant Point Sources (December 1979) (APCP, 1979).

⁵⁰ State of Missouri, Air Pollution Control Program, State Implementation Plan, Lead, July 1980 (the "1980 SIP Submission") (MDNR, 1980). The Doe Run facility was subject to regulation under the CAA for emissions of other criteria pollutants, notably

1974 to 1980; a base-year emissions inventory for stationary and mobile sources; control strategies intended to create reductions in lead emissions from these sources; consent orders detailing schedules for installation of control equipment on certain stationary sources including the Doe Run facility; calculations of projected ambient air lead concentrations in areas with exceedances of the standards; and provisions for review of new and modified sources of lead emissions. The 1980 SIP represented the beginning of decades-long struggles with many complex technical issues involving demonstration of attainment, monitoring, emissions estimation, and dispersion modeling:

- The Dunklin High School monitoring station, located approximately one-half mile from the smelter stack and one-quarter mile from the Doe Run fenceline (Welch, 1979. DR5003547; MDNR, 1990), was the monitoring point selected to demonstrate attainment with lead standards. The High School station was selected because its monitoring data had exhibited the highest 90-day average concentrations in the Doe Run vicinity during the short-term monitoring program conducted in support of the 1980 SIP.
- The required emissions reductions imposed by the SIP were derived by comparing observed ambient monitoring data at the attainment point with the amount of estimated emissions at the sources during the monitoring period, then proportionally reducing the emissions allowed at the sources so that the standard would be achieved at the monitoring point (*e.g.*, air concentrations were 2x too high at the monitoring point, thus requiring 50% reductions in the amount of emissions from the corresponding sources).⁵¹ On the basis of this ratio technique, the 1980 SIP (MDNR, 1980) estimated that the SIP emissions controls required at Doe Run would result in a lead concentration at the High School monitoring station of 1.48 $\mu\text{g}/\text{m}^3$, thereby achieving attainment with the NAAQS.
- The SIP emission inventory at Doe Run identified a wide range of emissions sources (*e.g.*, stack, piles, buildings). Emissions factors for most if not all types of sources, and notably sources of fugitive emissions, were estimated using handbook emission factors (*e.g.*, US EPA's AP-42) derived from measurement data collected at other primary lead smelters and/or non-smelter source types (MDNR, 1980).⁵²
- Air dispersion modeling conducted by the State for the first SIP was found to correlate poorly with measured values from the short-term monitoring network around the Doe Run smelter. The State concluded that the poor model performance was related to the

Total Suspended Particulates (TSPs). The facility had been designated in nonattainment for the secondary TSP standard prior to the adoption of lead as a criteria pollutant. However, by the time of development of the lead SIP, regulators had observed three and one-half years of data showing improvements in the facility's TSP emissions with no violations of the standards during that period. This resulted in US EPA's proposal to designate the facility in attainment for TSP, Proposal to Approve Revision to Missouri SIP, 44 Fed. Reg. 61384 (October 25, 1979) (US EPA, 1979f).

⁵¹ 1980 SIP Submission, at 23 (MDNR, 1980). Missouri chose to base the attainment demonstration on actual monitoring data rather than the Industrial Source Complex (ISC) model because it concluded that efforts to calibrate the model to the emissions data for DR did not produce meaningful results that related monitored values to the estimated emissions. *Id.*

⁵² Such emission factors at this date were crude, often taken from other types of emissions (*e.g.*, coal piles) believed to be analogous to lead smelters. The inaccuracy of emissions factors from fugitive emissions sources proved to introduce significant error into the emissions inventory for the 1980 SIP, which in turn undermined the possibility of achieving attainment using the emissions controls imposed by the 1980 SIP. See Memorandum, Bradley W. Reynolds to Lead SIP File, Lead SIP Progress Report (July 1, 1982 – June 30, 1983) –St. Joe Lead Smelter (November 22, 1983) (the "1983 MDNR Lead SIP Progress Report") (Reynolds, 1983a).

lack of continuous quality-assured meteorological data and plant-specific fugitive lead emissions estimates, and ultimately decided to perform no further attempts at modeling in support of the SIP. As described above, monitoring data rather than modeling were thus used for demonstration of attainment in the first SIP.

- The SIP submission detailed the State's plan for long-term ambient air monitoring for lead in 5 areas, 3 of which were in the immediate vicinity of each of the 3 primary lead smelters in the state, including the Doe Run facility. The objectives of the long-term monitoring network were to generate quality-assured data sufficient to meet US EPA guidelines and to provide data support for future air dispersion modeling. As described in MDNR (1982. DR 9000959), 6 locations around the smelter were ultimately selected and approved by both the State and US EPA for the long-term monitoring plan. Consistent with the newly released US EPA guidance document "Guideline for Lead Monitoring in the Vicinity of Point Sources" (US EPA, 1981a), locations were selected to represent impacts of both stack and fugitive emissions. The long-term monitoring program commenced in July 1982, and quality-assured monitoring data have been collected at locations around the smelter since this time.

The SIP reflected exceedances of the lead standard in the available monitoring data for St. Louis and for 2 of the 3 primary lead smelters, AMAX and Doe Run. The SIP requested a two-year extension of the deadline for attainment, to October 1984, in the vicinity of these 2 smelters in order to implement both stack and fugitive emission controls.

US EPA gave partial approval to the initial lead SIP submission on April 27, 1981. However, US EPA disapproved the State's air quality modeling concerning the 3 lead smelters. US EPA eventually retracted its disapproval of the air quality modeling and granted final approval to the lead SIP as it applied to Doe Run (the 1980 SIP) on July 19, 1984.⁵³ This final approval required the facility to attain the lead NAAQS by October 31, 1984.

⁵³ Approval and Promulgation of Missouri State Implementation Plan for Lead, 46 Fed. Reg. 23412 (April 27, 1981) (US EPA, 1981c). US EPA's disapproval of the air modeling in the vicinity of the smelters reflected a disagreement with the state over the efficacy of conducting effective atmospheric dispersion modeling for primary lead smelters because the predicted results of the modeling performed by Missouri, using the Industrial Source Complex Long-Term (ISCLT) and the Industrial Source Complex Short-Term (ISCST) models, did not correlate with observed air quality monitoring data for the three facilities. As well, the DR monitoring network on which the modeling was based lacked sufficient meteorological monitoring stations and plant-specific fugitive emissions lead estimates to yield accurate results. US EPA committed in the Approval to work with the state to develop appropriate modeling for each of the lead smelters. US EPA later reversed its position about the purported modeling deficiencies and reversed its initial rejection of the demonstration provided by Missouri in its original SIP submission as satisfying the requirement for the modeling portions of the SIP submittal. Petition for Reconsideration of Lead Plan and Policy Change Regarding Attainment Date; Missouri, 48 Fed. Reg. 48978 (October 21, 1983) (US EPA, 1983b), Approval and Promulgation of Missouri State Implementation Plan (SIP) for Lead, 48 Fed. Reg. 48982 (October 21, 1983) (US EPA, 1983c). US EPA's reconsideration reversed its earlier decision to reject Missouri's demonstration and granted final approval to the Missouri Lead SIP. Approval and Promulgation of Missouri State Implementation Plan (SIP) for Lead, 49 Fed. Reg. 29218 (July 19, 1984) (US EPA, 1984).

The Consent Order proposed for Doe Run was executed by Doe Run and the State and became effective in August 1980 while the SIP awaited US EPA approval.⁵⁴ The Consent Order obligated Doe Run to perform all of the emissions control activities specified for it in the proposed SIP, including revamping "the ventilation in the blast furnace area, adding 5 new scrubbers in the sinter plant, install[ing] alarm systems on baghouses, and pav[ing] and clean[ing] plant grounds" (MDNR, undated).

The State's first implementation plan for attaining the lead NAAQS at the Doe Run facility was thus not finally approved by US EPA until 1984, 14 years after passage of the 1970 CAA, 8 years after the addition of lead to the list of criteria pollutants, 6 years after US EPA adoption of the lead NAAQS, 5 years after the deadline for US EPA approval of SIPs for lead, 2 years after the initial deadline for attainment of NAAQS pursuant to an US EPA-approved SIP, and in the same year as the extended deadline for demonstrating attainment applicable to the Doe Run facility. The passage of this much time and effort highlights the difficulty faced by regulators and industry in translating the goals and standards of the Clean Air Act into meaningful emissions control technologies and measures at facilities as complex as the primary lead smelters in Missouri. The subsequent iterations of Missouri lead SIPs discussed below demonstrate how difficult it has been for regulators and industry to select and implement emissions control technologies and measures that will actually achieve the standard, despite using the most advanced technologies and predictive tools available at the time.

11.4 1990 SIP

Upon completion of the first Missouri lead SIP, and during its review and approval by US EPA, the State oversaw compliance with the various emission control requirements of its SIP while monitoring air quality at designated locations to determine if the SIP would result in attainment of air quality standards. US EPA tracked the progress toward attainment through quarterly inspection reports and air quality data routinely forwarded to US EPA by the State and by the facility. The 1983 MDNR Lead SIP Progress Report noted that all but 2 of the items in the Consent Order, corresponding to 99 percent of the projected emissions reductions, had been accomplished by Doe Run, as had many of the engineering and research tasks proffered by Doe Run in the SIP.⁵⁵

⁵⁴ Air Conservation Commission, State of Missouri, In the Matter of St. Joe Lead Company, Consent Order, August 15, 1980 (MACC, 1980).

⁵⁵ 1983 MDNR Lead SIP Progress Report (Reynolds, 1983a).

The State was pleased with Doe Run's timely implementation of the 1980 SIP measures, noting the following in its 1983 *Evaluation Support Document*, "In general, the smelter has met the terms of their consent order, as agreed to in the July 1980 Missouri Lead SIP for actions to be completed 26 months into the time frame specified. The smelter has also initiated other improvements to smelter processes, as outlined in the research and engineering studies on page 24 of the Lead SIP, that should improve ambient air quality... In the final analysis, real reductions in the normal operation [lead] inventory have been achieved. Comparison with the 1979 inventory estimate yields a 35 ton per year reduction... St. Joe has made a conscious effort to further quantify their emissions in the hope of determining their effects on the area surrounding the smelter." (Reynolds, 1983b, pp. 2-3. DR3000314)

By October 1985, the facility had implemented all of the emissions control measures specified by the SIP and had completed a significant program of control measures not required by the SIP.⁵⁶ Nevertheless, all Doe Run attempts sanctioned by US EPA and MDNR or voluntarily undertaken by Doe Run failed in the short term to produce an emissions control program at Doe Run that would attain the NAAQS at the High School monitoring station.

Even before final approval of the 1980 SIP, monitoring data from the High School monitoring station, as cited in the 1983 MDNR Lead SIP Progress Report, indicated that the provisions of that SIP would not result in attainment of the lead standard at the High School station.⁵⁷ The 1983 MDNR Lead SIP Progress Report identified inaccuracies in the associated emissions factors on which the 1980 SIP was based, including underestimation in the initial inventory of fugitive emissions. In addition, excess emissions resulting from unscheduled blast furnace shutdowns were identified as a likely cause for the underperformance of the emissions controls in the 1980 SIP.

In early 1984, US EPA and the State reviewed upsets and malfunctions at the Doe Run plant to determine the cause of the exceedances of the lead NAAQS.⁵⁸ The facility attributed these exceedances

⁵⁶ Letter to Gene Cassin, Missouri Air Pollution Control Program, from Daniel L. Vornberg, St. Joe Lead Company, Annual Review Comments, Mo. Lead Sip, Herculaneum, October 3, 1985. at 4-8. DR9000922 -9000926 (discussion of "New Controls and/or Practices Not Reflected in SIP") (Vornberg, 1985).

