

still serves the analysis for determination of maximum values. Table 11-10 presents the highest values for each model plant in terms of wet and dry deposition and air concentration of both particles and vapors. (Note that dry deposition of vapors is not included in this table, as it is not an ISCST3 modeled value [see section 11.3.2.]) The location of each value in Table 11-10 is indicated by x and y coordinates in meters. Table 11-11 presents modeled concentrations at 2.5 km, 10 km, and 25 km, as are reported in the mercury multipathway analysis (chapter 7). The locations in Table 11-11 are described in terms of degrees from the polar grid origin. For this analysis the polar origin was North with degrees progressing clockwise.

Due to the disparate locations of the maximum modeled concentrations for each modeled plant, it is difficult to determine where the single site of maximum risk would be. It is likely that the maximum risks would be observed at the 50 m location because that is the location of maximum wet deposition. In all modeled cases, wet deposition represents a significantly larger share, by an order of magnitude or greater, of the environmental concentration than either dry deposition or air concentration. This data does not indicate that a re-analysis of the model plant risks is necessary because the effort required to determine the exact location of a maximum and average exposure scenario in a multipathway analysis is beyond the scope of this screening-level analysis.

11.6 SUMMARY OF RESULTS

The results of this assessment indicate that the predicted cancer risks associated with case #2 exposures to dioxin emissions from the model plants are not greater than 1×10^{-7} for the model adult and child resident scenarios. This is the case for both the direct and the indirect exposure pathways. However, risks of 1×10^{-6} or above are predicted for the indirect pathways of the case #1 scenarios. In particular, the subsistence fisher scenario results in a predicted risk of 2×10^{-4} . When factors influencing the magnitude of the risk to the subsistence fisher were examined in a sensitivity analysis, it appeared that the assumptions about the BSAF had the greatest impact on the predicted risk.

Taken one at a time, several other uncertainty factors have the potential to raise the risk estimate for the subsistence fisher above 2×10^{-4} ; these include fish consumption rates, the organic carbon content of sediment, and the fraction of fish tissue that is lipid. This assessment has been conducted using model plant data and two geographic locations selected to represent two potential scenarios. The location of the case #1 receptors was arbitrarily placed at a point of high wet deposition. This assumption was made for the purpose of providing a conservative estimate of the case #1 risk.

The case #1 scenario represents a sub-population that has the potential to receive high exposures due to relatively high ingestion rates, and assumed to be in a location for which the meteorology would

Table 11-10. Maximum Dispersion Modeling Locations and Concentrations

Model plant phase	Wet deposition		Dry deposition		Air concentration	Air concentration
	location in m (x,y)	Wet deposition (g/m ² /y)	location in m (x,y)	Dry deposition (g/m ² /y)	location in m (x,y)	concentration (μg/m ³)
LCH, vapor	0, -500	0.07430	-	-	0, 9000	0.00050
LCH, particle	0, -500	0.09158	Several	0.00026	Several	0.00046
SCH, vapor	0, -500	0.08372	-	-	Several	0.00344
SCH, particle	0, -500	0.10274	8314, -3444	0.00210	-3826, 9238	0.00302
LOH,vapor	0, -500	0.07846	-	-	Several	0.00105
LOH, particle	0, -500	0.14166	Several	0.00092	Several	0.00084
SOH, vapor	0, -500	0.09083	-	-	-2296, 5543	0.00951
SOH, particle	0, -500	0.16233	4619, -1813	0.00997	-1913, 4619	0.00792

also tend to result in high exposures for given rates of release of dioxins. The results of this analysis can be considered a potential representative example for utility boilers, yet they do not represent a specific plant or location. The analysis should be considered an analysis of hypothetical scenarios used for demonstration.

This analysis of noninhalation exposures to dioxin emissions is a screening analysis. Thus, these quantitative exposure and risk results, because of the many modeling and analytic uncertainties, are very uncertain and do not, therefore, conclusively demonstrate the existence of health risks of concern associated with exposures to utility emissions either on a national scale or from any actual individual utility. The lack of measured data around these sources precludes a comparison with modeled results. These results do suggest that exposures and risks of concern cannot at present be ruled out and that there is a need for development of additional scientific information to evaluate whether risk levels of concern may exist.

Table 11-11. Dispersion Modeling Concentrations at Specified Distances

Model plant, phase	Wet deposition location (°)	Wet deposition (g/m ² /y)	Dry deposition location (°)	Dry deposition (g/m ² /y)	Air concentration location (°)	Air Concentration (µg/m ³)
2.5 km concentrations						
LCH, vapor	180	0.01342	-	-	360	0.00015
LCH, particle	180	0.01414	360	0.00005	360	0.00014
SCH, vapor	180	0.01406	-	-	360	0.00040
SCH, particle	180	0.01535	360	0.00088	360	0.00196
LOH, vapor	360	0.01406	-	-	360	0.00040
LOH, particle	360	0.01970	360	0.00030	360	0.00036
SOH, vapor	180	0.01577	-	-	360	0.00681
SOH, particle	180	0.02141	112.5	0.00768	360	0.00607
10 km concentrations						
LCH, vapor	180	0.00217	-	-	360	0.00049
LCH, particle	337.5	0.00121	337.5, 360	0.00019	360	0.00045
SCH, vapor	180	0.00225	-	-	337.5	0.00344
SCH, particle	180	0.01890	112.5	0.00207	337.5	0.00302
LOH, vapor	180	0.00221	-	-	360	0.00100
LOH, particle	180	0.00211	112.5	0.00084	360	0.00083
SOH, vapor	180	0.00233	-	-	337.5	0.00852
SOH, particle	180	0.00210	112.5	0.00675	337.5	0.00679
25 km concentrations						
LCH, vapor	180	0.00046	-	-	337.50	0.00046
LCH, particle	180	0.00037	112.5	0.00026	135	0.00039
SCH, vapor	180	0.00047	-	-	337.5	0.00256
SCH, particle	180	0.00036	112.5	0.00099	337.5	0.00205
LOH, vapor	180	0.00046	-	-	337.5	0.00103
LOH, particle	180	0.00036	112.5	0.00080	337.5	0.00079
SOH, vapor	180	0.00047	-	-	360	0.00444
SOH, particle	180	0.00033	337.5	0.00205	360	0.00355

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12.0 LITERATURE REVIEW ON THE POTENTIAL IMPACTS OF HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE EMISSIONS

12.1 OVERVIEW

The information presented in this chapter and in Appendix H was collected to expand the EPA's knowledge of the potential impacts of HCl and HF emissions from utilities. The details and references are presented in Appendix H. This chapter presents a summary of the findings. The EPA is updating its current state of knowledge of potential health impacts; atmospheric chemistry (e.g., half-life, impacts on the acid rain phenomenon); potential human exposure through pathways other than direct inhalation; and possible ecological harm. The EPA's goal is to understand the potential impacts from HCl and HF emissions to any and all health and environmental areas. This chapter is not intended to provide a detailed, comprehensive treatise on the above subject area; rather, it is designed to provide general technical information that will identify possible problem areas that may call for additional, more detailed research.

Published evidence for potential impacts of HCl and HF was evaluated from a wide variety of sources. Overall, there is extensive information available on the toxicology of these two pollutants; however, literature pertaining specifically to HF and HCl atmospheric chemistry is relatively scarce, especially that pertaining to fine particulate matter and acid rain. Literature on HCl and HF from sources outside the United States and pertaining to emissions sources other than utilities has also been evaluated.

This chapter is organized so that the findings for HCl are presented first, followed by the findings for HF. Within each section, evidence from the literature for transport and transformation through atmospheric, terrestrial, and aquatic processes is presented first, followed by evidence for impacts on human health; vegetation; and wild, domestic, and aquatic animals.

12.2 SUMMARY OF FINDINGS

This chapter provides a synopsis of the information of interest found during the literature review on potential impacts (e.g., acid rain, fine particulate matter, visibility, and toxicity to various plant and animal species) of hydrogen chloride and hydrogen fluoride emissions from utilities.

12.2.1 Hydrogen Chloride

12.2.1.1 HCl Emissions and Formation. Utilities emit a substantial amount of the anthropogenic atmospheric emissions of HCl in the United States.¹ As shown in chapter 3 of this report, utilities were estimated to emit 146,000 tpy of HCl in the United States in 1990. Other important sources of HCl are industrial coal combustion and solid waste combustion. Natural sources of HCl emissions include

volcanic activity, marine plants and microorganisms, and land plant combustion.

According to available information, ambient concentrations of HCl in the United State ranged from none detected to $4 \mu\text{g}/\text{m}^3$. Rural sites can be expected to be at the low end of this range and urban sites are likely to be toward the high end. Human health effects are discussed in Appendix E.

HCl can be formed several ways in the atmosphere. Anthropogenic chlorocarbons can react with OH radicals to produce small amounts of HCl. Nonanthropogenic HCl can be formed from deliquescent sea-salt in the marine environment. HCl can also be created or destroyed through the interaction between fogwater and aerosols. Although information on HCl formation by-products is scarce, available sources indicate that reactions generating HCl can produce the following by-products in the atmosphere: NaNO_3 , Na_2SO_4 , hydrocarbon radicals, and NH_3 .

12.2.1.2 HCl Atmospheric Processes. The atmospheric lifetime of HCl is estimated to be between 1 and 5 days. HCl is a highly reactive gas that is removed from the atmosphere via wet and dry deposition.

12.2.1.3 HCl Atmospheric Transport. In general, because of its high solubility, HCl will be removed from the atmosphere much faster than SO_2 or NO_2 and will be deposited in close proximity to the emissions source. However, conditions exist under which SO_2 is subject to further transport. One study found evidence that HCl-enriched plumes, believed to originate from coal-burning utilities, reached a rural site two days after emissions release. Evidence was found that HCl may affect the atmospheric chemistry of mercury, and thus the toxicity of mercury emissions from utilities. HCl emissions are believed to contribute to some limited degree to the formation of atmospheric acidity and acid rain. In addition, HCl appears to indirectly contribute to some limited degree, to fine PM and visibility problems. However, there are significant uncertainties as to the extent of the impacts due to HCl emissions in these areas. Further research and evaluation are needed to determine if, and to what extent HCl contributes to acid rain, fine PM, and visibility issues.

12.2.1.4 HCl Terrestrial Processes. Information on the terrestrial behavior of HCl is scarce. The references found discuss the evidence that HCl can lower pH to the point that SO_2 oxidation is delayed, possibly altering the spatial deposition of acid species, and that gaseous HCl damages limestone.

12.2.1.5 HCl Aquatic Processes. The chemistry of ubiquitous chlorinated compounds in natural waters is affected by a number of factors that determine the persistence and toxicity of interim species. Chloride cycling in watersheds was found to be more complex than previously thought. The traditional view has been that atmospherically deposited chloride is rapidly transported. Further

research of chloride cycling would be needed to gain a better understanding of the aquatic processes.

12.2.1.6 HCl Human Health Impacts. Evidence of local irritation to the upper respiratory tract by HCl was found, and long-term exposure may cause tooth erosion. The WHO concluded in a review on HCl that there are no mutagenic, carcinogenic, or teratogenic effects related to HCl. Appendix E contains more information on health effects.

12.2.1.7 HCl Vegetation Impacts. Atmospheric and leaf chloride levels were found to be closely correlated. Atmospheric chloride can concentrate in and cause damage to foliar tissues. High chloride concentrations resulted in tissue death in coastal vegetation.

12.2.1.8 HCl Terrestrial Animal Impacts. HCl that reaches plants and soil via wet and dry deposition is then available for uptake by animals. The adverse health symptoms of HCl exposure in animals include eye, nasal, and respiratory tract irritation, with the respiratory tract being the primary target.

12.2.1.9 HCl Aquatic Animal Impacts. Toxicity of chlorinated compounds to aquatic biota varies widely. One study reported the 24-hour LC₅₀ for one marine species as 0.0018 mg/L, and the LC₅₀ for one sensitive freshwater species as 0.003 mg/L.

12.2.2 Hydrogen Fluoride

12.2.2.1 HF Emissions and Formation. Anthropogenic sources are responsible for most atmospheric fluoride. Anthropogenic emissions of hydrogen fluoride (HF) originate from coal combustion and the aluminum, phosphate, and steel-making industries. As shown in chapter 3, utilities are estimated to emit approximately 19,600 tpy of HF nationwide. Volcanoes are the primary natural sources of HF. Ocean spray, fires, and dust from soil and rock weathering contribute relatively minor amounts of fluoride to the atmosphere. Measured concentrations of HF at one monitoring station in the United States ranged between 1 $\mu\text{g}/\text{m}^3$ and 8 $\mu\text{g}/\text{m}^3$. Atmospheric concentrations of fluoride in remote rural areas are reported to be approximately 0.1 $\mu\text{g}/\text{m}^3$, which is at the limit of detection. Estimates of the relative proportions of gaseous to particulate emissions of industrial fluoride vary. Fluoride particulates range from distinct minerals to alumina with HF adsorbed to its surface, and particle diameters range from <0.1 μm to approximately 10 μm . Volcanic emissions are usually not predominately HF, but rather other fluoride-containing compounds that react in the atmosphere to form HF.

12.2.2.2 HF Atmospheric Processes. HF is described as moderately persistent in the atmosphere, with an estimated lifetime of approximately 1 to 5 days. Wet and dry deposition are the primary routes of HF removal from the atmosphere. HF atmospheric reaction products are primarily fluoride salts. HF does not biodegrade.

12.2.2.3 HF Atmospheric Transport. Fluoride emissions from utilities are transported on a regional scale. Fluoride has been used as an atmospheric tracer because the fluoride to sulfur oxide ratio is relatively constant in the coal-fired utilities examined, providing a characteristic utility emissions fingerprint. Evidence was found that coal-fired utility emissions contribute to measured concentrations of atmospheric fluoride at distances of up to 500 km. Another study found that elevated levels (18-21 ppm) of fluorides emitted from a utility could be detected in grape leaves at distances of up to 37 km. However, it has been reported that the measurement of fluoride transport and deposition have problems of accuracy due to limitations of analytical methods.

12.2.2.4 HF Terrestrial Processes. Fluoride is lost from the various surfaces on which it is deposited and leaves ecosystems at a rapid rate. The volatilization pathway as a route of fluoride export from ecosystems needs further investigation. Soil can be both a sink and source of fluoride, but fluoride is not usually available or labile in soils. Soluble fluoride-containing process water and leachate of phosphogypsum were shown to dissolve much of the fine soil clay fraction, as well as the smectite of the coarse clay fraction of soils. Several conditions are reported to facilitate rapid uptake of water-soluble fluoride and transport. The natural buffering capacity of soils or water, or dilution can reduce acidity added by the presence of HF. Sulfate and fluoride were found to slightly retard aluminum's mobility through soils.

12.2.2.5 HF Aquatic Processes. Fluoride is a major component of seawater, and natural and anthropogenic fluoride may accumulate in waterbody sediments. In freshwaters with pH greater than 5, fluoride is mainly present as fluoride ion.