⁵⁷ 1983 MDNR Progress Report, at 4. *See, also*, Letter to Nick Nikkila, MDNR, from Carl M. Walter, US EPA, March 7, 1984 (unless upsets and malfunctions are eliminated or reduced in number, air quality standards will continue to be violated no matter what control measures are implemented) (Walter, 1984).

⁵⁸ Letter to Nick Nikkila, Missouri Air Pollution Control Program, from Carl M. Walter, US EPA Air Branch Chief, March 7, 1984. DR5500077 (Walter, 1984).

in part to variability in the facility's operating conditions due to difficulties in obtaining sufficient feed materials from mines, labor disruptions, and generally poor economic conditions of the company.⁵⁹

In June 1986, US EPA published notice that it considered the Missouri lead SIP to be inadequate to attain the NAAQS and issued a call for revisions to the SIP to correct the perceived inadequacies.⁶⁰ Specifically, the notice observed that the "monitoring network . . . used to determine if the standards were actually met . . . [has] been in place since 1982. The monitors have shown that there are still violations of the lead standards even though all the controls which were contained in the plan have been implemented at the St. Joe smelter. This indicates that additional controls are needed in order to meet the standard."⁶¹ US EPA requested the State to revise the plan as it pertained to the area in the immediate vicinity of the St. Joe lead smelter, which was the only area US EPA determined the Missouri lead SIP to be substantially inadequate.

This 1986 request led to the second lead SIP applicable to Doe Run (the "1990 SIP"), which was finally approved in 1992. Stated another way, in its 1986 notice, US EPA acknowledged that, despite the years of effort and deliberation involved in developing the first SIP, the engineering assumptions and expectations that led to the emissions controls incorporated in the first SIP, which were developed, shared, and approved by US EPA, MDNR, and Doe Run, had not proven sufficiently accurate or effective to attain the NAAQS standard at which they were targeted. It required an additional 6 years of effort by MDNR, Doe Run and US EPA to develop the next iteration of a technical and regulatory strategy believed to be sufficient to achieve the lead NAAQS at Doe Run.

Following the 1986 call for a revised SIP, MDNR and Doe Run engaged in a lengthy dialogue intended to yield a revised consent order containing emissions controls that could be demonstrated to achieve attainment with the NAAQS. Much of the dialogue focused on how to use the data generated from the long-term monitoring network to demonstrate attainment and on the location of monitoring stations for use in modeling and attainment demonstration. An exhaustive effort was also made to identify all available emissions reductions that could be implemented at Doe Run. Throughout the development of the 1990 SIP, US EPA insisted that emissions data reflecting excess emissions caused by

⁵⁹ Letter to Gene Cassin, Missouri Air Pollution Control Program, from Daniel L. Vornberg, St. Joe Lead Company, Annual Review Comments, Mo. Lead SIP, Herculaneum, October 3, 1985. DR 9000918 (Vornberg, 1985).

⁶⁰ Approval and Promulgation of State Implementation Plan for Missouri, Notice of Inadequacy for the State Implementation Plan (SIP) for lead and call for revisions, 51 Fed. Reg. 23247 (June 26, 1986) (US EPA, 1986c).

⁶¹ *Id.*

upsets and other extreme causes of variability should not be excluded from the data set used to demonstrate attainment,⁶² an issue which persists to the present.

In contrast to the previous SIP, air dispersion modeling played a prominent role in the development of the 1990 SIP, ultimately leading to a significant change in the demonstration of attainment that was to be incorporated into the revised SIP. In the 1980 SIP, monitoring data were used as the basis for the demonstration of attainment, with the High School monitoring location (the sampling location exhibiting the highest measured ambient lead concentrations during the 1979-80 short-term monitoring program) serving as the point for demonstrating attainment. For the 1990 SIP, MDNR used dispersion modeling in its demonstration of attainment, which supported consideration of other monitoring locations for determining attainment.

Specifically, preliminary MDNR air dispersion modeling predicted higher lead values at locations where no monitors were located rather than at the existing monitoring locations, with the highest value "at the smelter fenceline 300 meters from the stack (about 150 to 200 meters from the sinter building) and on a radial line from the stack to the No. 3 monitor at the High School."⁶³ Based on the preliminary modeling results as well updated 1990 dispersion modeling results, MDNR determined that a new Hi-Vol sampling station would be required at the approximate location determined by the model as having the maximum ambient lead concentration at the projected attainment date of February 1, 1993 (*i.e.*, when all emissions reducing control measures were in place and operational). In response to this requirement, Doe Run implemented sampling at the Broad Street monitoring location beginning in second quarter 1991.

Provided to Doe Run in October of 1986, the preliminary MDNR air dispersion modeling was a motivating factor underlying a series of additional emission controls adopted by Doe Run at this time.⁶⁴ The MDNR modeling identified the most significant sources of lead emissions at the plant to be the

⁶² See, *e.g.*, Memorandum, Richard G. Rhoads, US EPA to William A. Spratlin, US EPA, Acceptability of a Modified Dispersion Modeling Technique for the St. Joe Lead Smelter, February 25, 1987 (data reflecting emissions variability and excessive emissions due to upsets should not be discarded or even flagged for purposes of determining whether an ambient standard has been violated, though such data may be useful for diagnostic purposes) (Rhoads, 1987).

⁶³ Letter from Todd Crawford, MDNR, to Dwayne Durst, US EPA, December 31, 1986 (Crawford, 1986). The purpose of the Crawford letter was to provide US EPA Region VII with the reasoning underlying the MDNR decision to not use the maximum model-predicted lead value as the design value for demonstration of attainment in the 1990 SIP Revision. As discussed in the letter, key rationale underlying this decision included uncertainties associated with (1) fugitive emission estimates, (2) the effect of terrain and building downwash close in to the smelter, and (3) particle size distribution and density data. The letter concluded that "To accurately assess the ambient air impact, the state will install a new hi-vol monitor for lead near the predicted maximum concentration location shown by the preliminary dispersion modeling."

⁶⁴ Memorandum, from Gene Cassin, MDNR, to Dan Vornberg, DR, October 10, 1986 (Cassin, 1986).

Sinter Plant South End scrubbers, the Blast Furnace Baghouses, the Dross Furnace Roof Vents, and the Sinter Plant Railroad loading point. Doe Run actively developed 9 projects to address these sources for inclusion in the SIP and the Consent Order, 6 of which had been completed by Doe Run prior to submission of the 1990 SIP.⁶⁵

This early modeling by MDNR, which relied upon the model ISCLT, Version 5,⁶⁶ also served as the basis for additional modeling performed by Doe Run using an experienced modeler, Shell Engineering. This modeling used a Gaussian plume model, ISC1, to evaluate the relationship between emissions and air quality. Although MDNR and US EPA approved the Shell Engineering modeling, such modeling was still rudimentary compared to practices today. Some model input emission factors were taken from analogous industries – building emissions from aluminum smelters and pile emissions from coal mining – and model calibration was minimal. Nevertheless, reasonable agreement was found between model predictions and actual High School measurements, within about a factor of 1.5, and the model was used as a predictive tool for determining emission controls.

During this period, MDNR enacted a new regulation (10 CSR 10-6.120, effective December 29, 1988) that required existing primary lead smelters to restrict point source and fugitive emissions. This allowed imposition of source-specific emissions limitations on lead smelters in addition to the ambient standards imposed by the NAAQS. Under this regulation, point source and fugitive emissions for lead smelters were "capped" for each emissions source at the level of emissions used in the SIP's attainment demonstration for that emissions source: "The purpose of the rule is to limit emissions at the measurable point sources, to provide for the operation and maintenance of all emissions control equipment and procedures that limit and reduce all lead emissions from the smelter, and initiate requirements for smelter reporting and MDNR compliance inspections regarding lead emissions" (MDNR, 1990). At Doe Run, this had the effect of restricting lead emissions to the amounts used in the dispersion modeling conducted to support the 1990 SIP. This regulation constituted a significant change in the regulatory environment for Doe Run's operations because it subjected Doe Run to potential regulatory violations if the emissions caps were exceeded at one or more sources even if Doe Run had implemented all of the required emissions controls specified by the SIP. This regulation also imposed on Doe Run the obligation to develop and implement a work practice manual with detailed procedures for managing operational activities that give rise to fugitive or point source emissions.

⁶⁵ Letter from Walter D. Nowotny, DR, to G. Tracy Mehan, MDNR, February 21, 1990 (providing status report on Doe Run Lead SIP Consent Order) (Nowotny, 1990).

⁶⁶ *Id.*, at 2.

To determine available and appropriate emissions reductions that could achieve attainment, Doe Run engaged a US EPA- and MDNR-approved contractor, Fluor Daniel, Inc., in 1988 to conduct a study of all reasonably available control technology (RACT) and to identify all potentially relevant emissions reductions for consideration at Doe Run. It is noteworthy that the RACT provisions in the Clean Air Act at this time did not apply to lead emissions. RACT provisions were imposed under Part D of the Clean Air Act authorizing nonattainment designations and imposing more stringent emissions control requirement on designated nonattainment areas. However, US EPA believed that Part D did not apply to the lead NAAQS prior to the 1990 CAA Amendments.⁶⁷ The RACT study approach was adopted as the strategy that would provide the most comprehensive analysis of available control technologies for Doe Run. The RACT study prepared by Fluor Daniel identified 14 potential emissions control improvements and was submitted in draft⁶⁸ to US EPA and MDNR, revised in response to agency comments,⁶⁹ and re-submitted as final on July 7, 1989.⁷⁰

Having assembled all potentially relevant emissions reductions in the RACT study, Doe Run prepared an accompanying Technical Memorandum identifying the specific emissions controls it would implement in order to attain the lead NAAQS. These emission controls were then evaluated using MDNR- and US EPA-approved modeling techniques to determine combinations of emissions control activities that would be predicted to achieve attainment with the ambient standard. The RACT study and the modeling results were used as the basis for revised Consent Orders under which Doe Run would implement the emissions controls deemed by MDNR to be sufficient to attain the NAAQS. In the absence of a specific requirement to adopt RACT, this was accomplished formally by the State's issuance of a Notice of Violation to Doe Run that required Doe Run to resubmit the RACT study and the accompanying Technical Memorandum. These materials were then incorporated into the consent order, which in turn provided the basis for the SIP revision.⁷¹

⁶⁷ State Implementation Plans; General Preamble for the Implementation of Title I of the Clean Air Act Amendments of 1990, 57 Fed. Reg. 13498, at 13549 (April 16, 1992) (1990 Amendments clearly defines US EPA's authority to designate areas for lead; states must submit SIPs which meet the requirements of Part D within 18 months of designation) (US EPA, 1992b).

⁶⁸ Fluor Daniel, Review Draft of Evaluation of Lead Emission Controls at the Doe Run Company's Primary Lead Smelter at Herculaneum, Missouri, April 24, 1989 (Fluor Daniel, 1989).

⁶⁹ US EPA, MDNR, Comments Directed to the Review Draft of Fluor Daniel's "Evaluation of Lead Emission Controls at the Doe Run Company's Primary Lead Smelter at Herculaneum, Missouri," dated April 24, 1989, June 16, 1989 (US EPA; MDNR, 1989).

⁷⁰ Fluor Daniel, Evaluation of Lead Emission Controls at the Doe Run Company's Primary Lead Smelter at Herculaneum, Missouri, July 7, 1989 (Fluor Daniel, 1989).

⁷¹ Letter from Roger D. Randolph, MDNR, to John E. Fitzsimmons, DR, June 21, 1989 (citing violations of the ambient air standard for lead at DR monitoring sites number 3 and 5 dating from the second quarter of 1986) (Randolph, 1989).

Missouri submitted a revised SIP on September 6, 1990, which included 2 Consent Orders for the plant dated March 9, 1990 and August 17, 1990, each of which required additional emissions controls at the plant. These consent orders adopted the emissions controls identified by the RACT study and the associated Technical Memorandum. The State also revised its air quality regulations and adopted a work practice manual applicable to the plant operations. The consent orders, the revised regulations, and the work practice manual were incorporated into the SIP in a revised submittal to US EPA on May 8, 1991.

Doe Run was required under the proposed revised SIP to perform 16 distinct emission control projects, 5 of which were listed in the proposal as having been completed at the time of submission. The breadth and depth of the required control projects reflected the comprehensiveness of the RACT study. These projects addressed all aspects of the Doe Run facility's operations, including: modifications to the Sinter Plant South End involving removal of scrubbers, replacement with baghouses, conversion from air cooling to water cooling and replacement of venting equipment; installation of wind skirts, ventilation and recirculation of the lead chute, and paving at the rail car loading area; numerous housekeeping improvements designed to reduce traffic-caused resuspension by improved cleanup and containment methods; and rigorous plant operating procedures specified in the work practice manual.⁷²

In addition to the impetus driving the 1990 SIP, passage of the 1990 CAA Amendments indirectly imposed requirements for more aggressive emissions control at Doe Run. Because the monitoring results from the facility indicated NAAQS exceedances, as reflected in the 1986 US EPA Notice of Inadequate SIP, the facility was subject, under the 1990 CAA Amendments, to be designated by US EPA as in Nonattainment Status. Under the 1990 Amendments, for the first time, designation as nonattainment for lead triggered the requirement that the State submit, within 18 months of designation, a revised SIP that met the applicable requirements of Part D of the Act, Plan Requirements for Nonattainment Areas.⁷³ The imposition of Part D requirements on lead SIPs was newly adopted in the 1990 Amendments.⁷⁴ The addition of these requirements to the lead SIP process gave rise to a complex transition process for lead SIPs, such as Missouri's, which were under development at the time of passage of the 1990 Amendments. Under the transition process, US EPA intended that states whose SIPs needed

⁷² MDNR, Missouri State Implementation Plan for Lead, 1990 SIP Revision Concerning a Demonstration of Attainment of the Lead NAAQS in the Vicinity of the Primary Lead Smelter – Refinery in Herculaneum, Missouri, July 1990, at pp. 23.7 – 23.9 (MDNR, 1990).

⁷³ 42 U.S.C. § 7514(a). Prior to the 1990 Amendments, this requirement of developing a Part D SIP for areas in non-attainment had applied only to criteria pollutants designated prior to 1977.

⁷⁴ State Implementation Plans; General Preamble for the Implementation of Title I of the Clean Air Act Amendments of 1990, 57 Fed. Reg. 13498, at 13549-13551 (April 16, 1992) (US EPA, 1992c).

correction prior to the 1990 Amendments should continue development of their SIP under the pre-1990 requirements even if the state expected to have an area designated as nonattainment under the new law, thereby triggering the requirement under the 1990 Amendments for submission of a SIP meeting Part D requirements.⁷⁵ This was the circumstance confronting Doe Run and the State in completing development of the 1990 SIP.

In accordance with this transition process, US EPA's August 21, 1991 notice proposing to approve the 1990 and 1991 Missouri lead SIP submissions (which became the 1990 SIP) announced its expectation that the Herculaneum facility area would be formally designated as nonattainment thereby invoking the need according to the 1990 Amendments for a further SIP revision (in addition to the 1990 SIP) to meet the Part D requirements. Nevertheless, US EPA's August 1991 notice proposed a "limited approval" of the extant SIP submissions, pending the nonattainment designation and the impending applicability of the requirements of Part D.⁷⁶ US EPA noted that the work practice manual required by newly adopted Missouri regulations and the provisions of the 2 Consent Orders were integral parts of the SIP that would require the facility to install numerous additional control measures on an expeditious and specific schedule.⁷⁷

US EPA gave its final "limited approval" to the 1990 SIP for the Herculaneum plant on March 6, 1992.⁷⁸ The deadline identified for Doe Run to achieve attainment under the 1990 SIP was February 1, 1993. The effect of this approval, under the 1990 Amendments, was to incorporate by reference all of the elements of the Missouri SIP submission into the Code of Federal Regulations and to render these elements directly enforceable by US EPA.

11.5 Part D SIP

As anticipated in US EPA's August 21, 1991 notice proposing approval of the 1990 SIP, the facility was formally designated as nonattainment with respect to the lead NAAQS on November 6, 1991.⁷⁹ US EPA then reiterated in its final March 6, 1992 limited approval of the 1990 SIP that Missouri was required, as a result of the nonattainment designation, to submit a Part D SIP revision, the third SIP

⁷⁵ *Id.* at 13551.

⁷⁶ Approval and Promulgation of Implementation Plans; State of Missouri, 56 Fed. Reg. 41500 (August 21, 1991) (US EPA, 1991b).

⁷⁷ *Id.*

⁷⁸ Approval and Promulgation of Implementation Plans; State of Missouri, 57 Fed. Reg. 8076 (March 6, 1992) (US EPA, 1992c).

⁷⁹ Designation of Areas for Air Quality Planning Purposes, 56 Fed. Reg. 56694 (November 6, 1991) (US EPA, 1991c).

for Doe Run, no later than July 6, 1993 to meet the further requirements of Part D of the CAA. In addition to the requirements that would apply to SIPs that were not subject to Part D requirements, Part D SIPs were required to include, among other things, reasonably available control measures (RACM), which includes RACT, as well as contingency measures.⁸⁰ In US EPA's view, RACM for lead was to include control measures addressing both historical emissions as well as current direct emissions, such as controls on fugitive emissions resulting from re-entrainment of historically deposited lead.⁸¹ Contingency measures were to be implemented in areas failing to maintain reasonable further progress toward attainment or failing to attain NAAQS by the applicable attainment date.⁸²

Missouri submitted an initial SIP revision to satisfy the Part D requirements on July 2, 1993 in response to US EPA's nonattainment designation. Of note, some of the additional control measures incorporated into this submittal were to address increased emissions caused by the emissions controls required by the 1990 SIP. These emissions were themselves contributing to violation of the NAAQS, again demonstrating the difficulty of identifying effective emissions controls despite the rigorous and comprehensive efforts that went into development of the 1990 SIP.⁸³ The Consent Order incorporated into MDNR's 1993 SIP revision submission committed Doe Run to complete emissions control projects to build air-filtering systems, enclose buildings, and improve material handling. It also required Doe Run to implement additional controls as contingency measures if the NAAQS for lead was not met. US EPA concluded in September 1993 that the July 1993 submission lacked sufficient emission limits to assure attainment of the standard. Moreover, on October 7, 1993, US EPA notified Missouri that the SIP must contain contingency measures that would take effect without further action by the State or US EPA in the event of failure to attain the standards by the applicable deadline.⁸⁴

⁸⁰ State Implementation Plans; Addendum to the General Preamble for the Implementation of Title I of the Clean Air Act Amendments of 1990, 58 Fed. Reg. 67748, 67749 (December 22, 1993) (US EPA, 1993b).

⁸¹ *Id.* Examples of such controls cited by US EPA guidance included paving unpaved traffic surfaces and parking lots, covering haul trucks, dust control measures for material storage piles, storm water drainage to prevent erosion onto paved roads and other similar projects. *Id.*, Appendix I-Available Fugitive Lead-bearing Dust Control, at 67552-67553.

⁸² 42 U.S.C. § 7502(C)(9). Examples of contingency measures cited by US EPA guidance included paving more roads, increasing enclosure of buildings, increasing operation and maintenance procedures, reducing hours of operation and reducing the occurrence of malfunctions.

⁸³ Approval and Promulgation of Implementation Plans; State of Missouri, 60 Fed. Reg. 22274, 22275 (May 5, 1995) (US EPA, 1995d). See, also, The Doe Run Company, Technical Memorandum, Lead Emission Reductions, Herculaneum Lead Smelter, February 9, 1993 (projects installed in sinter plant pursuant to 1990 lead SIP have created unintended fugitive emissions causing exceedances of lead standard at Broad Street sampling station) (Doe Run, 1993). MDNR had notified DR on February 1, 1993 that the 1992 data indicated that the lead standard would not be attained and that a new SIP would be required to correct the nonattainment conditions. MDNR, Lead SIP Revision (1993) (MDNR, 1993), at p. 23.12.

⁸⁴ *Id.*

Missouri addressed these US EPA concerns in a further submission on June 30, 1994. This submittal included another Consent Order between Missouri and the facility, signed on March 31, 1994 (and modified on September 29, 1994 in response to certain inadvertent omissions observed by US EPA), which imposed additional specific contingency measures. Following is the final set of 5 contingency measures contained in the approved SIP: conduct street sweeping once per week on nearby affected roadways; consume inventory of lead concentrate on-site to reduce inventory size to a working minimum; consume inventory of sinter on-site to reduce inventory size to a working minimum; run water and sweeper trucks inside plant grounds on 2 shifts; and cover all remaining stockpiles with dust-impervious material.

US EPA deemed this assemblage of additional control measures to have satisfied the Part D requirements of the 1990 Amendments and gave final approval to the Part D SIP on May 5, 1995.⁸⁵ US EPA determined, based on dispersion modeling, that these control measures would result in attainment of NAAQS for lead in the vicinity of the Herculaneum plant by June 30, 1995. The date of attainment was driven by the Part D requirement that lead nonattainment areas must reach attainment as expeditiously as practicable but no later than 5 years from the date the area was designated nonattainment,⁸⁶ which would have been January 6, 1997.

Of note, the revised Part D lead SIP required the implementation of all RACM as expeditiously as practicable, including the adoption of all RACT requirements as newly required in the 1990 Amendments. The RACT study undertaken by Doe Run as part of the development of the 1990 SIP, much of which was already incorporated in the 1990 SIP, was further supplemented in the 1993 draft SIP which MDNR submitted for US EPA review to meet the Part D requirements. Accordingly, the 1990 SIP and the Part D SIP, as reviewed and approved by MDNR and US EPA, each purported to adopt all RACT and RACM to achieve the lead NAAQS at Doe Run. The 1993 draft SIP submission by MDNR acknowledged this, stating that "[Doe Run] has applied RACT emission control equipment and construction to the smelting and refining processes at the smelter on a continuing basis. Two significant upgrades of RACT equipment and RACM took place under State supervision in the initial lead 1980 SIP and the 1990 lead SIP revision."⁸⁷ Indeed, the emissions controls in place at the time of the 1993 draft SIP submission were deemed by the State to be RACT for all stack and process fugitive emission

⁸⁵ Approval and Promulgation of Implementation Plans; State of Missouri, 60 Fed. Reg. 22274 (May 5, 1995) (US EPA, 1995d).

⁸⁶ 42 U.S.C. § 7502(A)(2)(a).