12.2.2.6 HF Human Health Impacts. Adverse effects of fluoride on human health include dental fluorosis, gastric disturbances, reductions in urinary concentrating ability, skeletal fluorosis, and even death. Optimally fluoridated water has been shown not to be associated with a detectable risk of cancer in humans. Fluoride exposure is not associated with birth defects, and there is no indication that organ systems are affected by chronic, low-level fluoride exposure. Genotoxicity studies have yielded contradictory results. There is disagreement about whether the increased prevalence of dental fluorosis observed in the United States since the 1940s is a toxic effect. Crippling skeletal fluorosis has not been and is not a public health problem in the United States. Beneficial effects of high fluoride regimens in reducing osteoporosis have not been demonstrated. Further epidemiological studies are required to determine whether or not an association exists between various levels of fluoride in the drinking water and bone fractures.² Appendix E contains more information on health effects of HF.

12.2.2.7 HF Vegetation Impacts. Inherent differences in the resistance of some tropical tree species to fluoride may be related to

their capacity to accumulate aluminum. Although some plant species are tolerant of elevated fluoride levels, the storage of large amounts of fluoride in plant tissues may present a risk to ecosystems. Plant uptake of fluoride was found to be limited to the smaller, water-soluble, and labile fractions. The major pathway of fluoride to plants is atmospheric deposition.

Atmospheric fluoride is capable of injuring certain plant species at lower concentrations than any other air pollutant. However, most plant species are relatively resistant to fluoride. No morphological damage to lichen species exposed to high concentrations of fluoride was found. Fluoride was found to be the most important pollutant contributing to vegetation damage in one section of a tropical rainforest.

12.2.2.8 HF Terrestrial Animal Impacts. Two studies on the toxicity of fluoride to several rodent species found the animals to exhibit visible incisor lesions after fluoride ingestion. Bone fluoride loads in four predatory bird species were found to be greater in males of all species examined and higher than average in more industrial regions.

Conflicting information was found concerning whether fluoride accumulates in food chains. Variations in fluoride concentrations within plant organs can result in animal species with differing feeding niches ingesting different amounts of fluoride. Contamination of foliage with soil may constitute an important route of fluoride transfer to large herbivores in situations where soil has been treated with phosphate fertilizer or exposed to substantial airborne deposition of fluoride.

12.2.2.9 HF Aquatic Animal Impacts. Biomagnification in aquatic animals is reported to be negligible to very slight. Two trout species were demonstrated to be more resistant to fluoride than freshwater benthic macroinvertebrates. Diatoms appear to be tolerant of, and stimulated to grow by, high fluoride concentrations; the ecological significance of this is uncertain. Limited evidence exists for fluoride-containing effluent effects on both abundance and diversity of estuarine/marine organisms at relatively low fluoride levels.

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13.0 ALTERNATIVE CONTROL STRATEGIES FOR HAZARDOUS AIR POLLUTANT EMISSIONS REDUCTIONS

This chapter presents methods of reducing HAP emissions through precombustion controls, combustion controls, postcombustion controls, and alternative controls. Also, strategies for maximizing total HAP control or minimizing total HAP emissions are reviewed.

The HAPs of concern include the trace elements identified in chapter 5 as potential health risks. These consist of arsenic, cadmium, chromium, lead, manganese, mercury, and nickel; dioxins and furans (due to the toxicity of the organic chemical); and HCl and HF (due to the estimated emission quantities of the compounds).

13.1 PRECOMBUSTION CONTROLS

To reduce SO₂ emissions and thereby comply with the Phase II requirements of the Acid Rain Provisions of the Act, some utilities will switch to fuels that contain lower amounts of sulfur. The effects of fuel switching on HAP emissions are briefly reviewed in this section. Emissions of trace elements from coal-fired units may be controlled through precombustion control techniques such as coal cleaning and coal gasification. The effectiveness of these control techniques is also reviewed.

13.1.1 Fuel Switching

Utilities that switch fuel may change from higher to lower sulfur-containing coal (less than 1.5 weight percent sulfur) or elect to burn a different type of fuel (e.g., switching from oil to natural gas combustion). A potential concern with fuel switching is whether or not it will increase HAP emissions, due to potentially increased concentrations of trace elements in the fuel and different fly ash characteristics that impact effective PM and HAP control with existing APCDs (e.g., ESPs).

The qualitative effects of switching the type of fuel may be noted through comparisons of the averages of trace element concentrations in utility fuels. Table 13-1 lists the arithmetic average, as well as the standard deviation of the average, for trace element concentrations in coal, residual oil, and natural gas. As indicated by the magnitude of the standard deviations listed in Table 13-1, trace element concentrations vary considerably in coal and residual oil. Some of the standard deviations are large enough that comparable concentrations of trace elements may occur in some coal and residual oil samples. For discussion purposes, any overlap in trace element concentrations was ignored, and generalizations on the effects of fuel switching were made from comparisons of average trace element concentrations in the three fuels.

Table 13-1. Comparison of Average Concentrations of Trace Elements in Utility Fuels^{a, b}

	Coal ^c	Residual	Natural gas ^d
Sulfur	(lb/MMBtu)	(lb/MMBtu)	(lb/MMBtu)
average ^e	1.24	0.31	0.00006
SD (mean) ^f	0.19	0.07	0.00006
No. averages	26	13	2
	Coal ^c	Residual	Natural gas ^e
Trace elements:	(lb/trillion)	(lb/trillion)	(lb/trillion)
Arsenic			
average	660	17	0.19
SD (mean)	120	11	0.06
No. averages	26	6	2
Cadmium			
average	60	5.4	--
SD (mean)	30	3.9	--
No. averages	26	3	--
Chloride			
average	27,000	7,400	--
SD (mean)	6,600	3,300	--
No. averages	20	11	--
Chromium			
average	600	17	--
SD (mean)	98	3	--
No. averages	26	11	--
Fluoride			
average	5,300	600	--
SD (mean)	720	200	--
No. averages	26	3	--
Lead			
average	800	73	--
SD (mean)	190	43	--
No. averages	26	5	--
Mercury ^{1,2}			
average	7.7	0.6	0.001
SD (mean)	0.6	0.3	1
No. averages	152	4	
Nickel			
average	700	1,300	--
SD (mean)	69	200	--
No. averages	26	13	--

^a The coal data listed in Table 13-1 were not weighted for coal production by State of coal origin.

^b There were only two sets of data for concentrations of trace elements in natural gas in Table 13-1.

^c With the exception of the mercury data, coal values were determined from modified U.S. Geological Survey (USGS) data, by State of coal origin, and coal shipment data for coals that originated from three States. Modified USGS data are USGS data that were modified to account for the effects of bituminous coal cleaning. Mercury data were reported by EPRI for samples of coal shipments.² None of the data were weighted for coal production.

^d Natural gas values were determined from the preliminary EPRI test reports for Sites 120 and 121. The listed values are detected concentrations.

^e Averages of averaged data sets.

^f This is the standard deviation of the number of averages directly below.

13.1.1.1 Switching to Natural Gas Combustion. As shown in Table 13-1, natural gas has the lowest average concentrations, on a lb/trillion Btu basis, of sulfur, arsenic, and mercury when compared with the corresponding values for residual oil and coal. The averages listed for coal and residual oil exceed those listed for natural gas by factors that range from approximately 100 (for the concentration of arsenic in residual oil) to as much as approximately 21,000 (for the concentration of sulfur in coal). Thus, of the three utility fuels, natural gas contains the least amounts of the trace elements, and switching from coal or residual oil to natural gas combustion would ultimately reduce emissions of trace elements. Some total and seasonal conversion of coal- and oil-fired units to natural gas firing is expected to affect compliance with the various ozone and NO_x control provisions of Titles I and IV of the Act. However, a complete conversion of all utility boilers to natural gas is not practical. Even though the natural gas transmission network is expanding, delivery of natural gas to each utility unit cannot yet be accomplished. In addition, there is concern over the long-term availability of natural gas (particularly with respect to other fuels) given the projected usage (and increase in usage) in the residential, commercial, and industrial sectors and the estimates of proved and supplemental reserves of natural gas. Estimates of "proved reserves" of natural gas have decreased each year (but one) for the past 10 years.

13.1.1.2 Switching from Coal to Residual Oil Combustion. As shown in Table 13-1, with the exception of the average concentrations of nickel, the average concentrations of trace elements listed for coal exceed those listed for residual oil by factors that range from approximately 4 (for the concentrations of sulfur and chloride) to as much as approximately 40 (for the concentration of arsenic). However, the average concentration of nickel in coal is approximately half the corresponding value for residual oil. Thus, switching from coal to residual oil combustion could result in increased emissions of nickel and decreased emissions of the other trace elements.

13.1.1.3 Switching from Higher to Lower Sulfur Coals. The effects of coal switching will be reviewed first for mercury and then for the other trace elements.

Figure 13-1 shows the relationship between the concentrations of mercury and sulfur in 153 samples of coal shipments.² As shown in Figure 13-1, there is no relationship between the sulfur and mercury content in the sampled coal shipments; mercury concentrations below approximately 15 lb/trillion Btu are present in coal with both higher sulfur concentrations (above 2.5 lb/MMBtu) and lower sulfur concentrations (below 1.5 lb/MMBtu).

A conceivable control strategy would involve blending higher mercury-containing coals with lower mercury-containing coals to reduce mercury emissions. Such a practice would be comparable to blending high and low sulfur-containing coals in order to meet SO₂ emission

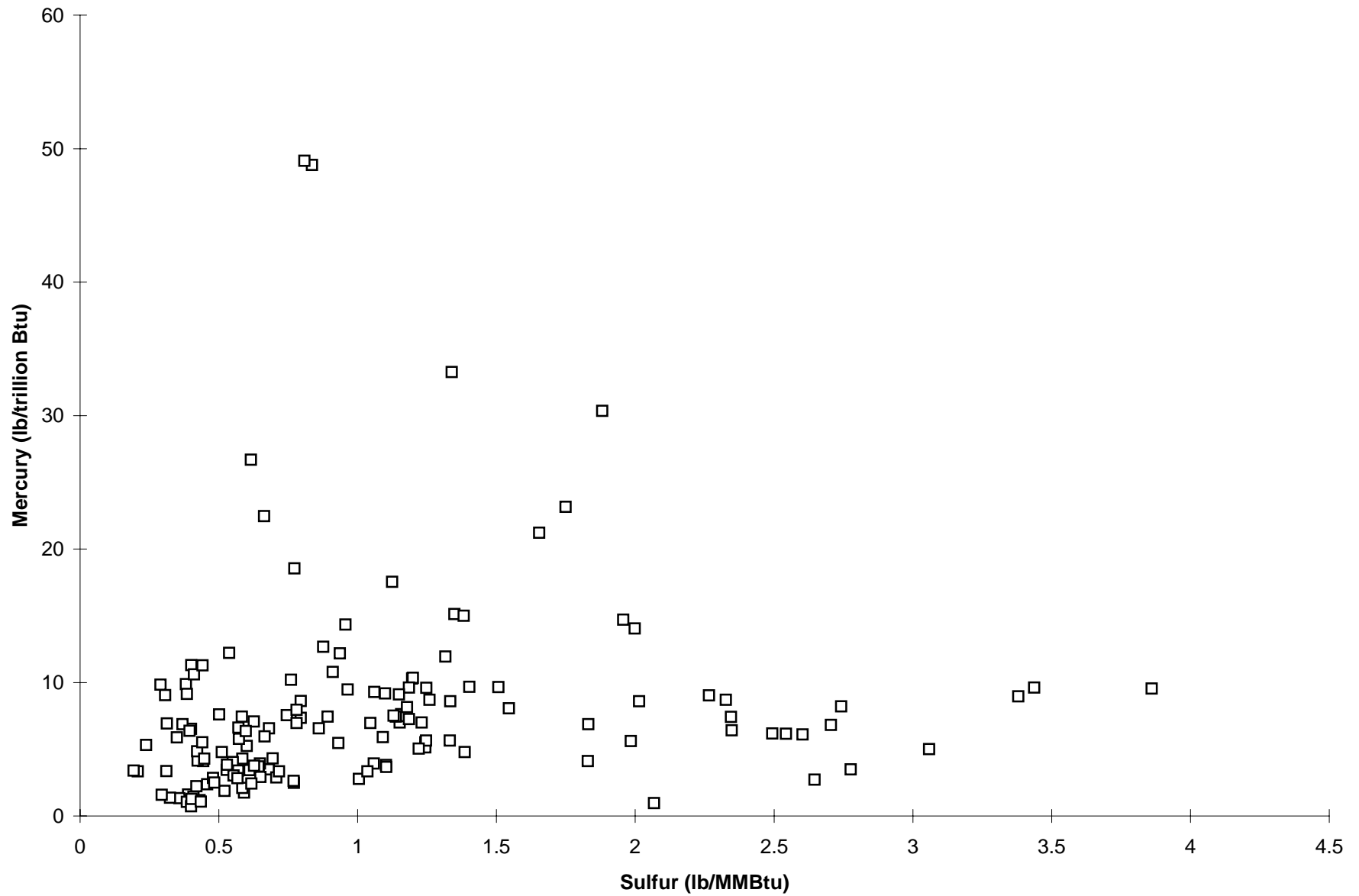


Figure 13-1. Relation between the concentrations of mercury and sulfur in 153 samples of coal shipments.²

limits. However, coal blending for mercury control is not a proven control strategy. Changes in the electrical resistivity and amount of flyash resulting from coal blending could reduce PM capture efficiencies by ESPs and subsequently lead to increased emissions of PM and HAP metals. However, these effects on ESP performance can be addressed by gas conditioning and/or modifications to the ESP. Blending for mercury control could also increase levels of other HAPs or sulfur. Another uncertainty with coal blending for mercury control would be the possibility of changing the distribution of the elemental and oxidized forms of mercury that could affect mercury control with existing control devices. Another factor is that the blending of two different coals might change the higher heating value of the resulting mixture, with subsequent effects on the quantity of fuel required for combustion.

The qualitative effects of switching to lower-sulfur-containing coals on other metallic HAPs are examined in Figure 13-2(a-g) through plots of the average concentrations of each HAP, excluding mercury, with sulfur content in coal. As shown in Figure 13-2(a-g), the average concentration of trace elements in coal shipments, as approximated by the modified U.S. Geological Survey (USGS) data (modified for the effect of coal cleaning on bituminous coals), generally show no clear trends with sulfur content (i.e., decreasing the sulfur content of coal does not generally lead to reduced concentrations of trace elements in coal).

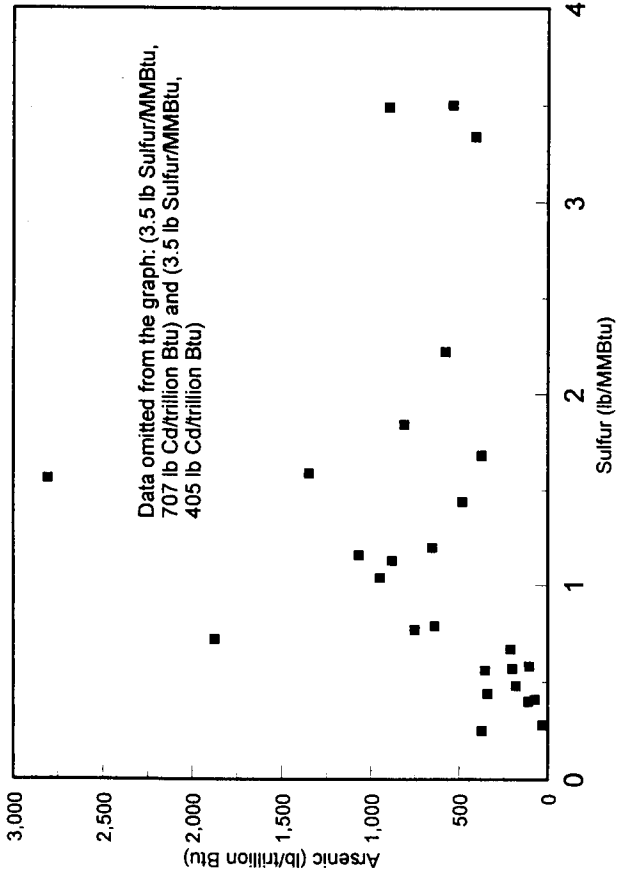
Based upon average concentrations of trace metals in coal from the modified USGS data, fuel switching to lower-sulfur-containing coals will not generally result in consistently reduced emissions of the trace elements. Trace elements associated with the PM (e.g., arsenic, cadmium, chromium, lead, and nickel) could be removed from coal-fired flue gas with a PM control device.