⁸⁷ State of Missouri Implementation Plan for Lead, 1993 Revision Concerning Demonstrations of Attainment of the Lead NAAQS in the Vicinity of the Primary Lead Smelter – Refinery in Herculaneum, Missouri April 1993), p. 23.12 (MDNR, 1993).

sources.⁸⁸ A review of 1991 US EPA RACT/RACM Guidance for Lead Nonattainment Areas identified 5 additional control items to be incorporated into the Part D SIP, consisting of chemically stabilizing or paving 3 specific areas at the plant and developing written guidelines to control fugitive emissions from construction projects and from temporary sources of dust on paved roads.⁸⁹ Thus, Doe Run's compliance with RACT and RACM had proven to be both timely and complete.

11.6 2002 SIP

In the early to mid-1990s, Doe Run built air-filtering systems, enclosed buildings, and improved materials handling, as stipulated in the 1990 and Part D SIPs and the accompanying Consent Orders. Doe Run also continued expansion of a physical buffer started in 1988 by purchase of near plant downwind properties (this purchase program also served to advise the community of lead issues at this time).

Despite these ongoing activities and continued progress in controlling emissions, a new cycle of SIP revisions was initiated when the Herculaneum facility did not achieve attainment by June 30, 1995, the attainment date predicted and required by the Part D SIP. On March 27, 1996, MDNR notified Doe Run of the need to revise the SIP because of exceedances of the NAAQS at Doe Run's air quality monitoring network.⁹⁰ This was occasioned by persistent nonattainment at the newer Broad Street sampling location at the facility fence-line, and less frequent nonattainment at the High School and the Bluff sampling stations.^{91,92} On August 27, 1996, US EPA notified the State that monitoring data from the facility demonstrated that it had failed to reach attainment by that deadline, citing a total of 8 violations of the standard observed at multiple monitoring sites in the vicinity of Doe Run.⁹³ The letter also stated US EPA's expectation that all contingency measures specified in the Part D SIP would be implemented without further action on the part of US EPA or the State.

⁸⁸ *Id.*, at 23.14.

⁸⁹ *Id.*

⁹⁰ Letter from David A. Shorr, MDNR, to Jeffrey Zelms, DR, March 27, 1996 (Shorr, 1996). This letter also "recognize[s] the previous emission reduction efforts at this facility. Although the national standard has not yet been achieved, the area out of compliance has shrunk considerably."

⁹¹ The Bluff monitoring location has formerly been referred to as either the Ice's House or Rutz's House monitor.

⁹² See MDNR, 2000 Revision of the State Implementation Plan for Lead for the Doe Run Resources Corporation Primary Lead Smelter, Herculaneum, Missouri, Adoption December 7, 2000 (2002 SIP), at p. 9, Table 1, Lead Ambient Air Quality Data, Vicinity of Herculaneum Smelter (MDNR, 2000).

⁹³ Letter from Dennis Grams, US EPA, to Mel Carnahan, Governor of Missouri, August 27, 1996 (Grams, 1996).

MDNR took the further action of notifying Doe Run on September 6, 1996 that, although MDNR inspection of the facility indicated that it had complied with the implementation and construction of all of the control measures required in the Part D SIP, it was necessary for Doe Run to comply with the stack emission limits established under the MDNR's 1988 regulation limiting fugitive and point source emissions (10 CSR 10-6.120). MDNR requested Doe Run to undertake stack testing to demonstrate compliance with the stack emission limits. At this point, MDNR announced its intention to enforce source-specific emission limits in addition to enforcing the implementation of the emissions control measures specified in the SIP.

In the Federal Register on March 5, 1997, US EPA issued a proposed notice of failure to attain the NAAQS for lead and issued a call for revision of the SIP that would become effective after consideration of public comment on the proposed notice.⁹⁴ This notice would have also formally triggered the contingency measures specified in the Part D SIP; however, Missouri and Doe Run had already implemented these contingency measures prior to the proposed notice. On August 15, 1997, US EPA finalized its notice of failure to attain the NAAQS. This final notice triggered the CAA requirement that the State file, within one year of the notice, a revised SIP that would bring the area into attainment.⁹⁵ This notice led to the development and submission by MDNR of a revised SIP, which was submitted by MDNR to US EPA in 2001 and approved by US EPA in 2002 (the "2002 SIP").

Continuing through this time period, persistent non-attainment at Broad Street caused Doe Run and the agencies to struggle with both modeling and pollution control technology issues. There remained large uncertainties in how to identify and model low level dispersed emissions ("fugitive emissions") from throughout the plant, which by this time were realized to be the most significant remaining factors to control. Technology to control such emissions also was still evolving. Enclosure of fugitive emission sources, so as to allow ventilation and treatment, was now viewed as necessary and technologically feasible throughout the smelting industry. Previously, such approaches at smelters were viewed as dangerous to occupational health due to carbon monoxide and heat buildup (US EPA, 1979a), but technology had advanced to the point where this could be dealt with effectively.

⁹⁴ Approval and Promulgation of Implementation Plans; State of Missouri, 62 Fed. Reg. 10001 (March 5, 1997) (US EPA, 1997d).

⁹⁵ Approval and Promulgation of Implementation Plans; State of Missouri, 62 Fed. Reg. 43647 (August 15, 1997) (US EPA, 1997e).

Based on continued Broad Street non-attainment, Doe Run continued its efforts with more stringent emission control even while the SIP was being revised. Doe Run installed new high efficiency filter bags in the baghouses and aggressively pursued a number of other blast furnace/dross plant and sinter plant improvement projects to reduce emissions. These activities were performed at Doe Run's initiative during the several year period in which US EPA, MDNR and Doe Run were developing the 2002 SIP and before the Consent Judgment with the State was finalized for inclusion in the revised SIP. These activities are summarized in the 2002 SIP among a list of 21 emission control projects implemented by Doe Run since the Part D SIP.⁹⁶

Representing a major innovative step towards advancing the understanding of emissions sources at the smelter as well as a significant level of effort, it was decided to use a receptor modeling approach to compliment and enhance the current air dispersion modeling effort in the development of the 2002 SIP. For this large and complicated undertaking, Doe Run hired consultants including TRC and Cooper Environmental Services to perform an emission inventory and additional modeling. In an effort to determine significant sources, Doe Run's consultants measured about 45 emission sources, including the sinter plant, dross plant, blast furnace, and performed an elemental fingerprinting study ("chemical mass balance," CMB) to link impacts at various monitoring stations throughout Herculaneum with specific emission sources (TRC, 1999; MDNR, 2000). This effort was innovative and successful at identifying the significant remaining sources, many of which were building "leaks."

Due in part to the incorporation of the receptor modeling approach, the process of developing the 2002 SIP and its associated control strategy was complex and time consuming, as noted in the SIP submission:

These tasks included gathering emissions and meteorological data, developing chemical profiles of emissions and ambient samples, developing independent dispersion and receptor modeling approaches and a plan for reconciling the models, preparing initial engineering designs and cost estimates for emission reduction strategies, evaluating the effectiveness of individual controls, and developing a chosen set of controls and an associated demonstration of the attainment of the standard.⁹⁷

The complicated nature of the project and the development of the receptor modeling were also cited in the SIP submission as the cause for US EPA's issuance, on July 28, 1999, of a Finding of Failure To

⁹⁶ 2002 SIP, at p. 3 (MDNR, 2000).

⁹⁷ 2002 SIP, at p. 2 (MDNR, 2000).

Submit a Revised SIP for Lead at the Missouri, Doe-Run-Herculaneum Lead Nonattainment Area.⁹⁸ This notice constituted the triggering event for 2 significant provisions of the 1990 Amendments, an 18-month time clock for imposition of mandatory sanctions on the state,⁹⁹ and a two-year time clock after which US EPA would be authorized to issue a Federal Implementation Plan in place of the SIP, thereby taking control of the implementation plan process away from the state.

Missouri submitted a revised SIP for the Herculaneum area on January 10, 2001 (which became the 2002 SIP).¹⁰⁰ This SIP established August 14, 2002 as the attainment date for the area, based on dispersion modeling (ISCST3 model version 99155) and receptor modeling (CMB receptor model version 7) of the proposed revised control strategy. A high degree of confidence in the modeling results and the attainment date was reported in the SIP:

The models used in this study are US EPA approved models. The attainment demonstration dispersion modeling study used maximum throughputs for all processes to show that even under these conditions the area would attain the standard. This is a conservative approach because it is not likely that the maximum throughputs will ever be reached, particularly in all processes at once. Consequently, this conservatism is reflected in the attainment demonstration results presented as part of this SIP revision.¹⁰¹

The 2002 SIP consisted of a revised Missouri Department of Natural Resources lead regulation containing emission limits and a work practice manual containing operating procedures for specific plant processes at Doe Run. In addition, it included an executed Consent Judgment, dated January 3, 2001, between Missouri and the facility specifying the control measures required of the facility by the revised plan, as well as further contingency measures to be implemented in the event of a violation of the lead NAAQS. Additional control measures required under the Consent Judgment included enclosure projects, improved ventilation systems routed to stacks, improved material handling conveyors, and installation of air pollution control baghouses. US EPA expected that the 2002 SIP control strategy would result in approximately a 99 percent reduction in fugitive lead emissions from sources that were fingerprinted by the modeling as contributing significantly to the nonattainment conditions (US EPA, 2001).

⁹⁸ 64 Fed. Reg. 40767 (July 28, 1999) (US EPA, 1999e).

⁹⁹ 42 U.S.C. § 7509(b) authorizes US EPA to impose significant sanctions on a state if it fails to submit a required implementation plan for an area designated in nonattainment. The sanctions include reduction of federal highway funding for the designated area and reduction in the value of emissions trading credits for new or modified sources.

¹⁰⁰ 2002 SIP (MDNR, 2000).

¹⁰¹ 2002 SIP, at p. 2 (MDNR, 2000).

The 2002 SIP also imposed a set of contingency measures that were designed to escalate in stringency depending on the degree of severity of a violation. Among the contingency measures included in the SIP was an agreement by the facility to enclose portions of the facility and to adopt more stringent process controls. If these measures failed, the facility agreed to curtail production in 1 of 3 alternative ways.

US EPA proposed to approve this revised SIP on December 5, 2001¹⁰² and issued final approval of the 2002 SIP on April 16, 2002.¹⁰³ US EPA reported that the company expected to spend \$8.5 million on these new SIP projects to control and reduce fugitive emissions of lead that were affecting the NAAQS for lead at Doe Run.¹⁰⁴ US EPA noted that the requirements of Maximum Achievable Control Technology Standards (MACT) applied to the facility represented a further ratcheting up of the stringency of required control measures. Under the MACT standard, if an emissions control technology was found to be achievable at any other comparable facility, it would be required to be adopted at Doe Run. The effect of the MACT standard on the 2002 SIP was to impose 1 additional requirement beyond the RACT/RACM standards: that Doe Run prepare and use an SOP manual for all baghouses used to control process, process fugitive, or fugitive dust emission sources for lead.¹⁰⁵

The facility achieved attainment at all monitoring stations for 10 consecutive quarters after the August 2002 attainment date (from the third quarter of 2002 to the fourth quarter of 2004). The facility implemented all of the control measures required by the SIP and also implemented the first set of contingency measures as a voluntary compliance activity even though no violation of the NAAQS had occurred to trigger their implementation. Nevertheless, neither implementation of all the SIP emissions control measures nor all of the contingency measures was sufficient to prevent occasional nonattainment in the vicinity of the plant. In the first 3 quarters of 2005, exceedances at the Broad Street sampling station returned.

On December 19, 2005, in response to the observed exceedances of the NAAQS, US EPA issued a Finding of Substantial Inadequacy of Implementation Plan, Call for Missouri State Implementation

¹⁰² Approval and Promulgation of Implementation Plans; State of Missouri, 66 Fed. Reg. 63204 (December 5, 2001) (US EPA, 2001).

¹⁰³ Approval and Promulgation of Implementation Plans; State of Missouri, 67 Fed. Reg. 18497 (December 5, 2002) (US EPA, 2002).

¹⁰⁴ 66 Fed. Reg. 63204, 63207 (US EPA, 2001).

¹⁰⁵ *Id.*, at 63206-63207.

Revision."¹⁰⁶ US EPA proposed to require Missouri to develop a revised SIP that demonstrated attainment as expeditiously as practicable, within 2 years of issuance of the final notice of substantial inadequacy, following public comment on the proposed notice. US EPA concluded that, "because the violations recorded in 2005 have occurred despite implementation of all the control measures contained in the SIP, including all contingency measures that were to address the violations, US EPA believes the SIP is substantially inadequate to attain and maintain the NAAQS for lead."¹⁰⁷ Following the public comment period, US EPA issued final notice of inadequacy on April 14, 2006,¹⁰⁸ requiring Missouri to submit a revised SIP within 12 months or be subject to the sanctions described above. The revised SIP must include a revised emissions inventory, a modeled attainment demonstration, adopted control measures shown to be necessary for attainment, and contingency measures.

As revision of the SIP progressed in 2006, Doe Run continued to proactively implement a variety of engineering and administrative controls, showing some improvements in monitoring results including achievement of the NAAQS at all monitoring stations in fourth quarter 2005 and second quarter 2006 but also additional exceedances at the Broad Street monitor in the first and third quarters of 2006 (Doe Run Company, 2006a, 2006b, 2006c, 2006d). In addition, although the Broad Street monitor registered its lowest reading (1.2 $\mu\text{g}/\text{m}^3$) in 3 years, 2006 fourth quarter results for the Main Street Herculanum monitor (also known as the City Hall monitor) exceeded the NAAQS (Doe Run Company, 2006e). This pairing of a low value at the Broad Street monitor with an exceedance at the Main Street Herculanum monitor further illustrates the challenges that Doe Run has faced over the years to consistently achieve the standard at all monitoring locations despite continuous efforts to identify appropriate controls and measures to do so. With the exception of the Broad Street and Main Street Herculanum monitors, all other monitors, including the Dunklin High School monitor as well as several additional newly located monitors, have consistently shown attainment of the NAAQS since 2002.

On April 26, 2007, the Missouri Air Conservation Commission (MACC) unanimously approved the 2007 revised MDNR SIP for Herculanum (Doe Run Company, 2007a). The 2007 revised SIP (MDNR, 2007), which is currently under review for completeness and approvability at US EPA, contains approximately 60 engineering and administrative controls. These 60 additional engineering and administrative control projects, which include major projects such as a blast furnace relocation as well as

¹⁰⁶ 70 Fed. Reg. 75093 (December 19, 2005) (US EPA, 2005d).

¹⁰⁷ *Id.*, at 75094.

¹⁰⁸ Finding of Substantial Inadequacy of Implementation Plan; Call for Missouri State Implementation Revision, 71 Fed. Reg. 19432 (April 14, 2006) (US EPA, 2006b).

procedural changes such as for delivery of lead ore concentrate, reflect Doe Run's continuous re-assessment of potentially viable control strategies and the never-ending evolution in understanding of significant emission sources, some of which is gained through updated emission inventories and air dispersion modeling but also through practical research and trial-and-error. Prior to the MACC approval of the 2007 revised SIP, Doe Run proactively implemented many of these controls, including: modification of ventilation systems to improve dust-capturing efficiency, installation of automated baghouse malfunction alerts, upgraded control of air injection into the blast furnace, installation of improved baghouse bags, improved bag-cleaning technology to increase dust-capturing efficiency, and a wheel tunnel enclosure and ventilation system (Doe Run Company, 2007a). Coinciding with its proactive control efforts, Doe Run met the lead NAAQS at all ten of the Herculaneum-area monitors in first quarter 2007 (Doe Run Company, 2007b).

In second and third quarters 2007, Doe Run met the lead NAAQS at nine of the 10 monitors, with the Broad Street monitor showing slight exceedances of the lead NAAQS (Doe Run Company, 2007c, 2007d). During this period, Doe Run was steadily working to implement additional SIP initiatives, including the major project where the No. 1 blast furnace was relocated. Doe Run is committed to implementing all 60 of the engineering and administrative controls in the 2007 revised SIP by April 2008 (Doe Run Company, 2007d), and the fourth quarter 2007 monitoring data may already reflect some early returns from the rapid progress on implementing these initiatives. All ten of the Herculaneum monitors, ranging from 0.2 to 1.4 $\mu\text{g}/\text{m}^3$, met the US EPA lead NAAQS of 1.5 $\mu\text{g}/\text{m}^3$ in fourth quarter 2007 (Doe Run Company, 2007e). Doe Run continues to make progress in its goal of consistent attainment of the lead NAAQS in Herculaneum.

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Tables

Table 1-1
Pre-Clean Air Act Landmark Air Pollution Events

Date	Event
1881	First US municipal smoke abatement legislation enacted in Chicago, IL.
1906	A Utah district court enjoined four Utah smelters not to operate in response to litigation launched by farmers alleging injury to crops and livestock.
1907	Municipal smoke inspectors formed the International Association for the Prevention of Smoke, later known as the Air Pollution Control Association and currently the Air & Waste Management Association.
1914	Selby Smelter Commission released its comprehensive report investigating conditions in and around the Selby Smelting and Lead Company smelter in Contra Costa County, California.
1919	US Bureau of Mines launched one of the most comprehensive air pollution studies to date in Salt Lake City, Utah, to identify the sources of the city's smoke problems.
1921	General Motors researchers identified tetraethyl lead as an effective anti-knock agent in gasoline.
1926	Surgeon General's committee affirmed the safety of tetraethyl lead for general use in gasoline, but recommended further federal study (studies never funded).
1927	US Public Health Service (PHS) quantified the loss of daylight due to smoke in New York City, reporting an average loss of 21.5 percent for yearlong measurements in Manhattan.
1930	Strong atmospheric inversion occurred between December 1 and 5 in Belgium's Meuse Valley, trapping industrial air emissions at ground level and contributing to more than 60 deaths and thousands of illnesses.
1943	First smog episodes recognized in Los Angeles, California.
1947	California adopted the Air Pollution Control Act, authorizing the formation of county air pollution control districts.
1948	Acute air pollution episode occurred in the small industrial town of Donora, PA, with an intense temperature inversion trapping particulates and other industrial emissions at ground level over a 4-day period, causing an estimated 20 deaths and between 5,000 and 7,000 illnesses among a population of approximately 14,000.
1950	First US Technical Conference on Air Pollution held in Washington, D.C., with over 750 people attending.
1950	Dr. Arie Haagen-Smit of the California Institute of Technology proposed a photochemical mechanism for smog formation, identifying nitrogen oxides and hydrocarbons from automobiles and the petroleum industry to be key causative agents.
1951	Oregon passed first state law providing statewide authority to a state air pollution control agency.
1952	London "killer fog" event occurred, with official reports blaming the thick sulfur and particulate-laden fog that occurred between December 5 and 9 for over 4,000 deaths over a 2-week period.
1953	New York City experienced its first major acute air pollution episode, with an estimated 160 to 220 deaths.

- 1953 The Public Health Service established the National Air Sampling Network (NASN), later renamed the National Air Surveillance Network.
 - 1955 US Air Pollution Control Act of 1955 passed; major provisions provide for federal technical assistance to state air pollution control and funding for Public Health Service to conduct air pollution studies.
 - 1955 National Air Pollution Control Administration (NAPCA) founded within the US Department of Health, Education, and Welfare (DHEW).
 - 1962 Rachel Carson's *Silent Spring* is published, bringing to the public's attention the unforeseen harm that human actions can have on the environment.
 - 1963 Air pollution inversion event resulted in over 400 deaths in New York City.
 - 1963 First Federal Clean Air Act enacted, giving the federal government enforcement authority to combat both interstate and intrastate air pollution problems and providing grants for initiation and development of local or state air pollution control programs.
 - 1965 Motor Vehicle Air Pollution Control Act enacted, authorizing the development of federal emissions standards for new motor vehicles.
 - 1965 Dr. Clair Patterson of the California Institute of Technology published the seminal paper "Contaminated and Natural Lead Environments of Man," challenging the current paradigm that human exposures to lead were in large part natural in origin and that the body had adapted over time to handle chronic lead exposure.
 - 1967 Federal Air Quality Act of 1967 enacted, with key provisions authorizing the federal government to define the atmospheric areas of the nation, designate air quality control regions (AQCRs), publish Air Quality Criteria (AQC)s and Control Technology Documents for use by the states in setting air quality standards, require the development of state implementation plans (SIPs), and expand ongoing air pollution control research.
 - 1969 National Environmental Policy Act (NEPA) passed in Congress.
 - 1970 US Environmental Protection Agency (US EPA) established.
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Table 4-1
Key Dates in the Development and Application of Direct Sampling Methods
Used to Collect Suspended Particulate Matter

Year	Sampling Method
1900s	• Dustfall collectors gained usage in early air pollution investigations
1920s	• Owens Jet Dust Counter developed • Greenburg-Smith Impinger developed
1930s	• Midget Impinger developed
1940s	• Precursor to modern Hi-Vol Sampler developed • First cascade impactor developed • American Iron and Steel Institute (AISI) Spot Tape Sampler developed
1950s	• Hi-Vol sampler selected for usage in Public Health Service's NASN
1960s	• Modified Andersen Cascade Impactor developed and applied to ambient suspended particulate matter
1970s	• Hi-Vol promulgated as federal reference method for TSP and Pb • Modified Andersen Cascade Impactor selected by US EPA for usage in NASN cascade impactor network • Dichotomous sampler gained usage as size-selective sampler
1980s	• PM₁₀ replaced TSP as NAAQS, and PM₁₀ federal reference methods first developed
1990s	• PM_{2.5} NAAQS promulgated and PM_{2.5} federal reference methods first developed

Table 4-2

Timeline of Analytical Methods Used to Determine Particulate Lead

Table	Analytical Method
1920s	• Chromate method (<i>i.e.</i>, modified Fairhall method) gains usage for lead determination, in particular for PHS investigations of tetraethyl lead
1940s	• Colorimetric dithizone gains acceptance as standard method for lead determination
1950s	• PHS first employs optical emission spectroscopy (OES) for trace metal analysis of NASN samples • Birth of modern AAS
1960s	• First applications of AAS for particulate lead determination • Commercial AAS instruments become available • Early applications of graphite furnace atomic absorption (GFAA) and ICP-AES for elemental analysis
1970s	• AAS promulgated as federal reference method for lead determination in suspended particulate matter • GFAA and ICP-AES become commercially available
1980s-present	• ICP-MS becomes commercially available • Methods such as GFAA, X-Ray Fluorescence Spectrometry (XRF), ICP-OES, ICP-AES, ICP/MS attain federal equivalent method status for particulate lead determination

Table 6-1
Key Events in the Development and Application of
Major Particulate Air Pollution Control Technologies at Smelters