It should be stressed that the effects of coal switching were drawn from comparisons of average concentrations of trace elements in modified USGS coal data. The concentrations of trace elements in actual coal shipments may vary from the USGS averages.

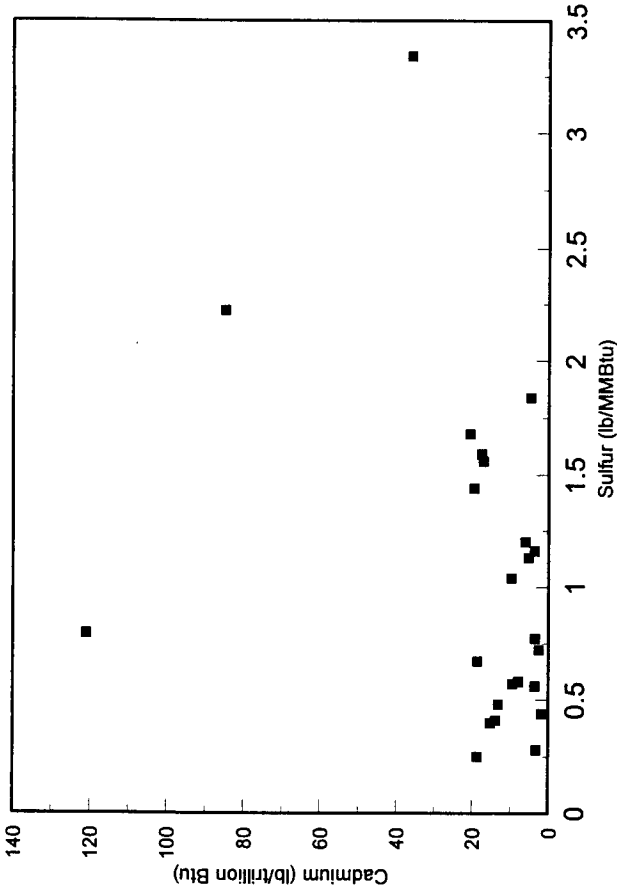
13.1.2 Coal Cleaning

Approximately 77 percent of eastern and midwestern³ bituminous coal shipments are cleaned to meet customer specifications on heat, ash, and sulfur content. Subbituminous and lignite coals are not routinely cleaned.⁴ Conventional coal cleaning removes mineral matter and, in the process, may also remove some of the trace elements contained in the mineral matter. The mineral matter is removed from the coal by either crushing and screening or by coal washing (through the difference in specific gravities of the constituents or by surface-based floatation).⁵ In the process of removing the mineral matter, coal cleaning generates solid refuse that contains trace elements; the solid refuse must be disposed of properly. Any coal cleaning liquid wastes will also contain trace elements, but the liquid wastes may be properly clarified and then recycled.

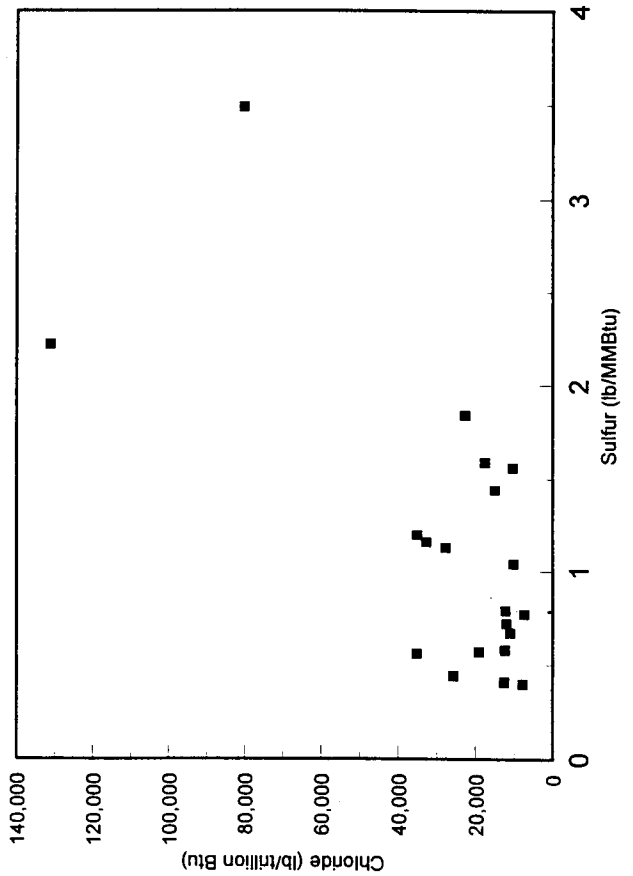
(a) Arsenic



(b) Cadmium



(c) Chloride



(d) Chromium

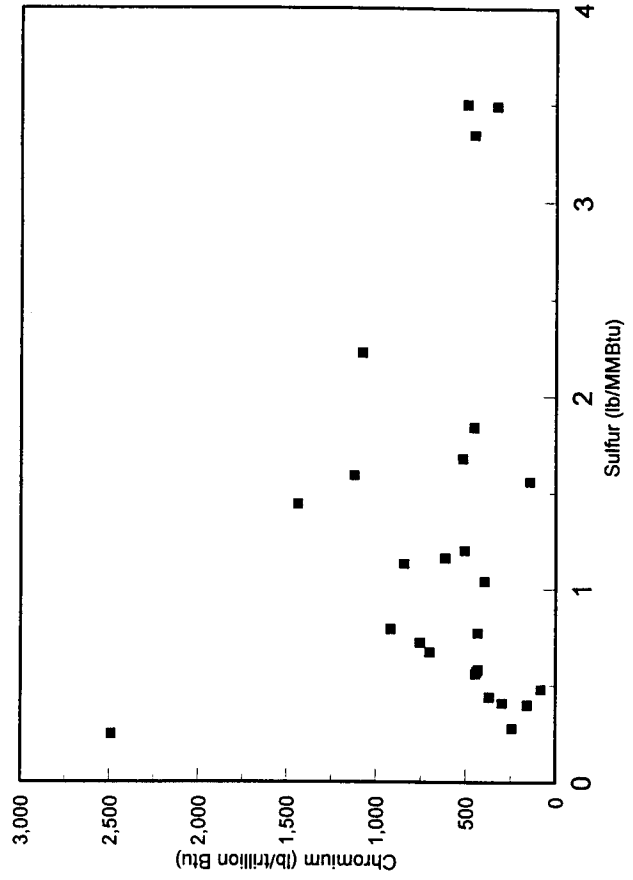
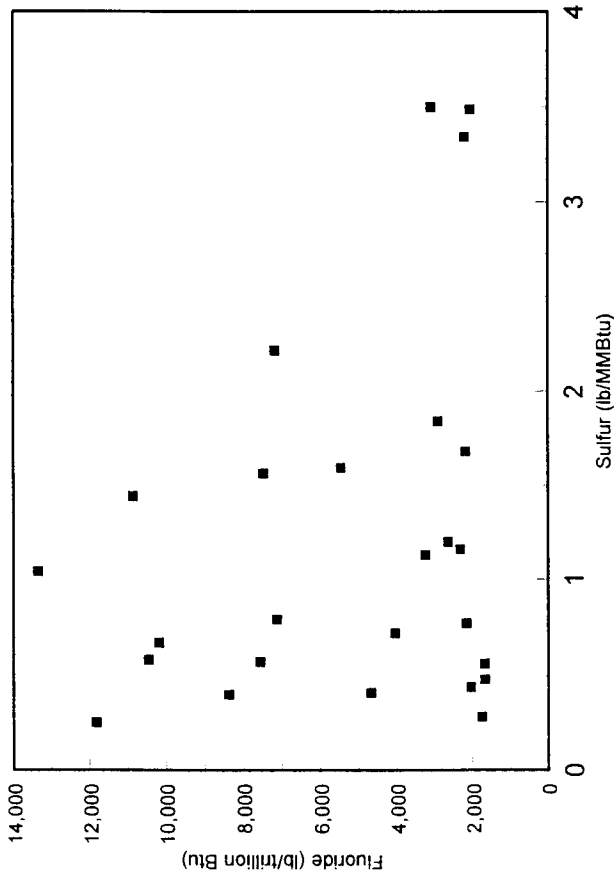
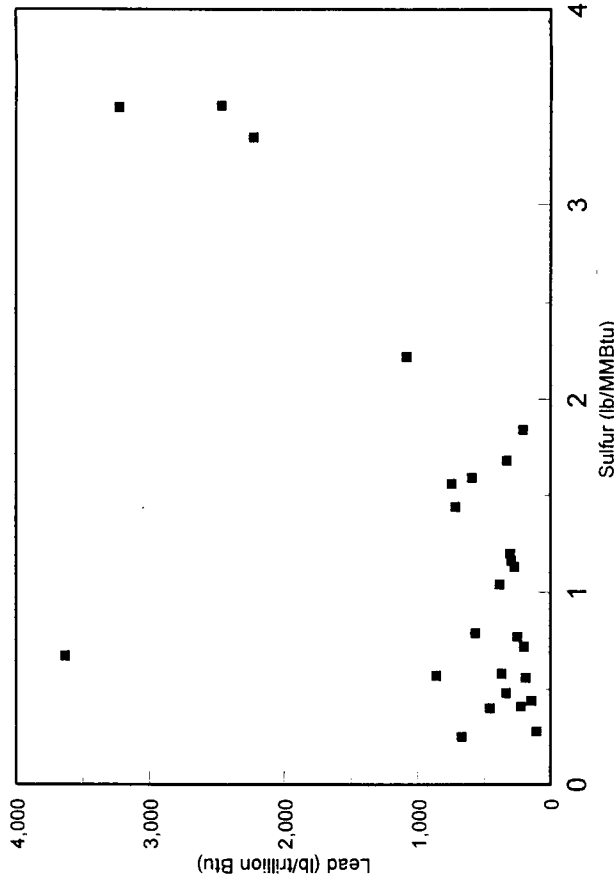


Figure 13-2 (a-g). Relation between concentration of selected trace elements and sulfur in modified USGS data.

(e) Fluoride



(f) Lead



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(g) Nickel

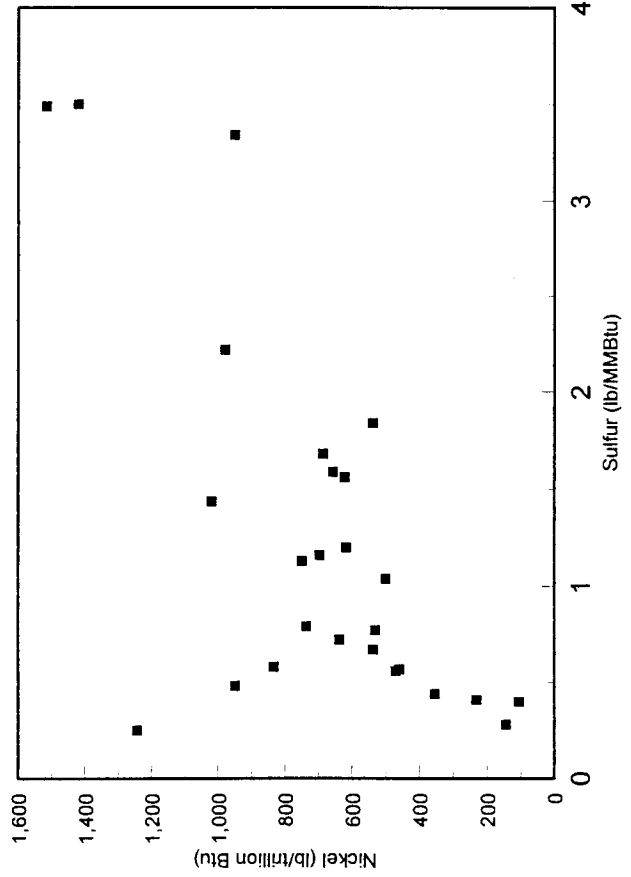


Figure 13-2 (a-g). continued.

Table 13-2 lists the limited amount of available data on trace element reductions achieved through conventional coal cleaning. In Table 13-2, some of the trace element reductions are negative. Negative percentages occur when part of the coal is removed but the element is not contained in the extracted portion of the coal, so that the same weight of the element that was contained in the uncleaned coal is contained within a relatively smaller weight of the cleaned coal. Because the weight of the trace element does not change, negative removal percentages are considered to indicate that no trace element reduction occurred or that the trace element reduction was effectively 0 percent.

As shown in Table 13-2, for the limited amount of available data, trace element removal percentages may vary for coals obtained from the same seam. The variability occurs because trace element concentrations, in the mineral portion of coal, vary from coal to coal. For the data listed in Table 13-2, the variation in trace element reductions may also be due to the use of various cleaning methods, the accuracy of the analytical techniques used to measure concentrations of trace elements in cleaned and uncleaned coals, and sample collection methods. With regard to analytical techniques, CONSOL, Inc., noted the following difficulties in analyzing mercury concentrations in coal: the volatility of mercury compounds, low mercury concentrations in coal, large variability of approximately 50 percent in the interlaboratory reproducibility of mercury concentrations, lack of certified mercury-in-coal standards, and lack of standard sample preparation and analysis methods.^{6,7}

The average trace element reductions, listed in Table 13-2 for a limited amount of available data, were determined with the negative percentages treated as 0 percent removal and the averages not weighted by coal production since the EPA does not believe sufficient data exist at this time to follow a production-weighted approach. The average values for the limited amount of available data indicate that, in general, lead concentrations were reduced the most (approximately 55 percent) while mercury concentrations were, on average, reduced the least (approximately 21 percent). It should be stressed that better and worse trace element reductions may be found for specific coals. For instance, mercury removals of at least 50 percent should occur during conventional cleaning of Upper Freeport coal, based upon the modes of occurrence of mercury and available conventional coal cleaning data.⁸ In Table 13-2, mercury removals were reported for three samples of Upper Freeport coal; two indicated approximately 62 percent removal while the third indicated effectively no mercury removal. More research is needed to establish trace element removal efficiencies, achieved through conventional coal cleaning, on a statistically representative sampling of commercially viable coal seams. Additional information on advanced coal cleaning is provided in section 13.6.1.