Year	Event
<u>Baghouses (Fabric Filters)</u>	
1900s-1910	First used at lead, copper, and zinc smelters in California, Colorado, Missouri, and Utah for roaster and blast furnace gases
1930s	Common industrial use (cotton or wool bags)
1955	Efficiency >99%; use limited to gas temperatures <250° F
1950s	Development of synthetic fiber filter bags
1965	Efficiency = 99.7% overall (99.5% for 0-5 µm particles)
late 1960s	First use of synthetic fiber (fiberglass) filter bags at a smelter
1969	Baghouses and ESPs - principal particulate control technologies used at primary lead smelters
1980	Efficiency between 95-99.9% at primary lead smelters
c. 1990	Development of ceramic fabric bags that withstand temperatures up to 900° F
1990s	Continued development of specialty fabric bags with greater chemical resistance and thermal resistance up to 1,000° F
1999	Baghouses (or equivalent) required as part of EPA's final NESHAP rule for primary lead smelting
<u>Cyclones (Centrifugal Separators)</u>	
c. 1890s	First used for industrial gas particulate cleaning
1955	Efficiency of 50-90% for 5-10 µm particles; cyclones used in series called multi-cyclones
1962	Usage noted at primary lead smelters
1966	Used as pre-cleaners ahead of ESPs
1969	Efficiency >95% for >40 µm particles; very low efficiency for <5 µm particles
1977, 1980	Cyclones were not noted by EPA to be used at any primary lead smelter
<u>Electrostatic Precipitators (ESPs)</u>	
1906	Dr. Frederick Cottrell first successfully electrostatically-precipitated sulfuric acid fumes
1907	First commercial ESP demonstration; first ESP installed at a gold smelter for collection of sulfuric acid fumes
1910	First large ESP used for particulate collection at the Anaconda, MT copper smelter
1930s	Common industrial use; efficiencies near 95%
1939	By this time, ESPs had revolutionized recovery of acid mists, lead and arsenic fumes, and precious metals at smelters
early 1950s	Efficiency up to 98-99%
1969	Baghouses and ESPs - principal particulate control technologies used at primary lead smelters
1969	Efficiencies of 90-98+% (dry applications) and up to 99+% (wet applications)
mid-1970s	Efficiency >99.5%
<u>Wet Collectors (Wet Scrubbers)</u>	
early 1930s	Common industrial use
1940s	Development of venturi scrubber (most efficient of wet collectors) for particulate removal
1962	Use of various wet collectors (including scrubbing and spray towers and venturi scrubbers) noted at primary lead smelters
1965	Efficiency = 99.5% overall (99.0% for 0-5 µm particles) for venturi scrubbers
1960s	Wide variety of wet collectors in industrial use, including: spray chambers, wetted filters, mist eliminators, and scrubbers (centrifugal, impingement plate, packed bed, venturi, etc.)

Table 10-1
Timeline of Ambient Lead and Primary Lead Smelter Regulatory Activity

Year	Regulatory Activity
1970	Clean Air Act
1973	Leaded gasoline phasedown promulgated
1975	NRDC suit to make lead a criteria air pollutant
1976	Standards of performance promulgated for new and modified primary lead smelters
1976	Court order requiring designation of lead as criteria air pollutant
1977	First US EPA Air Quality Criteria document for lead issued
1978	Lead Primary and Secondary NAAQS promulgated
1986	US EPA issued revised Air Quality Criteria document for lead
1990	Clean Air Act Amendments
1990	US EPA issued supplement to 1986 Air Quality Criteria document for lead
1991	US EPA retained lead NAAQS of 1.5 µg/m ³ following completion of review process
1996	Leaded gasoline phasedown completed
1999	National Emission Standards for Hazardous Air Pollutants (NESHAP) adopted for primary lead smelters
2004	US EPA initiated review process for lead NAAQS
2006	US EPA issued final lead Air Quality Criteria document
2007	US EPA issued final lead Risk Assessment Report and final lead Staff Paper; US EPA issued Advance Notice of Proposed Rulemaking (ANPR) for lead NAAQS

Figures

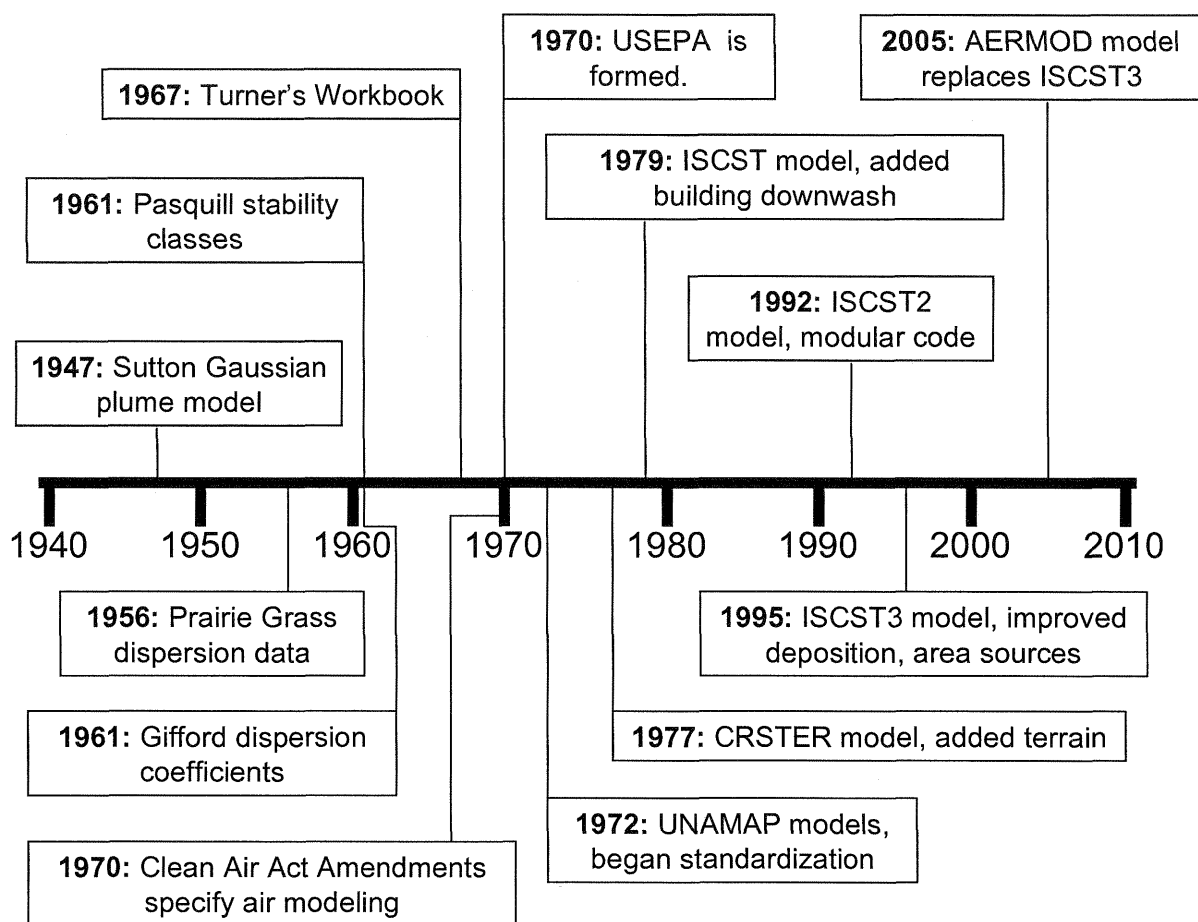


Figure 5-1
Timeline of Important Events in Air Dispersion Modeling

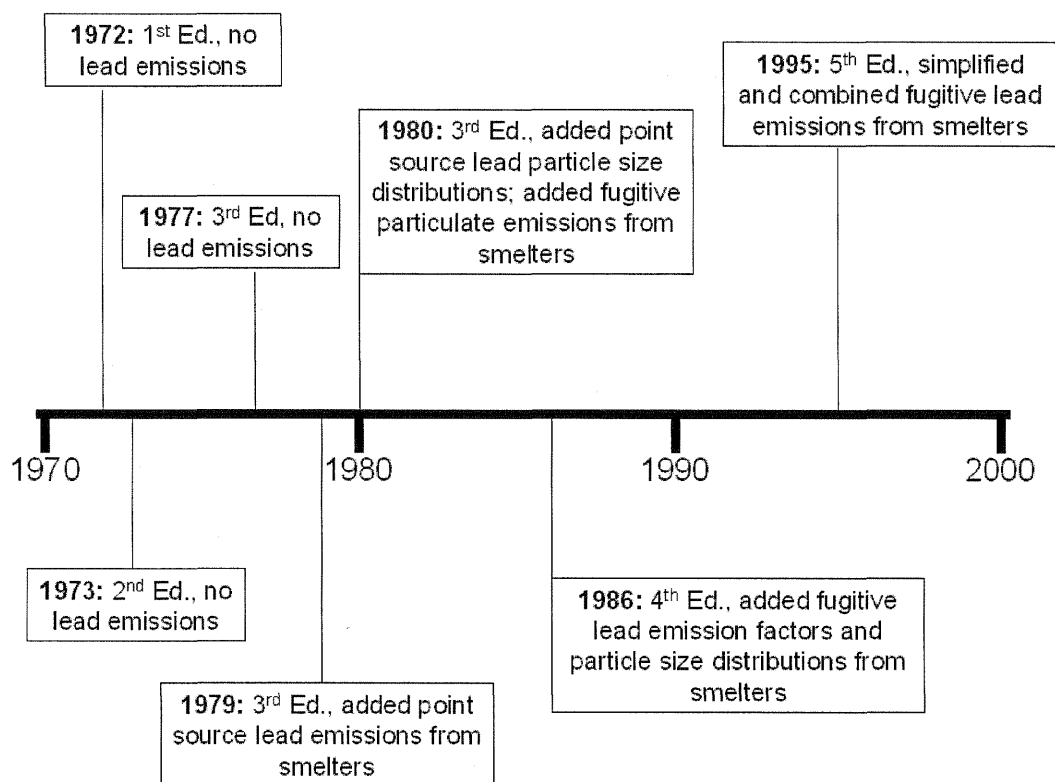


Figure 5-2
Timeline of AP-42 Changes for Lead Emissions from Primary Lead Smelters

Appendix A

Resume of Dr. Neil S. Shiffrin



20 University Road
Cambridge, MA 02138
617-395-5000

Neil S. Shifrin, Ph.D.
President and Founder
nshifrin@gradientcorp.com

Areas of Expertise

Environmental engineering, contaminant fate & transport, PRP cost allocations, cost recovery, waste management standard of care, hazardous waste site remedy negotiation/renegotiation, cleanup level negotiation, M&A environmental issues, monitoring/investigation program design, water quality.

Education

Ph.D., Environmental/Civil Engineering, Massachusetts Institute of Technology, 1980.

B.S., Chemical Engineering, University of Pennsylvania, 1971.

Massachusetts Licensed Site Professional (No. 1009).

Professional Experience

1985 - Present GRADIENT CORPORATION, Cambridge, MA
President and cofounder of consulting firm specializing in the fate of and risks of chemicals in the environment from contaminated sites as well as from manufactured or recycled products. Individual technical practice area is contaminant fate and transport. Business role includes full range of P&L and executive management responsibilities.

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Technical Director of the Consulting Division and Corporate Quality Assurance Officer. Environmental data analysis and hazardous waste landfill remediation.

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- Board of Trustees and co-chair of Strategy Committee, New England Aquarium
- Chairman, Boston Chamber of Commerce "Business of the Year" Selection Committee (Retired).
- Board of Directors, New England Environmental Business Council (Retired).
- "Chemistry for Non-Chemists," a 2-day course sponsored by Government Institutes, Inc.
- Cochairman, "Managing the Superfund Process," a 2-day course presented twice yearly and sponsored by Executive Enterprises, Inc.
- Invited member, Environmental Task Force, Massachusetts Attorney General Scott Harshbarger.