Table 13-2. Trace Element Reductions Achieved Through Conventional Coal Cleaning^a

Seam	State	Reference	% Removal arsenic	% Removal cadmium	% Removal chromium	% Removal fluoride	% Removal lead	% Removal mercury	% Removal nickel
C. App. A		a	39	14	75		57	-11	50
C. App. B		a	22	33	67		65	8.3	39
IL	IL	e	54	59	21		38	55	24
IL #6	IL	a	47	76	72		35	43	40
IL #6	IL	c	3	32	23	27	37	-8.3	21
IL 2,3,5	IL	d	30		44	41	68	17	58
IL 2,3,5	IL	d	48		46	60	59	42	37
Ky #11	Ky	d	52		60	83	88		68
Ky #11	Ky	d	13		69	92	84	20	73
Ky #9 & 14	Ky	c	40	53	29	42	49	13	33
Lower Kittanning	Pa	c	66	43	44	64	59	23	35
Pittsburgh	Pa	b	74		71	-459	67	20	33
Pittsburgh	Pa	c	53	57	56	67	65	15	51
Pittsburgh	Pa	c	27	20	24	30	34	7.7	31
Pittsburgh A	Pa	a	65	40	42		37	27	51
Pittsburgh B	Pa	a	67	58	66		69	36	62
Pittsburgh C	Pa	a	67	63	63		63	7.1	53
Pittsburgh D	Pa	a	77	55	64		63	-20	69
Pittsburgh E	Pa	a	50	50	71		72	20	69
Pratt	Al	d	29	0	48	19	58	3.4	46
Pratt	Al	d	7.1	0	54	54	24	29	21
Pratt/Utley	Al	d	29	0	41	65	53	21	54
Sewickley	Pa	c	36	52	46	57	94	0	52
Upper Freeport	Pa	b	38		11	47	53	-200	26
Upper Freeport	Pa	d	73	40	50	80	8.3	64	15
Upper Freeport	Pa	d	74	42	45	75	61	60	30
Utley	Al	d	23	0	17	6.5	28	21	24
All seams:									
min			3.4	0	11	-459	8.3	-200	15
max			77	76	75	92	94	64	73
average			45	38	49	50	55	21	43

13-9

^a Negative percentages are listed as entries. However, averages were determined with negative percentages treated as zero removal.

Table 13-2. (continued)

References

Data for references a - d were taken from the report:

Akers, David, Robert Dospoy, and Clifford Raleigh, The Effect of Coal Cleaning on Trace Elements, Draft Report, Development of Algorithms, December 16, 1993, prepared for EPRI by CQ Inc.

Data for reference e were taken from the report:

Demir, Ilham, Richard D. Harvey, Rodney R. Ruch, Heinz H. Damberger, Chusak Chaven, John D. Steele, Wayne T. Frankie, Ken K. Ho, "Characterization of Available Coals from Illinois Mines," draft report, December 28, 1993, Illinois State Geological Survey file number to be assigned.

Specific references that were mentioned in the report by Akers, Dospoy, and Raleigh:

^a DeVito, M., L. Rosendale, and V. Conrad, "Comparison of Trace Element Contents of Raw and Clean Commercial Coals," presented at the DOE Workshop on Trace Elements in Coal-Fired Power Systems, Scottsdale, AZ, April 1993.

^c Ford, C. and A. Price, "Evaluation of the Effects of Coal Cleaning on Fugitive Elements: Final Report, Phase III," DOE/EV/04427-62, July 1982.

Although there is variability in trace element reductions, the data suggest that coal cleaning techniques may be useful in reducing trace element concentrations in selected coals. More studies are needed on diverse samples of coal to establish the effectiveness of coal cleaning in reducing trace element concentrations and to determine the causes of variability in cleaning effectiveness.

13.1.3 Coal Gasification

Coal gasification converts coal to a syngas-fuel form that emits lower quantities of pollutants at the utility boiler than if the coal were not converted. Although there are some disadvantages to this process (the cost of gasification and the addition of another combustion source), the total quantity of air pollutants emitted from the combination of gasification and combustion is expected to be lower than burning coal in a conventional system.^{9,10}

The gasification process typically described for near-term generation projects uses integrated gasification combined cycle (IGCC) technology and conventional cold-gas cleanup. In this process, gas from coal is used to generate electricity from both a steam turbine and a gas turbine. Steps in the process, shown in Figure 13-3, include coal preparation, coal oxidation and gasification, gas cooling, and gas cleanup. A large part of the pollutant mass is transferred to the slag or ash produced during gasification, and more of the impurities are transferred to water streams used in the gas cleanup. Slag or ash from the gasification step may be treated for recovery of salable products, and the stream from gas cleanup may be treated for recovery of sulfur. Heat transferred from the cooling step is used to produce steam for the steam turbine generator, while fuel gas made from the coal is burned to produce more electricity from the gas turbine generator. The IGCC technology can produce up to 25 percent more electricity from a given amount of coal than is currently obtained from conventional boilers.⁹

Statements by the DOE⁹ suggest that IGCC technology is almost certain to be one of the lowest-cost fossil fuel options for generating electricity in the 21st century. When used to refurbish an existing plant, the technology is less expensive than building a conventional coal-fired plant. Other claims include higher thermal efficiency (to about 40 or 45 percent from about 35 percent), higher plant output (by 50 to 150 percent), and lower SO₂ and NO_x emissions as described above. The IGCC process has been demonstrated in a limited number of commercial-scale projects. In addition, IGCC is being utilized in several DOE CCT projects.

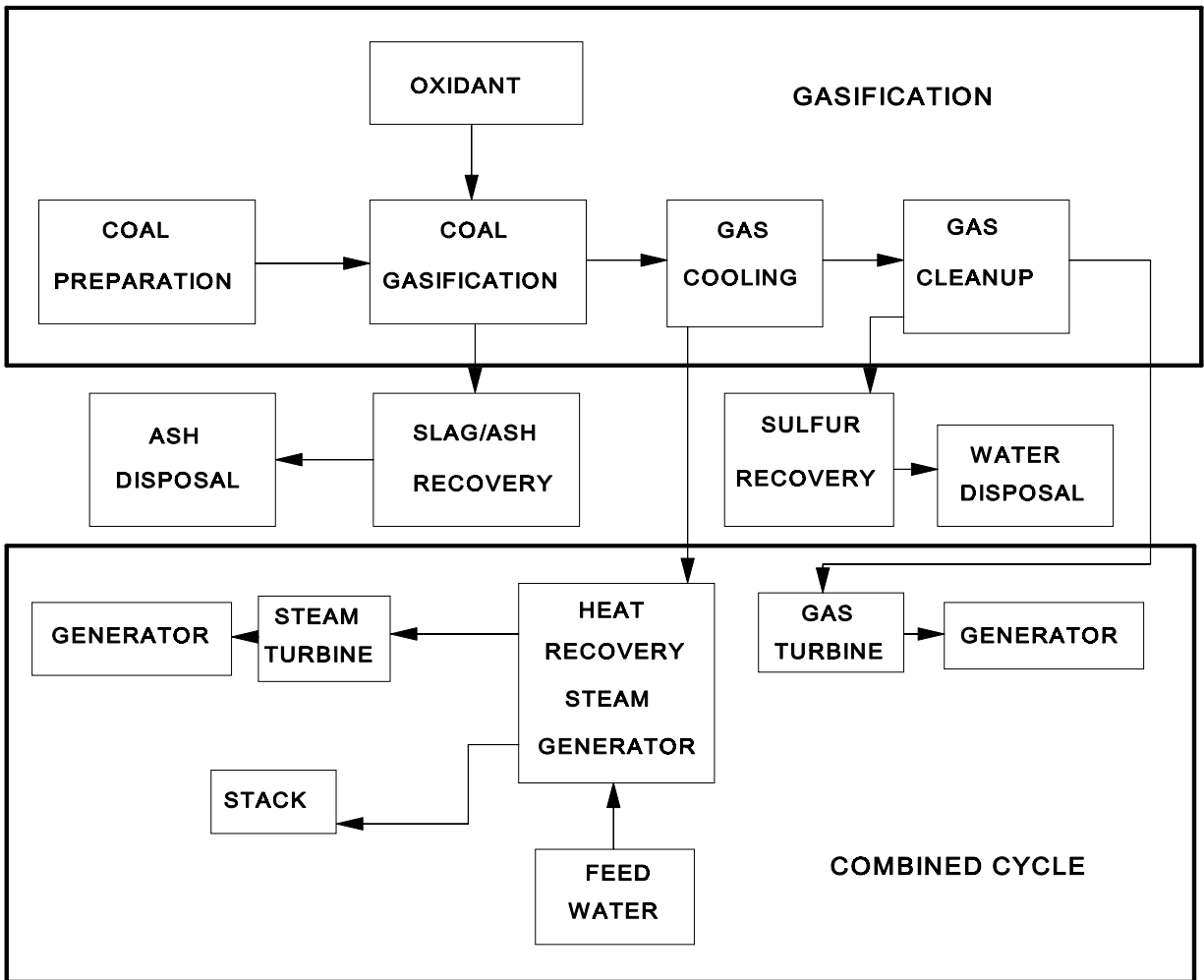


Figure 13-3. Coal gasification combined cycle technology.

There are limited data available on the impact of IGCC on HAP emissions. Experiments with a different gasifier, an air-blown, fixed-bed gasifier coupled to a turbine simulator, produced trace metal concentrations as shown in Table 13-3.¹⁰ The hot gas from the gasifier was treated in a moving bed with zinc titanate sorbent,

13.2 COMBUSTION CONTROL

Combustion control deals with the effect of furnace type (firing method and bottom type) and furnace modifications (such as the addition of low-NO_x burners) on HAP formation. Since the recent emission testing on utility units provided a significant amount of information on the generation and control of trace metals but considerably less information on organic HAPs, trace metals are used

Table 13-3. Emissions from an Air-Blown, Fixed-Bed Gasifier

Trace metal	Emissions to flare, $\mu\text{g}/\text{Nm}^3$	Emissions from turbine simulator, $\mu\text{g}/\text{Nm}^3$	Total air, $\mu\text{g}/\text{Nm}^3$
Arsenic	639	8	647
Cadmium	16	0.19	16.2
Chromium	155	20	175
Mercury	20	2	22
Nickel	1,530	26	1,556
Selenium	68	0.56	68.6

to analyze the effect of combustion control. The trace metals for coal-fired units examined in this section are arsenic, beryllium, cadmium, chromium, lead, manganese, and mercury; those for oil-fired units are arsenic, lead, nickel, and mercury.

While the majority of recently collected HAP data has focused on metals, some small-scale studies have been conducted to evaluate changes in combustion conditions on organic HAPs. In one test, coal was burned at normal and elevated excess air levels and with air staging to simulate combustion modification NO_x controls.¹¹ A large number of organic HAPs were sampled in each case. Some increases in HAP emissions were noted for the air-staging conditions, but the conclusion was that this increase would not result in emissions at significant levels, even for a large utility boiler. During a second small-scale test, combustion conditions were varied between very high excess air and substoichiometric conditions.¹² This study concluded that low- NO_x firing conditions did not necessarily exacerbate emissions of organic HAPs. In both studies, the organic emissions were found to be one or more orders of magnitude less than emissions of any of the metallic HAPs, even under the worst combustion conditions tested. Although these results are from small-scale units and are relatively limited in their scope, they provide additional information supporting the position that, in general, organic HAP emissions are not likely to increase significantly due to the installation of low- NO_x combustion equipment.

The effect of NO_x control on metallic HAP generation was examined by developing an average emission output in lb/trillion Btu from one oil- and several coal-fired units. These units were tested before and after the installation of NO_x control or after the addition of greater NO_x control to an existing NO_x -controlled unit. As shown in Table 13-4, there appears to be a trend toward reductions in HAP emissions through the addition of NO_x control. However, this trend is neither uniform

Table 13-4. Comparison of Electric Utility Emissions Before and After Application of NO_x Control or Application of Greater NO_x Control on a Unit With Lesser NO_x Control (lb/trillion Btu) ^{1,3-16}

Trace metal	EPRi Site 110 (with low NO _x burners)	EPRi Site 110 (with low NO _x burners and offset air)	EPRi Site 110 percentage change	EPRi Site 114 (without NO _x control)	EPRi Site 114 (with overfire air and return burners)	EPRi Site 114 percentage change	EPRi Site 113 (without NO control)	EPRi Site 13 (with burners out of service)	EPRi Site 13 percentage change	EPRi Site 16 (with overfire air)	(with overfire air and low NO burners)	EPRi Site 16 percentage change
Arsenic	141.73	64.15	-121%	137.22	151.4	9%	7.1	3.7	-92%	1789.01	1805.89	1%
Beryllium	43.87	45.26	3%	39.86	36.21	-10%	ND	ND	ND	108.33	130.43	17%
Cadmium	448.83	120.9	-271%	17.38	20.41	15%	10.13	13.84	27%	10.93	21.07	48%
Chromium	745.12	743.02	-0.28%	241.77	164.57	-47%	2.95	8.95	67%	934.26	845.76	-10%
Lead	878.75	503.23	-75%	1365.7	1007.17	-36%	8.02	4.6	-74%	437.31	351.15	-25%
Manganese	1021.84	999.7	-2%	392.1	375.22	-4%	4.7	7.84	40%	745.42	890.91	16%
Mercury	3.58	0.02	-17981% ^a	6.47	4.48	-44%	0.23	0.17	-36%	7.06	10.74	34%
Nickel	538.55	511.13	-5%	1073	1437.58	25%	1827.15	1355	-35%	664.17	655.97	-1%
Average Overall Percentage Change	↑	↑	-67%	↑	↑	-11%	↑	↑	-15%	↑	↑	10%
	Lesser NO _x control	Greater NO _x control		Lesser NO _x control	Greater NO _x control		Lesser NO _x control	Greater NO _x control		Lesser NO _x control	Greater NO _x control	

ND = This trace metal was below the detection limit in both the coal feed and the boiler exit emissions on both tests.

^a This percentage difference seems too large and is not used in the average overall percentage change calculation.

(see arsenic, beryllium, and cadmium percentage change between Sites 110 and 114) nor universal (see Site 16 compared to all other sites). The differences in the percentage change could be due to the variability of trace metal concentrations in the oil or in different sources of bituminous coal; differences in the carbon, chloride, or ash content of the coal burned; differences in the age or operating condition of the units; or a combination of all of these or other factors.

The effect of the bottom type (furnace type) on HAP generation was examined by analyzing an average emission output of coal-fired units (see Table 13-5) with either a wet bottom furnace or a dry bottom furnace, both burning pulverized coal. Emissions were further segregated by coal type. Since there was only one test done on a conventional, dry bottom, lignite-fired unit, no lignite-fired units were analyzed. Site 111, which burned a mixture of bituminous and subbituminous coal, was grouped with the subbituminous coal-fired units for this analysis. To support the emission results, the EMFs for these furnaces and the concentrations of the trace metals found in feed coal are also included in Table 13-5. In this way, the effects of furnace type and low-NO_x operation and of trace metal concentration in the coal can be observed. Furnace type, with and without low-NO_x operation, may affect the partitioning of ash between bottom ash and fly ash. Trace metal concentration in the coal affects the trace metal concentration in the flue gas in either vapor or solid form. Oil-fired units could not be separated into wet or dry bottom configurations, as all oil-fired units use dry bottom furnaces. Therefore, the impact on HAP emissions of bottom type is not addressed for oil-fired boilers.