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Metropolitan District Commission: Instream treatment of the Charles River, Project Engineer. Pilot plant design and operation of 2-year field study.

Projects – Cost Allocation, Liability Evaluation, NCP Consistency

Berry's Creek Superfund Site: Technical factors-based allocation of \$18 million study over 158 parties (NJ).

Pipeline Oil Spill: Insurance cost recovery (Guam).

Connecticut Power & Light: Cost allocation between current utility successor and a former utility holding company for 13 manufactured gas plants. Examination of the level of control of operator status at the plants and contaminant causation during various time periods.

General Electric: Insurance cost recovery claim for PCBs in sediments of several rivers. Electrical manufacturing standard of care.

Teleflex Cost Recovery: Opinions on whether environmental conditions were appropriately disclosed at time of sale, site response appropriateness, and site response costs (for buyer).

City of Bangor: Source of MGP tar in river.

South Carolina Utility: Evaluation of a holding company's role as owner/operator for CERCLA liability.

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ITT Financial Services (Accurate Die Casting): NCP consistency of remedial activities at a former manufacturing facility in New York.

Organic Chemicals, Inc./Total Petroleum: Developed environmental cleanup cost allocation at a site formerly used successively for various purposes including petroleum refining, custom chemical manufacturing, and solvent recycling.

Velsicol Chemical Corporation: Cost allocation at an Ohio Superfund Site between a chemical Toll Manufacturer and its customers.

Ocean View Capital, Inc. (Triangle Wire Co.): Cost allocation of Superfund remedies at a municipal landfill built on coal mine waste.

Stauffer/Rhone-Poulenc: Expert testimony on remedy appropriateness at 5 sites (chemical plants and landfills).

Conrail: Source of contaminant plume, formation/transformation of chlorinated solvents in ground water.

Goddard Corporation: Source of VOC contaminant plume in an industrial park.

Pirelli-Armstrong Rubber: Contribution to liability of naphtha, toluene and tire leachate at the Beacon Heights Landfill (CT).

Alcoa/Alcotec: Evaluation and expert testimony on multi-source VOC plume mixing in Traverse City, MI. Determination of the precise source of downgradient contaminant concentrations.

Cabot Corporation: Cost allocation among wood treating, pine oil products, and auto dealership facilities, Gainesville, FL.

Cabot Corporation: Site investigations, data interpretation, remedy design and cost allocation negotiations between PRPs primarily for PCBs in soils from heat exchangers at a TiCl_4 manufacturing plant.

Salt River Project (Phoenix, AZ): Data review and modeling to demonstrate that a local water utility did not contribute to VOC contamination in the Scottsdale aquifer.

Pepper, Hamilton & Scheetz (Washington, DC): Data interpretation, monitoring program development and PRP cost apportionment for a site contaminated with dioxin and wood treating chemicals in St. Louis.

Time Oil Co. (Tacoma, WA): Evaluation of the contribution of a waste oil recycling operation to a regional VOC contamination problem.

Saltwater Trust (Plymouth, MA): Investigation of chemical wastes and identification/allocation of responsible parties at the Cannon Engineering hazardous waste storage tank site.

NJ Department of Law: Timing of releases from the A-Z Automotive facility.

NJ DEP: DDT contamination in the Delaware River from a chemical manufacturing facility.

Projects – Manufactured Gas Plants – Historical Practices & Remediation

Everett Tar Refinery: Response cost insurance claim for tar refiner and coke works in Boston.

Keyspan/Brooklyn Union Gas: Response cost insurance claim for 4 MGPs in New York.

MGP and Tar Refiner, Minnesota: Source differentiation of tar in bay sediments.

Keyspan/Boston Gas: Response cost insurance claim for 4 MGPs in Boston.

Keyspan Energy Services: Response cost insurance claim related to former MGPs in Laconia, Concord, Nashua, Dover, Manchester, and Keene, NH.

Manufactured Gas Plant (MGP), Manchester, NH: Cost allocation -- evaluation of the role of a holding company in historical plant operations.

New Jersey Natural Gas Company: Role of MGP demolition practices in causing contamination.

Long Island Lighting Company: Response Cost insurance claims at 8 former MGPs.

Consolidated Edison: Historical waste practices at a former MGP in Tarrytown, New York.

New Jersey Natural Gas Company: Historical waste practices at former MGPs.

General Public Utilities Corporation (First Energy): Cost allocation at the Dover Gas MGP Superfund Site (Delaware). Development of a monitored natural attenuation protocol proposal to US EPA.

West Coast Utility: Confidential MGP litigation support.

Stone & Webster Inc.: Need for and appropriateness of remediation at the former Columbus (GA) MGP site.

South Jersey Gas Co.: Expert report on historical practices (1890 – 1975) at MGPs and waste/byproduct handling at MGPs *versus* US industry.

Midwest Gas Utility: Strategic planning, site investigation, and remediation of 15 MGP sites. Projects and activities include: site prioritization and master planning; development of an MGP Risk Assessment Manual; development and oversight of a bioremediation research program; preparation of a report on the chemistry, fate and risks of Blue Soils; ground water modeling oversight; design and oversight of soils and ground water field investigations; and agency negotiations for site remedies and cleanup levels.

Northeast Utilities: Fate-related properties of contaminants from MGP sites.

Projects – Historical Waste Practices

Rhodia PCBs and Pesticides: Response cost insurance claim -- examination of the causation, timing, and historical standards of care related to PCB contamination from transformer use at a New Jersey factory.

Doe Run/Smelter: Evolution of air quality management for lead – measurement, modeling, control technologies, and standards.

Lead Ore Railroad Transport: Evaluation of the contemporaneous standard-of-care for lead ore railroad transport from the 1970s to 1990s.

Montana Fish Hatchery: Examination of historical uses and the environmental understanding of PCB fate and persistence from use of PCB in paint.

Ohio Landfill: Standard care for subsurface land disposal of toluene diisocyanate (TDI) factory wastes – TDI residue and contaminated vacuum pump oils – from 1964 to 1976 in the context of contemporary regulations and waste handling practices.

Roadside Flare Manufacturer: Standard of care for manufacturing and waste management at a flare company using potassium perchlorate from 1957 to 1987 – wastewater lagooning, incineration, landfilling, and ground water contamination.

PCB Site: Evaluation and expert testimony on the historical operations involving PCB use in a still-operating transformer manufacturing facility in the Southeastern U.S. Examination of the scientific and regulatory history of PCBs, PCB measurement in environmental samples, and evaluation of the evolution of stormwater and wastewater management regulations during the relevant period of PCB use. Evaluation of claims relating to whether dioxin contamination was related to the PCB contamination.

Pfizer, Inc.: Response cost insurance claim -- historical landfill practices associated with Connecticut and Indiana pharmaceutical manufacturing plants compared to industry in general.

Schlumberger Industries: Response cost insurance claim -- historical handling and waste practices for PCBs in electrical capacitor manufacturing.

PCBs in Paper Recycling: Response cost insurance claim -- expert report on the development of wastewater treatment in the paper industry in Michigan from 1940 to 1980 and PCBs at paper recycling (deinking) pulp operations.

Projects – Portfolio Environmental Assessment

AstraZeneca: Estimation of environmental costs at 20 former chemical plants, as part of an insurance claim settlement.

Cabot Corporation: Arbitration hearings on the cost-effectiveness of PCB cleanup at natural gas compressor stations in Texas in defense of Seller who claimed Buyer over-remediated.

Fortune 500 Company: Evaluation of 45 gas field sites for environmental cleanup liabilities raised during company M & A negotiations.

Fortune 100 Manufacturer: Expert panel member - prioritization of hazardous waste sites.

Projects – Regulatory Comment

Chemical Manufacturers Association - PCB Consensus Panel: Critique of US EPA's proposed "PCB Megarule" (TSCA cleanups) with particular emphasis on sampling program design.

American Petroleum Institute: Superfund reform - study of cost savings if US EPA used more realistic risk assessments.

Chrysler Corporation: Critique of Michigan Act 307 hazardous waste rules, including cleanup standards and site scoring models.

US EPA, Office of Research and Development: 5-year Agency research strategy for municipal wastewater control technology, Project Manager.

US Congress National Commission on Water Quality: Assessment of the impact of the 1972 Federal Water Pollution Control Act on the Charles River and Boston Harbor, Project Engineer/Manager. Technical review and modeling study.

Projects – Toxic Torts – Fate/Transport & Historical Exposures

Cabot Corporation: Toxic tort testimony on the likelihood of toluene exposures decades after closure of pine tar settling lagoons – fate of historical toluene source.

Keyspan/Bayshore MGP: Exposures to nearby residents from former MGP.

Monsanto Anniston PCB: Evaluation of historical industrial practices and the evolution of environmental regulations as they related to client's manufacturing and waste disposal practices; historical knowledge of environmental fate, transport and persistence of hydrophobic chemicals.

Glass Manufacturer: Arsenic in glass manufacturing and wastes – standard of care during wastewater generation and during Superfund remediation.

Publications – Journals, Proceedings & Books

Beck, BD; Seeley, MR; Ghosh, RS; Drivas, PJ; Shifrin, NS. 2006. "Human health risk assessment of cyanide compounds in water and soil." In *Cyanide in Water and Soil: Chemistry, Risk, and Management*. (Eds: Dzombac, D; Ghosh, R; Wong-Chong, GM), Taylor & Francis, Boca Raton, FL, p309-330.

Shifrin, NS. 2005. "Water pollution management in the twentieth century." *ASCE Journal of Environmental Engineering* 131(5):676-691.

Merrill, DE; Fendley, JE; Cohen, JT; Shifrin, NS. 1999. "Cleanup level averaging – A simple concept with huge payback for site remediation." In *Proceedings of the Environmental Solutions Exchange, The IT Group, Inc. Conference, Orlando, FL*, February 4-6.

Shifrin, NS; Beck, BD. 1999. "Debating RBCA (Letter to the Editor)." *Civ. Eng.* 69(2):10-11.

Chapnick, SC; Sharma, M; Roskos, D; Shifrin, NS. 1998. "An alternative to the inappropriate use of Toxicity Characteristic Leaching Procedure (TCLP)." *American Environmental Laboratory* 10(7):18-19.

Shifrin, NS; Toole, AP. 1998. "Historical Perspective on PCBs." *Environmental Engineering Science* 15(3):247-257.

Shifrin, NS. 1997. "The Role of Risk Assessment in Sediment Standards (Chapter 3D)." In *Proceedings of the Washington Bar Association, Science & Law Conference, Seattle WA*, February 28.

Sharma, M; Shifrin, NS; Gauthier, TD. 1996. "Application of a Solute Transport Model at a Former MGP Site to Assist in Remedy Selection." In *Proceedings of the New England Environmental Exposition, Longwood Environmental Management, Belmont, MA*, May.

Shifrin, NS; Beck, BD; Gauthier, TD; Chapnick, SD; Goodman, G. 1996. "Chemistry, Toxicology, and Human Health Risk of Cyanide Compounds in Soil at Former Manufactured Gas Plant Sites." *Regul. Toxicol. Pharmacol.* 23:106-116.

Bowers, TS; Shifrin, NS; Murphy, BL. 1996. "A Statistical Approach to Meeting Soil Cleanup Goals." *Environ. Sci. Technol.* 30:1437-1444.