When units firing bituminous and subbituminous coal were analyzed, their averages showed that arsenic, lead, and mercury seemed to be emitted in higher amounts by wet bottom units while beryllium, cadmium, chromium, and manganese seemed to be emitted in higher amounts by dry bottom units (see Figure 13-4a). When units firing only bituminous coal were analyzed, the same effect was observed (see Figure 13-5a). When units firing only subbituminous coal were analyzed, their averages showed that emissions of almost all HAPs stated above were emitted in higher amounts from dry bottom units than from wet bottom units (see Figure 13-6a). Mercury was the exception, being emitted in similar amounts by both bottom types. The percent removal by bottom type and the concentrations of trace metals in the feed coal show a logical relationship between the trace metal concentration observed in the feed coal and the amount emitted from the boiler. This relationship appears to be a consequence of the ash and trace metal partitioning in the boiler.

Table 13-5. Comparison of wet bottom vs. dry bottom electric utility boilers metallic HAP emissions, trace element removal, and trace metal concentrations in feed coal ^{13,14,16-33}

Compound	EPR1 Site 114 (without NO _x control)		EPR1 Site 114 (with overfire air and reburn burners)		DOE Niles test (with SNOX SCR)		DOE Niles		Northern States Power Riverside 8		EPR1 Site 102 (same as NSP A.S. King)		DOE Boswell		Fuel type	Average emissions	Average emissions	Average emissions	Average percent removal by boiler (1-average EMF)	Average percent removal by boiler (1-average EMF)	Average percent removal by boiler (1-average EMF)	Average trace metal concentrations in feed coal (microgram/gram)	Average trace metal concentrations in feed coal (microgram/gram)	Average trace metal concentrations in feed coal (microgram/gram)	
	WET	Cyclone	BIT	Cyclone	WET	Cyclone	BIT	Cyclone	WET	Cyclone	WET	Cyclone	WET	Cyclone											Subbituminous
Boiler emissions (lb/trillion Btu)																									
Arsenic	137.2		151.4	2349.3	1583.3	32.4	51.4	34.4							620	1055	620								39
Beryllium	39.9		36.2	55.6	41.3	5.0	3.1	11.7							28	43	28								7
Cadmium	17.4		20.4	4.8	2.6	2.1	1.9	11.0							9	11	9								5
Chromium	241.8		164.6	434.0	366.1	54.7	146.0	446.7							265	302	265								216
Lead	1365.7		1007.2	637.5	593.0	56.3	152.0	176.5							570	901	570								128
Manganese	392.1		375.2	420.4	322.5	66.4	599.0	6278.5							1208	378	1208								2315
Mercury	6.5		4.5	21.3	19.7	3.0	6.4	4.7							9	13	9								5
Boiler emission modification factors																									
Arsenic	0.15		0.25	0.85	0.58	0.51	0.48	0.23							56%	54%	56%								59%
Beryllium	0.15		0.15	0.30	0.26	0.08	0.04	0.60							77%	79%	77%								76%
Cadmium	0.01		0.01	0.20	0.11	0.16	0.02	1.00							79%	92%	79%								61%
Chromium	0.30		0.23	0.35	0.28	0.22	0.25	1.00							63%	71%	63%								51%
Lead	0.50		0.84	0.60	0.56	0.38	0.61	0.42							44%	38%	44%								53%
Manganese	0.20		0.18	0.19	0.15	0.13	0.33	0.57							75%	82%	75%								66%
Mercury	0.73		0.54	1.00	1.00	1.00	1.00	0.87							12%	18%	12%								4%
Trace metal concentrations in feed coal (microgram/gram)																									
Arsenic	12.0		8.1	34.0	33.3	0.7	1.3	1.4							13.0	21.9	13.0								1.1
Beryllium	3.6		3.3	2.3	1.9	0.7	0.9	0.2							1.8	2.8	1.8								0.6
Cadmium	39.0		47.0	0.3	0.3	0.2	1.0	0.1							12.5	21.7	12.5								0.4
Chromium	11.0		9.4	15.3	16.0	2.7	7.0	3.2							9.2	12.9	9.2								4.3
Lead	37.0		16.0	13.0	13.0	1.6	3.0	3.9							12.5	19.8	12.5								2.8
Manganese	26.5		27.0	26.7	25.3	5.5	22.0	102.0							33.6	26.4	33.6								43.2
Mercury	0.12		0.11	0.26	0.21	0.03	0.06	0.05							0.12	0.17	0.12								0.05

BIT = bituminous
SUB = subbituminous
SNOX = wet sulfuric acid-selective catalytic reduction process

Table 13-5. Continued

Compound Bottom Type Furnace Type	EPR Site 110 (w/LNB and offset air)		EPR Site 110 (w/LNB)		DOE Yates		EPR Site 15		DOE Cardinal		EPR Site 116		EPR Site 12		EPR Site 14		EPR Site 115		EPR Site 16 OFA		EPR Site 16 OFALNB	
	DRY Tangential	BIT	DRY Tangential	BIT	DRY Tangential	BIT	DRY Tangential	BIT	DRY Opposed	BIT	DRY Front	BIT	DRY Opposed	BIT	DRY Opposed	BIT	DRY Vertical	BIT	DRY Opposed	BIT	DRY Opposed	
	Fuel type																					
	Boiler emissions (lb/trillion Btu)																					
Arsenic	64.2		141.7		393.1		598.9		1043.2		61.5		498.4		230.4		38.2		1789.0		1805.9	
Beryllium	45.3		43.9		90.1		45.8		113.0		4.1		58.6		30.1		17.5		108.3		130.4	
Cadmium	120.9		448.8		23.8		7.4		32.4		0.6		33.8		5.3		4.0		10.9		21.1	
Chromium	743.0		745.1		2798.8		1164.3		976.0		71.8		1252.7		735.6		87.5		934.3		845.8	
Lead	503.2		878.8		688.6		811.3		623.0		23.9		381.2		115.2		167.1		437.3		351.2	
Manganese	999.7		1021.8		2055.9		1752.6		1350.8		71.8		1723.6		1152.2		334.3		745.4		890.9	
Mercury	0.02				12.4				1.7		2.2		7.6		0.8		1.7		7.1		10.7	
	Boiler emission modification factors																					
Arsenic	0.89		0.39		1.00		0.60		0.91		0.70		1.00		0.50		0.61		1.00		1.00	
Beryllium	0.93		0.43		1.00		0.54		0.96		0.35		1.00		0.92		0.52		1.00		0.82	
Cadmium	1.00		0.70		1.00		0.01		1.00		0.12		0.14		0.02		0.58		1.00		0.11	
Chromium	1.00		1.00		1.00		0.58		0.61		0.27		1.00		0.67		0.57		0.58		0.69	
Lead	1.00		0.36		1.00		1.00		1.00		0.26		1.00		0.79		0.38		1.00		0.66	
Manganese	0.71		0.76		1.00		0.81		0.27		0.21		1.00		0.93		0.58		0.60		0.88	
Mercury	0.66				1.00				0.41		0.97		0.74		0.74		0.78		0.64		1.00	
	Trace metal concentrations in feed coal (microgram/gram)																					
Arsenic	2.0		1.9		2.3				12.9		5.0		6.2		6.3		0.5		17.0		23.0	
Beryllium	1.3		0.6		1.1		1.1		1.3		0.7		0.7		0.5		0.2		1.4		2.2	
Cadmium	2.1		1.7		0.3		8.0		0.1		0.3		3.4		3.0		0.1		0.1		2.6	
Chromium	9.0		5.5		24.8		26.0		18.0		15.0		17.0		15.0		1.1		22.0		17.0	
Lead	17.0		5.0		8.0		4.0		6.8		5.3		2.4		2.0		2.1		5.1		7.3	
Manganese	16.0		17.0		23.4		28.0		57.3		19.0		18.0		17.0		4.2		17.0		14.0	
Mercury	0.08				0.08				0.05		0.13		0.14		0.24		0.02		0.15		0.14	

BIT = bituminous
SUB = subbituminous
SNOX = wet sulfuric acid-selective catalytic reduction process

Table 13-5. Continued

Compound	EPR1 Site 11 DRY	EPR1 Site 111 DRY	DOE Springenville DRY	NSP Sherburne 3 DRY	NSP Riverside 6,7 DRY				
Bottom Type	Tangential	Opposed	Tangential	Opposed	Front				
Furnace Type	SUB	SUB (BIT Mixed)	SUB	SUB	SUB	Total bituminous & subbituminous	Bituminous	Subbituminous	
Boiler emissions (lb/trillion Btu)									
Arsenic	124.1	5.8	81.0	64.4	47.1	Average emissions	Average emissions	Average emissions	Average emissions
Beryllium	9.9		93.4	21.8	9.4	437	606	64	64
Cadmium	58.7	16.6	172.4	7.0	10.3	55	62	34	34
Chromium	248.2		607.0	253.6	326.7	61	64	53	53
Lead	143.1		91.0	525.4	236.1	786	941	359	359
Manganese	1406.5		5627.6	4978.2	480.0	398	453	249	249
Mercury			5.4	6.0	4.3	1639	1100	3123	3123
						5	5	5	5
Boiler emission modification factors									
Arsenic	0.92	0.11	0.29	0.79	0.99	Average percent removal by boiler (1-average EMF)	Average percent removal by boiler (1-average EMF)	Average percent removal by boiler (1-average EMF)	Average percent removal by boiler (1-average EMF)
Beryllium	0.79		0.87	0.58	0.40	27%	22%	38%	38%
Cadmium	0.35	0.05	1.00	0.99	0.25	24%	23%	34%	34%
Chromium	0.72		0.68	0.49	1.00	39%	48%	47%	47%
Lead	1.00		0.19	0.49	0.19	23%	27%	28%	28%
Manganese	0.98		0.72	0.00	0.77	30%	23%	53%	53%
Mercury			1.00	1.00	1.00	24%	29%	38%	38%
						19%	23%	0%	0%
Trace metal concentrations in feed coal (microgram/gram)									
Arsenic	1.6	0.6	1.5	0.7	0.4	Average trace metal concentrations in feed coal (microgram/gram)	Average trace metal concentrations in feed coal (microgram/gram)	Average trace metal concentrations in feed coal (microgram/gram)	Average trace metal concentrations in feed coal (microgram/gram)
Beryllium	0.2		1.1	0.3	0.2	5.5	7.7	1.0	1.0
Cadmium	2.0	4.0	0.5	0.1	0.4	0.9	1.0	0.4	0.4
Chromium	4.1		9.2	4.4	2.6	1.8	2.0	1.4	1.4
Lead	1.4		5.0	9.1	10.5	12.7	15.5	5.1	5.1
Manganese	17.0		80.8		5.4	6.1	5.9	6.5	6.5
Mercury			0.04	0.02	0.001	23.9	21.0	34.4	34.4
						0.09	0.11	0.02	0.02

BIT = bituminous
SUB = subbituminous
SNOX = wet sulfuric acid-selective catalytic reduction process

Figure 13-4a. Average boiler emissions

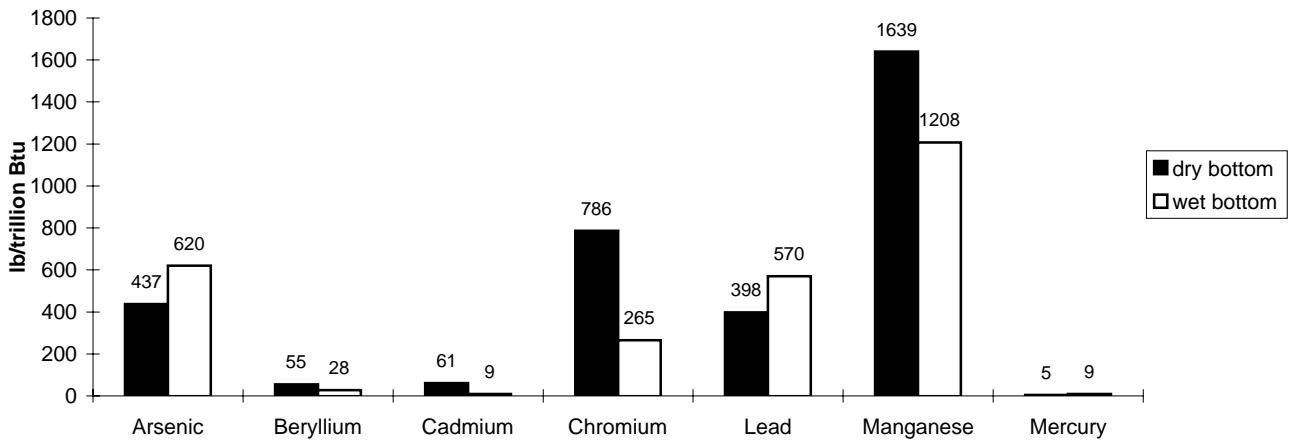


Figure 13-4b. Average trace metal removal by boiler

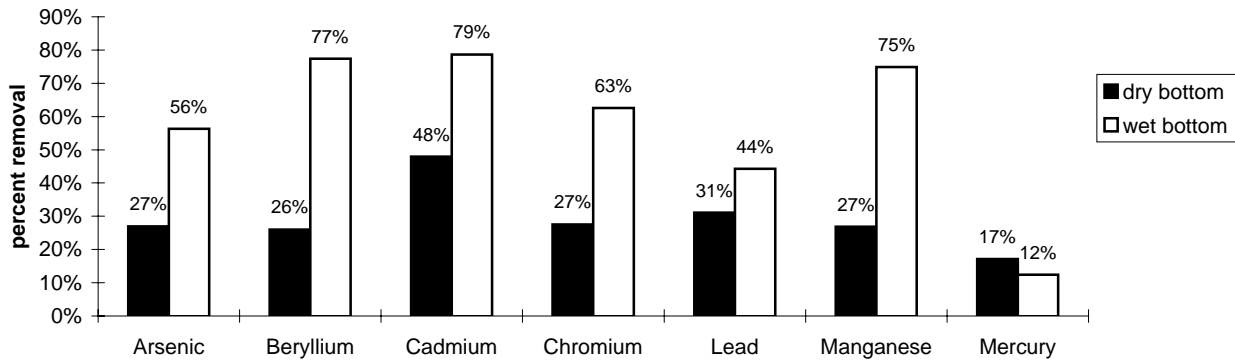


Figure 13-4c. Average trace metal concentration in feed coal

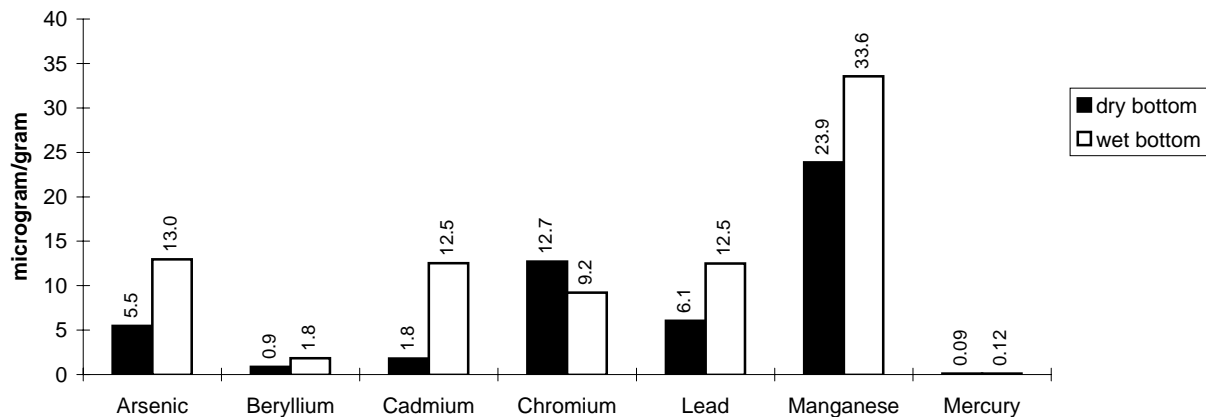


Figure 13-4 (a-c). Average coal-fired boiler emissions, trace metal removal, and average trace element concentration in feed coal vs. bottom type (bituminous and subbituminous coal)

Note: Data taken from Table 13-5.