Shifrin, NS. 1992. "Interpreting Environmental Chemistry Data: Data Quality First." Invited paper at the Environmental Data/Standard Methods session, Water Environmental Federation 65th annual conference, New Orleans, LA, September 20-24.

Shifrin, NS. 1992. "Practical Aspects of Implementing Soil Flushing." Invited paper at the RCRA Corrective Action session, Water Environmental Federation 65th annual conference, New Orleans, LA, September 20-24.

Wait, AD; Shifrin, NS; Chapnick, SD. 1992. "Ensuring Environmental Data Quality." Invited paper at the 85th Air & Waste Management Association Conference, Kansas City, June 21-26.

Shifrin, NS; Kaul, L; Benavides, L. 1990. "Bioaccumulation of TCDD in Lake Ontario fish: laboratory and field studies in support of hazardous waste landfill risk assessments." *New Risks: Issues and Management* (Eds: L.A. Cox, Jr. and P.F. Ricci), Plenum Publishing, New York.

Murphy, BL; Doherty, JD; Shifrin, NS. 1989. "Determining the Effectiveness of Soil Washing." Presented at the 6th HMCRI National Conference on Hazardous Waste and Hazardous Materials, New Orleans, LA, April 12-14.

Swallow, KC; Shifrin, NS; Doherty, P. 1988. "Hazardous organic compound analysis: lost data and misinformation for decisionmakers." Feature article, *Environ. Sci. Technol.* 22(2):136-142.

Shifrin, NS. 1986. "Bioaccumulation of TCDD in Lake Ontario Fish." Presented at the SETAC Annual Meeting, Alexandria, VA, Nov. 2-5.

Walsh, WW; Faust, C; Putzrath, R; Hawley, J; Shifrin, NS; Gianti, SJ; Slack, J; Goldweber, A. 1986. "Case Study: Use of Risk Assessment in Determining Certain Ground Water Remedies for the Hyde Park Landfill -- Risk Management Decisionmaking." Presented at the American Geophysical Union Winter Meeting, San Francisco, Dec. 8-12.

Shifrin, NS. 1984. "Oils from microalgae." *Biotechnology for the Oil and Fat Industry* (Eds: C. Rutledge *et al.*), Am. Oil Chem. Soc. Press.

Shifrin, NS; and Chisholm, SW. 1981. "Phytoplankton lipids: interspecific differences and environmental influences." *Journal of Phycol.* 17:374-384.

Shifrin, NS; Chisholm, SW. 1980. "Phytoplankton lipids." *Algae Biomass: Production and Use* (Eds: G. Shelef and C.J. Soeder), Elsevier North Holland Biomedical Press, Amsterdam.

Shifrin, NS. 1980. "The measurement of dissolved organic carbon released by phytoplankton." *Estuaries* 3(3):230-233.



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Organic Chemicals, Inc./Total Petroleum: Developed environmental cleanup cost allocation at a site formerly used successively for various purposes including petroleum refining, custom chemical manufacturing, and solvent recycling.

Velsicol Chemical Corporation: Cost allocation at an Ohio Superfund Site between a chemical Toll Manufacturer and its customers.

Ocean View Capital, Inc. (Triangle Wire Co.): Cost allocation of Superfund remedies at a municipal landfill built on coal mine waste.

Stauffer/Rhone-Poulenc: Expert testimony on remedy appropriateness at 5 sites (chemical plants and landfills).

Conrail: Source of contaminant plume, formation/transformation of chlorinated solvents in ground water.

Goddard Corporation: Source of VOC contaminant plume in an individual park.

Pirelli-Armstrong Rubber: Contribution to liability of naphtha, toluene and tire leachate at the Beacon Heights Landfill (CT).

Alcoa/Alcotec: Evaluation and expert testimony on multi-source VOC plume mixing in Traverse City, MI. Determination of the precise source of downgradient contaminant concentrations.

Cabot Corporation: Cost allocation among wood treating, pine oil products, and auto dealership facilities, Gainesville, FL.

Cabot Corporation: Site investigations, data interpretation, remedy design and cost allocation negotiations between PRPs primarily for PCBs in soils from heat exchangers at a TiCl₄ manufacturing plant.

Salt River Project (Phoenix, AZ): Data review and modeling to demonstrate that a local water utility did not contribute to VOC contamination in the Scottsdale aquifer.

Pepper, Hamilton & Scheetz (Washington, DC): Data interpretation, monitoring program development and PRP cost apportionment for a site contaminated with dioxin and wood treating chemicals in St. Louis.

Time Oil Co. (Tacoma, WA): Evaluation of the contribution of a waste oil recycling operation to a regional VOC contamination problem.

Saltwater Trust (Plymouth, MA): Investigation of chemical wastes and identification/allocation of responsible parties at the Cannon Engineering hazardous waste storage tank site.

NJ Department of Law: Timing of releases from the A-Z Automotive facility.

NJ DEP: DDT contamination in the Delaware River from a chemical manufacturing facility.

Projects – Manufactured Gas Plants – Historical Practices & Remediation

Keyspan/Bayshore MGP: Exposures to nearby residents from former MGP.

Keyspan/Liberty Hill MGP: MGP wastes and possible residential exposures from an uncontrolled landfill.

Manufactured Gas Plants (MGPs): Insurance claim for 4 MGPs in New York.

MGP and Tar Refiner, Minnesota: Source differentiation of tar in bay sediments.

Keyspan/Boston Gas: Insurance claim for 4 MGPs in Boston.

Keyspan Energy Services: Insurance litigation related to former MGPs in Nashua, Dover, Manchester, and Keene, NH.

Manufactured Gas Plant (MGP), Manchester, NH: Evaluation of the role of a holding company in historical plant operations.

New Jersey Natural Gas Company: Role of MGP demolition practices in causing contamination.

Long Island Lighting Company: Insurance claims for environmental response costs at 8 former MGPs.

Energy North: Historical waste practices and contamination continuity at the Concord and Laconia, NH former MGPs.

Consolidated Edison: Historical waste practices at a former MGP in Tarrytown, New York.

New Jersey Natural Gas Company: Historical waste practices at former MGPs.

General Public Utilities Corporation: Cost allocation at the Dover Gas MGP Superfund Site (Delaware). Development of a monitored natural attenuation protocol proposal to US EPA.

West Coast Utility: Confidential MGP litigation support.

Stone & Webster Inc.: Need for and appropriateness of remediation at the former Columbus (GA) MGP site.

South Jersey Gas Co.: Expert report on historical practices (1890 – 1975) at MGPs and waste/byproduct handling at MGPs *versus* US industry.

Midwest Gas Utility: Strategic planning, site investigation, and remediation of 15 MGP sites. Projects and activities include: site prioritization and master planning; development of an MGP Risk Assessment Manual; development and oversight of a bioremediation research program; preparation of a report on the chemistry, fate and risks of Blue Soils; ground water modeling oversight; design and oversight of soils and ground water field investigations; and agency negotiations for site remedies and cleanup levels.

Northeast Utilities: Fate-related properties of contaminants from MGP sites.

Projects – *Historical Waste Practices*

Roadside Flare Manufacturer: Standard of care for manufacturing and waste management at a flare company using potassium perchlorate from 1957 to 1987 - wastewater lagooning, incineration, landfilling, and ground water contamination.

Glass Manufacturer: Arsenic in glass manufacturing and wastes – standard of care during wastewater generation and during Superfund remediation.

PCB Site: Evaluation of level of care regarding PCBs at a transformer manufacturing facility.

Pfizer, Inc.: Historical landfill practices associated with Connecticut and Indiana pharmaceutical manufacturing plants compared to industry in general (insurance claim).

Schlumberger Industries: Historical handling and waste practices for PCBs in electrical capacitor manufacturing in an insurance cost recovery action.

Howrey & Simon (Washington, DC): Expert report on the development of wastewater treatment in the paper industry in Michigan from 1940 to 1980 and PCBs in paper recycling (deinking) pulp operations.

Projects – *Portfolio Environmental Assessment*

AstraZeneca: Estimation of environmental costs at 20 former chemical plants, as part of an insurance claim settlement.

Cabot Corporation: Deposition and expert testimony at arbitration hearings on the cost-effectiveness of PCB clean-up at natural gas compressor stations in Texas.

Fortune 500 Company: Evaluation of 45 gas field sites for environmental cleanup liabilities raised during company M & A negotiations.

Fortune 100 Manufacturer: Expert panel member - prioritization of hazardous waste sites.

Projects – *Regulatory Comment*

Chemical Manufacturers Association - PCB Consensus Panel: Critique of US EPA's proposed "PCB Megarule" (TSCA cleanups) with particular emphasis on sampling program design.

American Petroleum Institute: Superfund reform - study of cost savings if US EPA used more realistic risk assessments.

Chrysler Corporation: Critique of Michigan Act 307 hazardous waste rules, including cleanup standards and site scoring models.

US EPA, Office of Research and Development: 5-year Agency research strategy for municipal wastewater control technology, Project Manager.

US Congress National Commission on Water Quality: Assessment of the impact of the 1972 Federal Water Pollution Control Act on the Charles River and Boston Harbor, Project Engineer/Manager. Technical review and modeling study.

Publications – Journals, Proceedings & Books

- Beck, BD; Seeley, MR; Ghosh, RS; Drivas, PJ; Shifrin, NS. 2006. "Human health risk assessment of cyanide compounds in water and soil." In *Cyanide in Water and Soil: Chemistry, Risk, and Management*. (Eds: Dzombac, D; Ghosh, R; Wong-Chong, GM), Taylor & Francis, Boca Raton, FL, p309-330.
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- Shifrin, NS. 1992. "Interpreting Environmental Chemistry Data: Data Quality First." Invited paper at the Environmental Data/Standard Methods session, Water Environmental Federation 65th annual conference, New Orleans, LA, September 20-24.
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- Murphy, BL; Doherty, JD; Shifrin, NS. 1989. "Determining the Effectiveness of Soil Washing." Presented at the 6th HMCRI National Conference on Hazardous Waste and Hazardous Materials, New Orleans, LA, April 12-14.
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Shifrin, NS. 1980. "The measurement of dissolved organic carbon released by phytoplankton." *Estuaries* 3(3):230-233.

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2005. "Rebuttal Report: Historical Contamination at the Manchester, NH Former MGP." Prepared for McLane, Graf, Raulerson & Middleton. August.

2005. "Supplemental Expert Report: Historical Contamination at the Manchester, NH Former MGP." Prepared for McLane, Graf, Raulerson & Middleton. April.

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2005. "Perchlorate at Olin's Morgan Hill Flare Plant (Palmisano, *et al.* v Olin Corporation, *et al.*)" Prepared for Husch & Eppenberger, LLC. February.

2005. "Capitol Cleaners PCE Spill Study Report, Dover Gas Light Superfund Site [US EPA ID # DED980693550; DE-0057/DE-1018], Dover, Delaware. (Three Volumes) Prepared for FirstEnergy. January.

2004. "Expert report: Historical Contamination at the Nashua, NH Former MGP [re: EnergyNorth Natural Gas, Inc. v. Century Indemnity Co.]" Prepared for McLane, Graf, Raulerson & Middleton. October.

2004. "Historical Practices and Environmental Conditions at Four Boston Gas former MGPs: Commercial Point, South Boston, Braintree, & Everett (Two volumes) (Expert report)." Prepared for Dickstein, Shapiro, Morin, & Oshinsky. November.

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2001. "Kaiser-Nelson Steel and Salvage Company MGP Demolition Allocation of Environmental damages." Expert report prepared for Fitzgerald, McGroarty and Lipari, P.A. August 13.

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