Figure 13-5a. Average boiler emissions

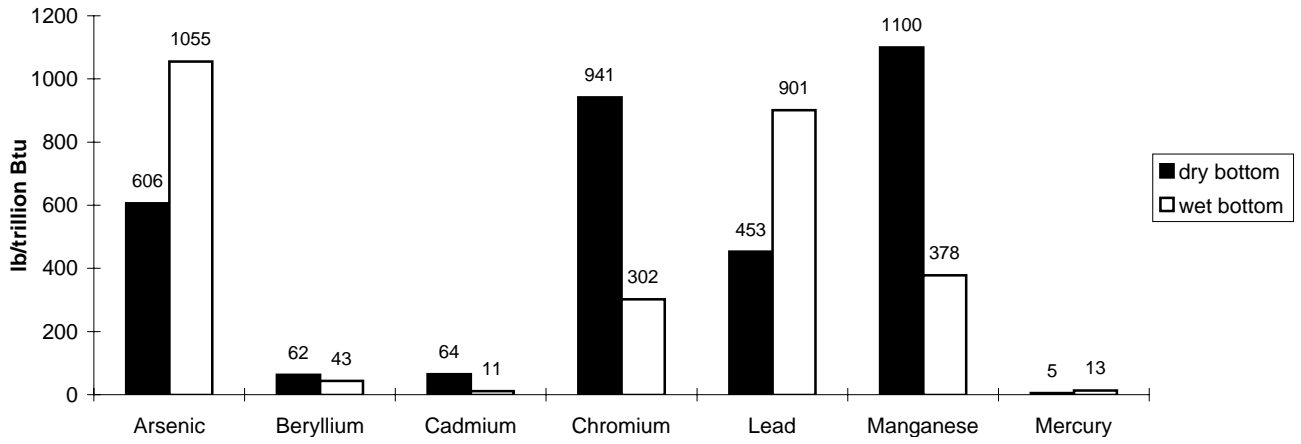


Figure 13-5b. Average trace metal removal by boiler

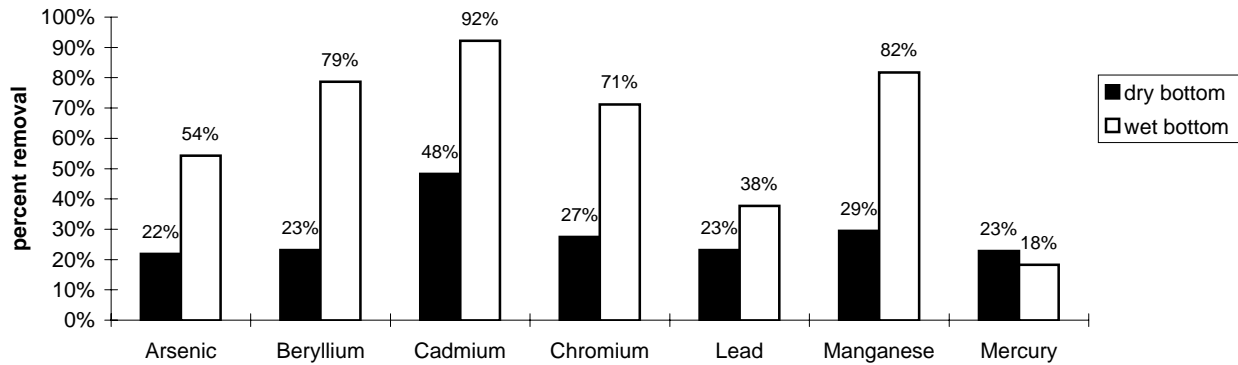


Figure 13-5c. Average trace metal concentration in feed coal

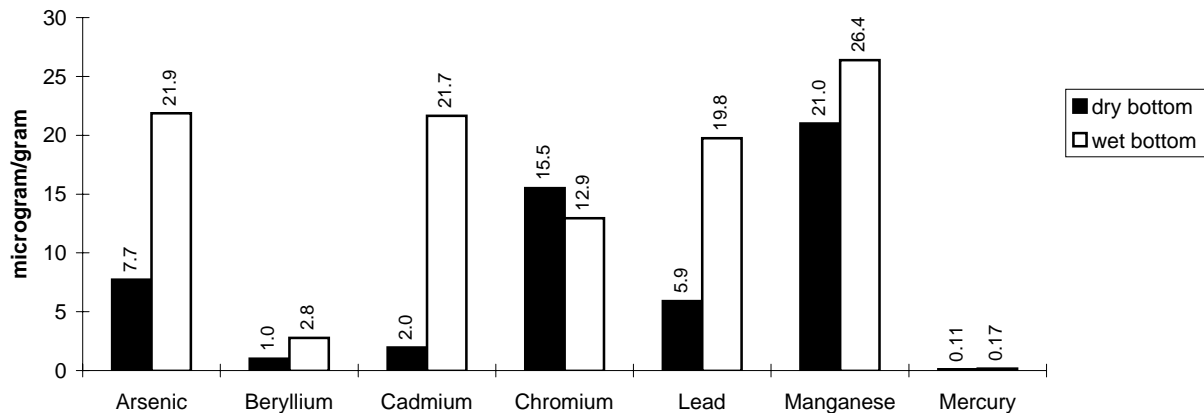


Figure 13-5 (a-c). Average coal-fired boiler emissions, trace metal removal, and average trace element concentration in feed coal vs. bottom type (bituminous coal-fired only)

Note: Data taken from Table 13-5.

Figure 13-6a. Average boiler emissions

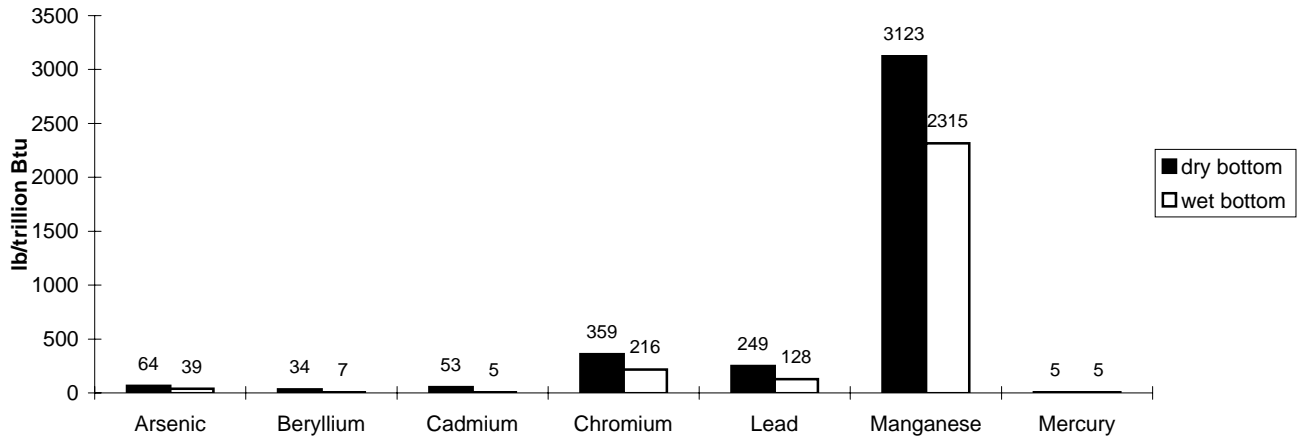


Figure 13-6b. Average trace metal removal by boiler

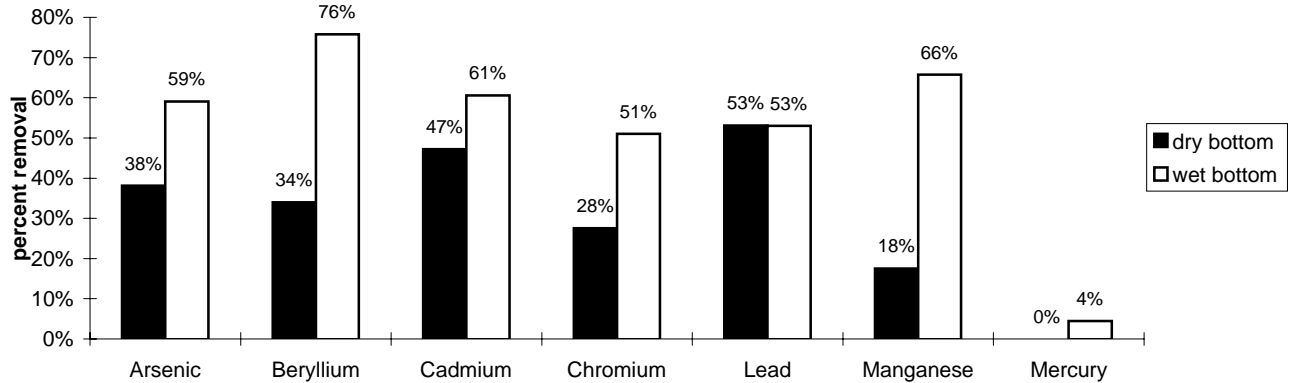


Figure 13-6c. Average trace metal concentration in feed coal

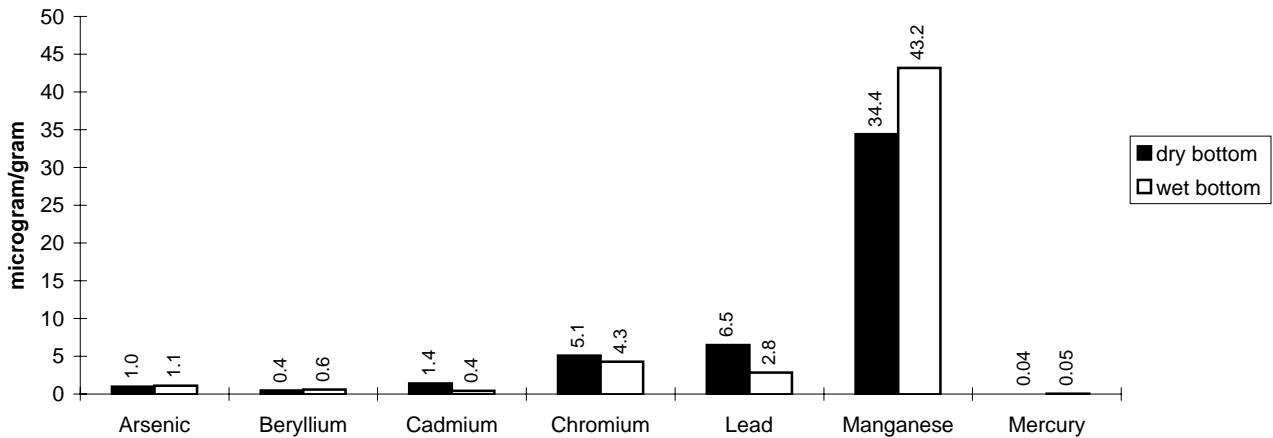


Figure 13-6 (a-c). Average coal-fired boiler emissions, trace metal removal, and average trace element concentration in feed coal vs. bottom type (subbituminous coal-fired only)

Note: Data taken from Table 13-5.

Based on this analysis, wet bottom furnaces seem to have better trace metal removal than dry bottom furnaces. Trace metal removal in a furnace is likely due to the partitioning mentioned above. A possible explanation for the effect would be that bottom ash in a wet bottom furnace is kept in a molten state, and, thus, the trace metals in the bottom ash are less likely to reentrain into the fly ash. It needs to be emphasized that these analyses are based on limited data and may not hold true for all units and coals. More data and analyses are needed.

It needs to be noted that the averages in Figures 13-4(a and b), 13-5(a and b), and 13-6(a and b) were computed from data with EMFs limited to a maximum of 1.0, meaning that no more HAP could exit a device than entered it. All of the data used in these figures had at least one instance in which an EMF of 1.0 was used. This situation did not occur in Figures 13-4(c), 13-5(c), or 13-6(c) because these data were taken directly from the coal feed without modification. The result of this methodology is several sets of data averages where more HAP is emitted than was present in the feed coal. These data averages were composed of a large number of EMFs of 1.0.

13.3 POSTCOMBUSTION CONTROL

To comply with various local, State, and Federal requirements, utilities routinely use postcombustion technologies for the control of PM and SO₂. The following sections assess how different APCDs affect removal of selected HAPs from fossil-fuel-fired electric utility flue gas.

13.3.1 Particulate Phase Controls

Figures 13-7 through 13-14 and Tables 13-6 through 13-9 show the relationship between the HAP metal removal and PM collection efficiency of different particulate controls (namely ESPs and FFs). The HAP removal effectiveness is shown in the tables in this section as percent removal. Percent removal is equivalent to 1 minus the EMF (see chapter 3, section 3.4.6). A 90 percent removal indicates that 90 percent of that HAP has been collected by a PM control device. The HAP metals that exist primarily in particulate form are readily controlled by PM control devices. These HAPs include arsenic, beryllium, cadmium, chromium, lead, and manganese. Table 13-10 shows the percentage of data, for all listed HAPs other than mercury, with a control device HAP removal efficiency greater than 90 percent. For example, 90 percent of the particulate from metallic HAPs data points for cold-side ESPs fall into the 90 percent or better removal category. For the two oil-fired sites for which ESP removal data were available, the control of particulate metallic HAPs was not clear. It should be noted that the concentrations of metallic HAPs in oil, with the exception of nickel, which is not discussed here, are significantly lower than those in coal, and the fuel-ash characteristics are also quite different. These factors could explain the spread of PM HAP removal of 51 to 93 percent.

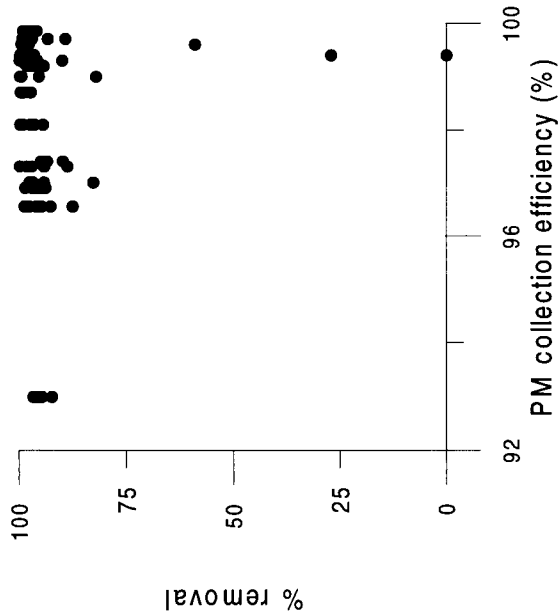


Figure 13-7. Removal of Metallic HAPs by Electrostatic Precipitators (Cold-side, Coal) (Includes, Arsenic, Beryllium, Cadmium, Chromium, Lead, and Manganese)

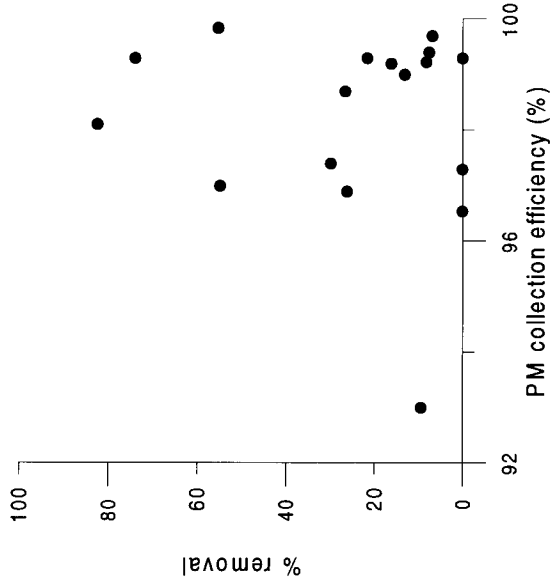


Figure 13-8. Removal of mercury by electrostatic precipitators (cold-side, coal)

	Mean	Median	Sdev	Min	Max	Count
Arsenic	98	99	2.1	94	>99	18
Beryllium	94	98	17	27	>99	18
Cadmium	80	92	31	0	98	18
Chromium	97	97	2.3	93	>99	18
Lead	93	97	15	34	>99	18
Manganese	98	97	1.5	95	>99	18
Mercury	25	16	26	0	82	17

Table 13-6. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-7 and 13-8

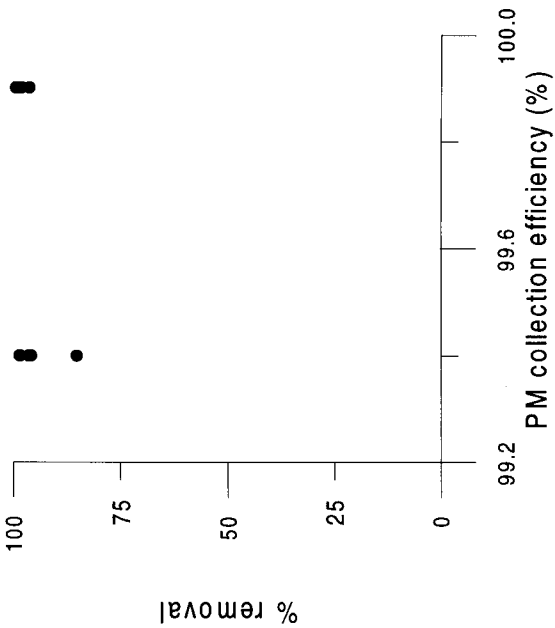


Figure 13-9. Removal of Metallic HAPs by Electrostatic Precipitators (Hot-side, Coal) (Includes, Arsenic, Beryllium, Cadmium, Chromium, Lead, and Manganese)

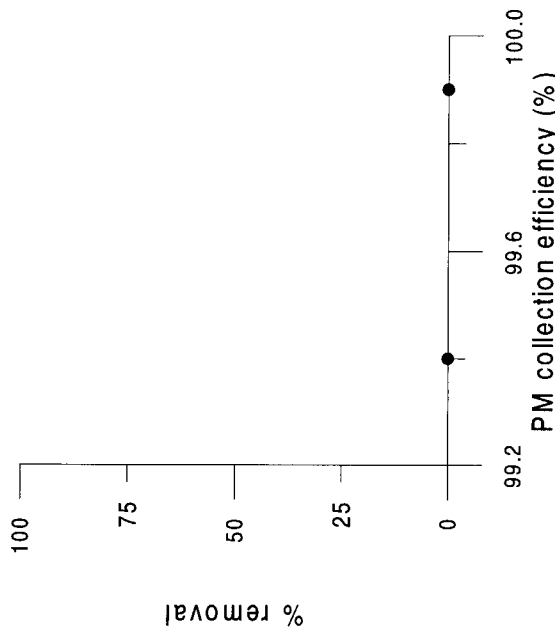


Figure 13-10. Removal of Mercury by Electrostatic Precipitators (Hot-side, Coal)

	Mean	Median	SDev	Min	Max	Count
Arsenic	92	92	10	85	99	2
Beryllium	99	99	0.1	99	99	2
Cadmium	99	99	0.7	99	> 99	2
Chromium	97	97	1.6	96	98	2
Lead	97	97	1.2	97	98	2
Manganese	97	97	1.5	96	99	2
Mercury	0	0	0	0	0	2

Table 13-7. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-9 and 13-10

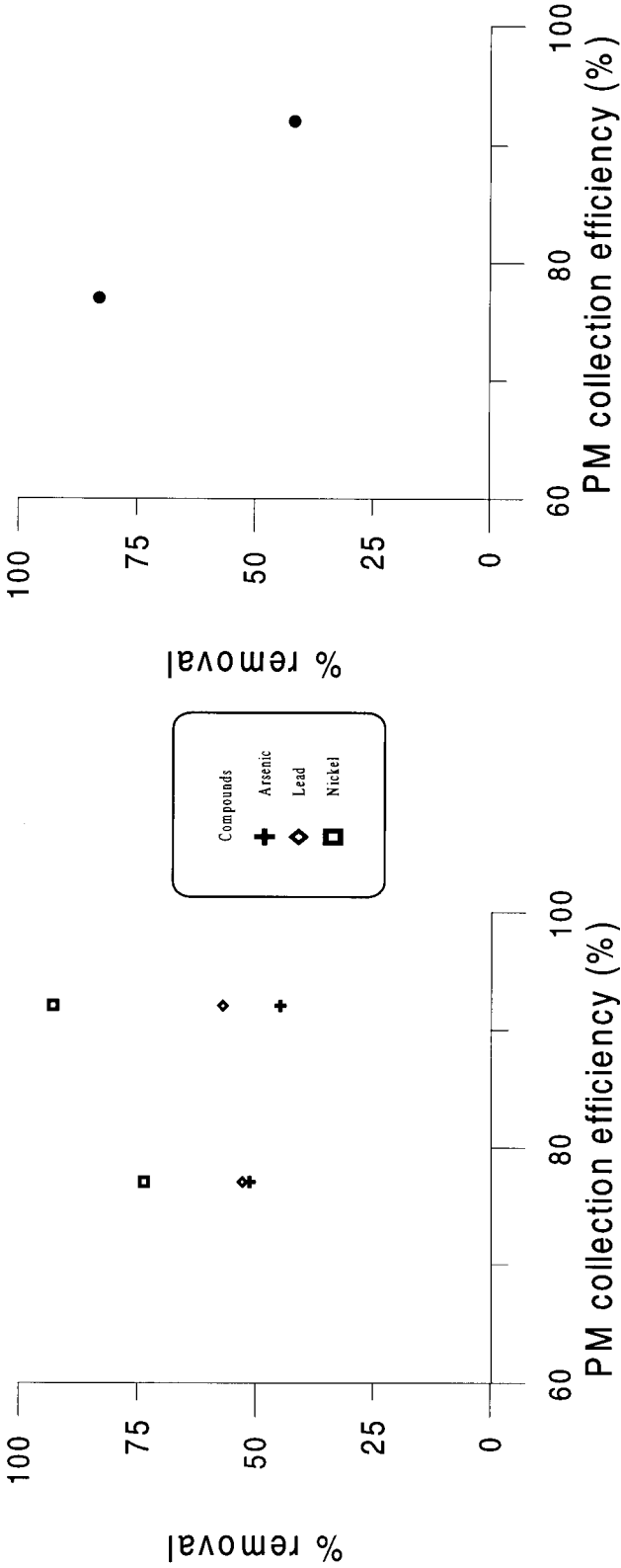


Figure 13-11. Removal of Metallic HAPs by an Electrostatic Precipitator (Oil) (Includes, Arsenic, Lead, and Nickel)

Figure 13-12. Removal of Mercury by an Electrostatic Precipitator (Oil)

	Mean	Median	S.Dev	Min	Max	Count
Arsenic	48	48	4.6	45	51	2
Lead	55	55	2.9	53	57	2
Mercury	62	62	29	42	83	2
Nickel	83	83	14	73	93	2

Table 13-8. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-11 and 13-12

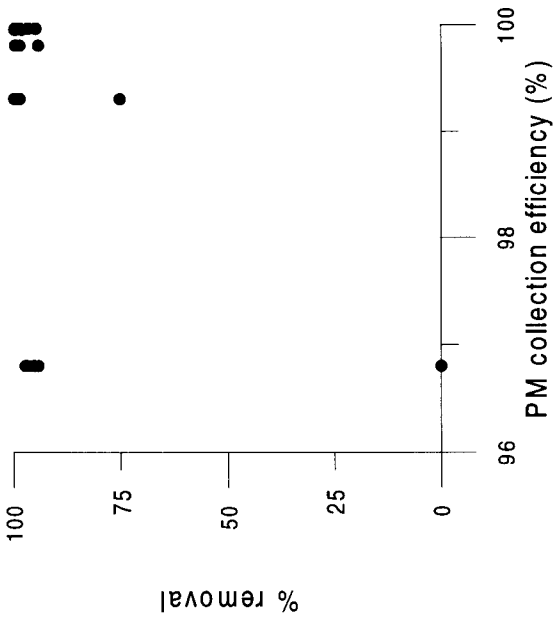


Figure 13-13. Removal of Metallic HAPs by a Fabric Filter (Coal) (Includes, Arsenic, Beryllium, Cadmium, Chromium, Lead, and Manganese)

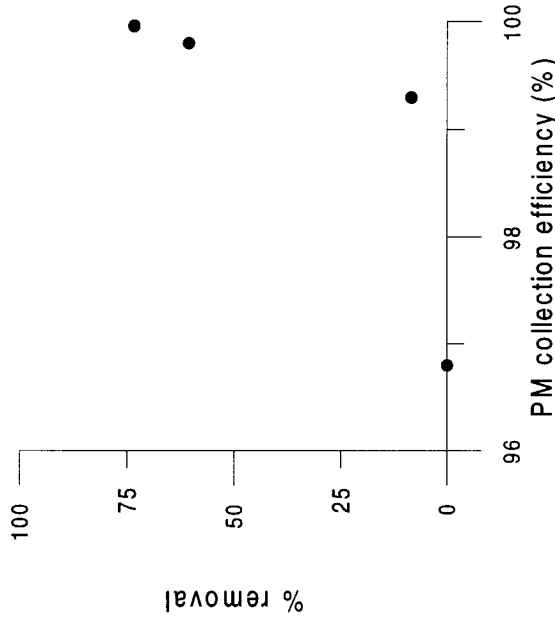


Figure 13-14. Removal of Mercury by a Fabric Filter (Coal)

	Mean	Median	Sdev	Min	Max	Count
Arsenic	99	99	1.4	97	>99	5
Beryllium	99	>99	2.4	94	>99	5
Cadmium	72	95	48	0	99	4
Chromium	94	99	10	75	>99	5
Lead	99	99	1.3	97	>99	5
Manganese	98	99	1.8	95	>99	5
Mercury	36	34	37	0	73	4

Table 13-9. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-13 and 13-14

18, 27-29, 41

Table 13-10. Particulate Metallic HAP Removal Percentage from ESPs and FFs (Excluding Mercury)

Particulate control device (coal)	Number of data points	Percentage of data with a HAP removal efficiency greater than 90 percent
ESP (cold-side)	108	89
ESP (hot-side)	12	92
FF	33	89

ESP = electrostatic precipitator

FF = fabric filter

HAP = hazardous air pollutant

Mercury, however, is not well controlled by PM APCDs. This situation would be expected because mercury is emitted as a mixture of solid and gaseous forms. Mercury removals and current investigations on the control of mercury are further discussed in section 13.6.

Dioxin removal in utility boiler PM control equipment has been measured at one coal-fired boiler and one oil-fired boiler. In both cases, measurements contained many values of uncertain accuracy. However, removal efficiencies could be estimated for one dioxin and three furans at the coal-fired boiler. This unit was a 615-MWe boiler firing Pennsylvania bituminous coal that had an ESP with an overall PM efficiency of 99 percent. The ESP's apparent efficiency for the following compounds was:

- 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin 7 percent
- 2,3,7,8-tetrachlorodibenzofuran 38 percent
- 2,3,4,6,7,8-hexachlorodibenzofuran 35 percent
- 1,2,3,4,6,7,8-heptachlorodibenzofuran 29 percent.

The oil-fired boiler was an 850-MWe unit firing residual oil and had an ESP with an overall PM collection efficiency of 92 percent. All of the measurements for this site indicated negative efficiencies for dioxins and furans in the ESP.

Under certain conditions in MWC systems, dioxins and furans can be formed in the particulate-laden flue gas stream upstream of or within the associated PM control equipment at temperatures in the range of 480° to 1,020° F (250° to 550° C).⁴²⁻⁴⁴ Units that are equipped with hot-side ESPs (ESPs upstream of the air preheater operating at temperatures in the range of 600 to 750°F [316° to 400° C]) are of

particular concern with regard to this formation mechanism since their operating temperatures typically fall within this range. Little information is available regarding dioxin formation in utility particulate removal equipment, however, and additional information is needed to adequately quantify the potential for dioxin formation in utility pollution control systems. Thus, at utility plants, any strategy for dioxin control must consider adequately treating large volumes of gas in order to remove relatively small concentrations of dioxin.

13.3.2 Vapor Phase Controls

Figures 13-15 through 13-18 and Tables 13-11 and 13-12 show the relationship between HAP metal removal and the inlet temperature for SO₂ control devices. The correlation between FGD scrubber inlet temperature and HAP metal removal is difficult to determine. This difficulty is compounded by having a maximum of eight data sites at which four of the eight test sites employ flue gas bypass in their design. A bypass means that part of the flue gas is diverted around the FGD or SDA/FF while the majority of the flue gas is treated by these control devices. Bypass is used to minimize the size and the lime/limestone cost of the FGD unit while still meeting SO₂ emission limits. Another factor is that FGDs usually follow an ESP or an FF; thus, the concentrations of metallic HAPs that reach the FGDs are generally less than 10 percent of the amounts intercepted by primary PM control devices.

The HAP metal removal by SDA/FF-equipped units seems to follow the results found in FF PM-controlled units, i.e., metallic HAPs are controlled to approximately 90 percent or better. This situation follows because an SDA/FF contains an FF.

13.3.3 Acid Gas Control

There was a limited amount of data (using EPA Method 26a) available on the removal efficiencies for HCl and HF from air pollution control devices. Since utilities operate with varying amounts of bypass, removal percentages for FGDs and SDA/FFs were estimated for operations with 15 percent and 14 percent bypass, respectively. The test report data indicated that: ESPs removed less than 6 percent of the acid gases; FFs removed approximately 44 percent of the HCl and essentially none of the HF; an FGD with 15 percent bypass was estimated to remove approximately 80 percent of the HCl and approximately 29 percent of the HF; and an SDA/FF with 14 percent bypass was estimated to remove approximately 82 percent of each acid gas.⁴⁷ Despite the inconsistencies in removal efficiencies achieved for HCl and HF with FFs and FGDs, the data indicate that the SO₂ control devices remove more of the acid gases than do PM controls.

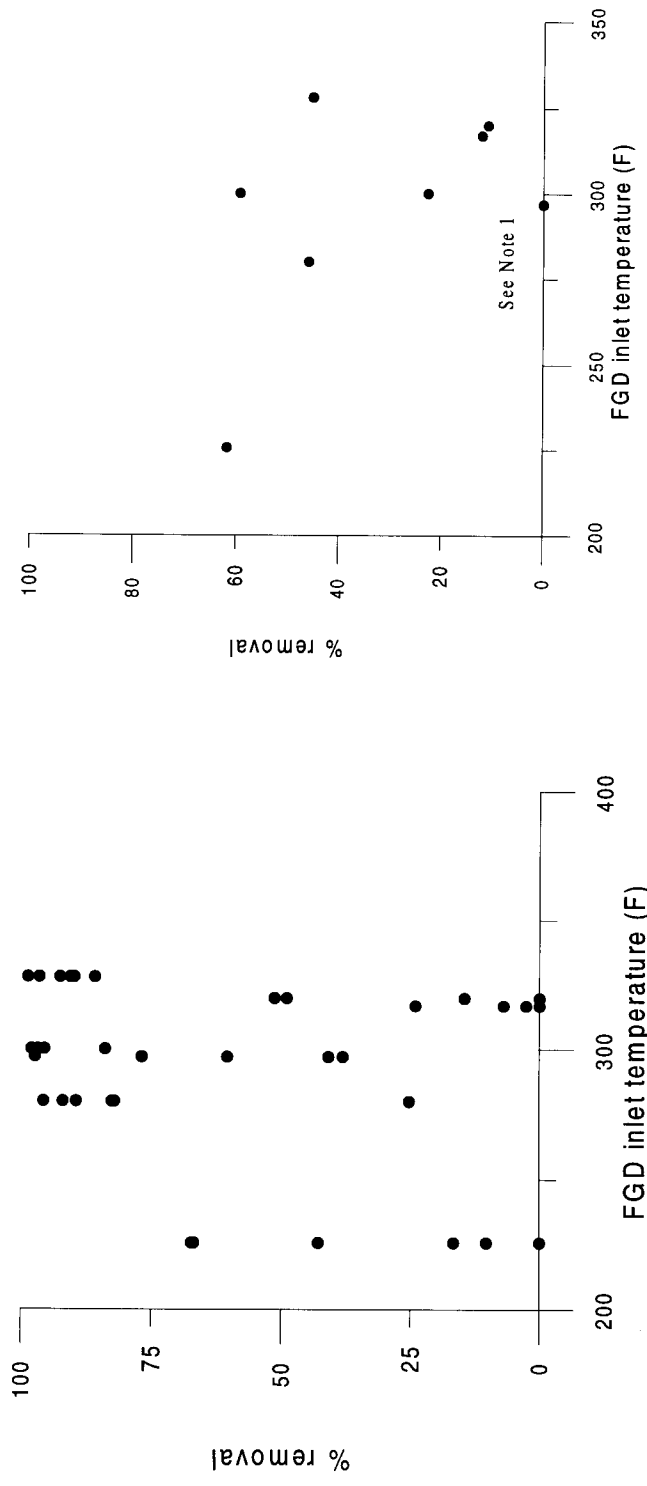


Figure 13-15. Removal of Metallic HAPs by an FGD (Coal) (Includes, Arsenic, Beryllium, Cadmium, Chromium, Lead, and Manganese)

Figure 13-16. Removal of Mercury by an FGD (Coal)

	Mean	Median	Sdev	Min	Max	Count
Arsenic	69	79	26.0	24	96	8
Beryllium	73	87	36	3	98	6
Cadmium	38	25	35	0	90	7
Chromium	55	57	35.8	0	97	8
Lead	57	61	39	0	98	8
Manganese	50	68	47.4	0	99	7
Mercury	31	23	23	0	62	9

Note 1 - This unit (EPR1 Site 12) was retested for mercury, but was tested as a combined ESP/FGD system. Since there was no way of determining which component was responsible for the mercury removal, the ESP was given the full credit for removal. This explains the "zero" data point in Figure 13-16. (The ESP for this site was given an "82" percent removal.)

21, 23, 25, 38, 45, 46, 48-50

Table 13-11. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-15 and 13-16

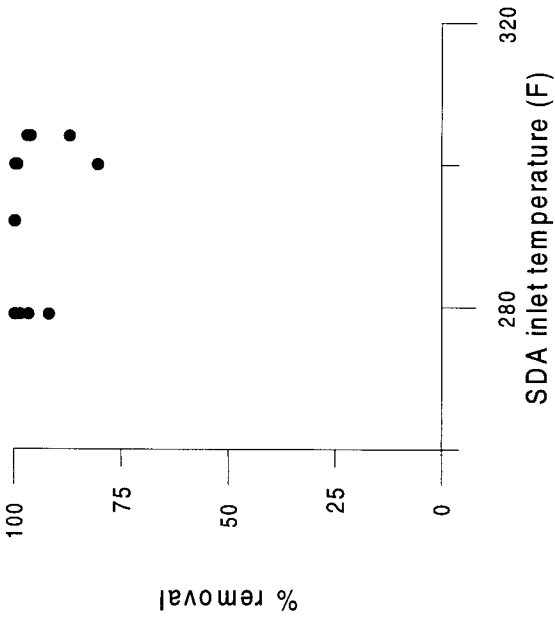


Figure 13-17. Removal of Metallic HAPs by a Spray Dryer Adsorber/fabric Filter (Coal) (Includes, Arsenic, Beryllium, Cadmium, Chromium, Lead, and Manganese)

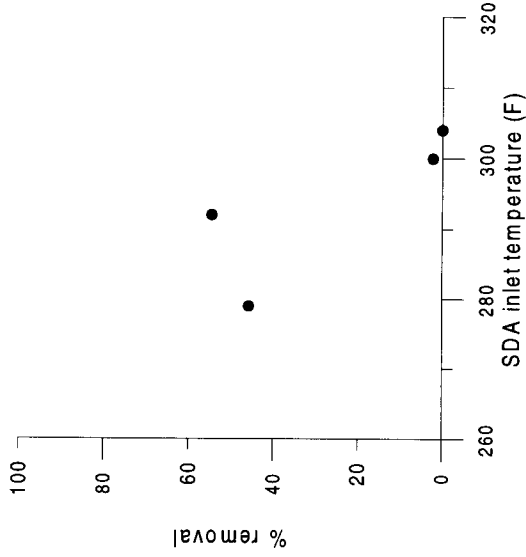


Figure 13-18. Removal of Mercury by a Spray Dryer Adsorber/Fabric Filter (Coal)

	Mean	Median	sDev	Min	Max	Count
Arsenic	99	> 99	1.8	96	> 99	4
Beryllium	> 99	> 99	0.3	99	> 99	3
Cadmium	90	90	8.2	81	> 99	4
Chromium	98	97	1.5	97	> 99	3
Lead	99	> 99	0.7	99	> 99	3
Manganese	> 99	> 99	0.1	> 99	> 99	3
Mercury	26	24	29	0	55	4

Table 13-12. Descriptive Statistics for HAP Removal Efficiencies Shown in Figures 13-17 and 13-18

13.3.4 Carbon Adsorption

A possible way of further reducing the amount of vapor phase HAPs emitted from utilities is through the use of carbon adsorption. Activated carbon (AC) is a specialized form of carbon produced by pyrolyzing coal or various hard, vegetative materials (e.g., wood) to remove volatile material. The resulting char then undergoes a steam or chemical activation process to produce an AC that contains multiple internal pores and has a very high specific surface area. With this internal pore structure, the AC can adsorb a broad range of contaminants.

Activated carbon can be introduced through the use of a fixed-carbon filter bed, a moving bed, a fluidized carbon filter bed, or through direct AC injection into the flue gas stream.

Other than for mercury (see section 13.6.1.2), no utility data were found for AC removal of HAPs. However, for other industries (e.g., MWCs and medical waste incinerators [MWIs]), dioxin removal from the flue gas stream has also been achieved by AC injection.

13.4 ALTERNATIVE CONTROLS

An alternative to pollution control systems applied directly to boiler systems is to use alternative, nontraditional control methods such as demand side management (DSM) and energy conservation. Demand side management addresses the issue of reducing potential HAP emissions by reducing the amount of electricity needed. This objective can be accomplished by several different methods.

Through the use of progressively higher efficiency electrical devices (e.g., more efficient home appliances, lighting systems, and industrial machinery), the overall tonnage of fossil fuel burned would be reduced.⁵¹ Also, campaigns to reduce the use of fossil-fuel-generated electricity have a positive effect on reducing HAPs by slowing down the necessity of building additional plants. Research into more efficient electrical generators and transmission equipment could produce units that deliver the same amount of energy for less fuel.⁵²

Another potential fuel option is the use of liquid or gaseous fuels derived from biomass. Currently, fuels such as ethanol and methanol, derived from corn, grains, and other crops, are being used to produce "gasohol" (a blend of up to 10 percent ethanol in gasoline). Future use of these fuels by utilities, as well as hydrogen fuels derived from biomass, could reduce (but perhaps not eliminate) HAP emissions. However, DOE has estimated that development of technologies to produce sufficient quantities of biomass-derived fuels may not be commercially viable until 2030.⁵³ Other assessments indicate that with realistic investments in research and development

in both crop production and generation techniques, biomass could be competitive (without subsidies) in niche markets within 5 years (with high energy prices, which are not currently forecast) and within 10 years in larger markets.⁵⁴

Another method would be to switch to a source of renewable energy (e.g., wind, solar), but to date these methods have been limited to certain geographic locations only. (However, such campaigns may also lead to slower introduction of new, more efficient fossil fuel-burning technologies.)

Future potential electrical transmission equipment could include the development and use of superconductive power lines, which could substantially reduce the amount of electricity that needs to be generated to move the high voltage electricity through power lines because of the negligible power loss (due to lower resistance).⁵⁵

13.5 POLLUTANT TRADEOFFS

13.5.1 HAP Increase/Decrease

The various strategies for limiting HAP emissions, discussed in sections 13.1 through 13.4, have different effects in controlling air emissions of all HAPs. Table 13-13 presents the qualitative effects of the different control strategies on air emissions.

Table 13-13 provides a comparison of HAP removal effectiveness of different existing and alternative control strategies. As shown in Table 13-13, the effect on HAP emissions of: (1) switching from a higher- to a lower-sulfur coal, (2) NO_x controls, and (3) boiler types cannot be predicted from the available data. Techniques that would reduce emissions of the HAPs of concern include: (1) switching from coal or oil to natural gas; (2) coal gasification; and (3) alternative controls, such as energy conservation or DSM. The remaining strategies control certain HAPs. Existing PM control devices, such as ESPs and FFs, generally do not remove the vapor-phase HAPs (i.e., organics, elemental mercury, HCl, and HF). (However, these controls do provide some reduction of ionic mercury emissions.) Emissions of the vapor-phase HAP, dioxin, are not controlled by ESPs but are controlled to some extent with FFs because dioxins adsorb onto the filter cake. As noted in section 13.3.1, there is the potential for dioxins to be produced in hot-side ESPs due to the temperature and catalytic effects of the fly ash. With the exception of elemental mercury emissions, the existing SO₂ control devices, namely FGDs and SDA/FFs, tend to reduce emissions of the HAPs and provide some reduction of emissions of ionic mercury.

Table 13-13. Qualitative Effects of Different Control Strategies on Air Emissions of HAPs

Type of alternative control strategy	Effect on particulate HAPs		Effect on mercury		Effect on acid gases (HCl, HF)	Effect on dioxin
	Primarily organically bound	Primarily inorganically bound	Primarily oxidized mercury	Primarily elemental mercury		
PRECOMBUSTION CONTROL						
Conventional coal cleaning	No removal	Decrease in emission	Decrease in emission (highly coal-specific)		Decrease in emission if chloride or fluoride is reduced	
Coal gasification	Decrease in emission		Cannot predict the effect		Decrease in emission	
<i>Fuel switching</i>						
From a higher to lower sulfur coal	Cannot predict the effect		Cannot predict the effect		Cannot predict the effect	
To western and certain eastern coals	Cannot predict the effect		Cannot predict the effect		Cannot predict the effect	
Coal or oil to gas	Decrease in emission		Decrease in emission		Decrease in emission	
COMBUSTION CONTROLS						
NO _x controls	Cannot be determined without further testing					
Boiler type	Cannot be determined without further testing					
POSTCOMBUSTION CONTROLS						
<i>Particulate phase controls</i>						
ESP	Decrease in emission		Some decrease in emission	No effect	No effect ^a	
FF	Decrease in emission		Some decrease in emission	No effect	No effect	Decrease in emission because of filter cake adsorption
<i>Vapor phase controls</i>						
FGD	Decrease in emission		Decrease in emission	No effect	Decrease in emission	
SDA/FF	Decrease in emission		Some decrease in emission	No effect	Decrease in emission	
Carbon adsorption	Decrease in emission. (Elemental and ionic mercury were removed, respectively, by impregnated and unimpregnated carbon adsorption, in pilot-scale studies.)					
NON-TECHNOLOGY-BASED CONTROL OPTIONS						
Demand management	Decrease in emission					

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^a There is the potential for dioxins to be produced in hot-side ESPs due to the temperature and catalytic effects of the fly ash.

Emissions of HAPs could be reduced through energy conservation or DSM. Finally, pilot-scale studies suggest that ionic and elemental mercury emissions could be controlled, respectively, with unimpregnated- and impregnated-carbon adsorption, but full-scale testing is needed to establish the effectiveness of these techniques.

13.5.2 Water/Solid Waste Considerations

Coal cleaning can produce a variety of waste problems.⁵⁶ The process creates a liquid waste containing fine coal particles and inorganic elements and compounds dissolved from the ash in the coal. The large volumes of water used in the cleaning process and the large amount of suspended solids generated dictate that process water be clarified and recycled. The usual means of clarification is retention in large sedimentation ponds. Contamination of surface water or groundwater can occur from coal wastepiles or storage piles if water is allowed to infiltrate them. Contaminants such as iron, manganese, and heavy metals (such as cadmium and silver) may leach from the wastes.⁵⁶

Precombustion controls such as fuel switching could have an effect on reducing this waste. If coal with lower amounts of ash and sulfur was mined, there would be less need to clean the coal and therefore fewer tailings would be created at the coal washing site. Switching from coal to natural gas would reduce the need to mine and wash the coal.

In either case, the amount of bottom ash and captured fly ash is quite large. Because the metals are not destroyed in the combustion process, the ash will have a higher concentration of metals than the coal, and water contamination may occur if water runoff from the ash is not controlled. The amount of metals in ash disposal pits is not likely to increase significantly if particulate controls are already in place. If new controls are installed, larger amounts of ash will require disposal, leading to an increase in the potential for water contamination from ash leachate.

Coal gasification would not necessarily reduce the waste potential of coal, but the processing of coal into a gasified form would tend to localize the waste and transfer it from a gaseous stream to a solid stream that could be more easily disposed of after being properly treated.¹⁰ For example, gasifier residue may contain contaminants in a nearly vitreous matrix that is not easily leached. In conventional coal combustion, these contaminants would largely appear in the flue gas stream.

Combustion controls, such as different boiler/furnace types or the adding of NO_x controls, would have the effect of changing combustion conditions in the coal-fired furnace and, thus, changing

the ratio of bottom ash to fly ash. Increasing the amount of bottom ash in the furnace would consequently reduce the amount of fly ash exiting the furnace. However, if the amount of fly ash exiting the furnace was increased, there would be greater fly ash loading on the PM controls. If the PM controls were not designed to accept this additional load, excess fly ash could cause stack opacity problems and higher HAP emissions.

The wet FGD processes use a liquid absorbent to absorb SO₂ gases. This absorbent is most likely an alkaline slurry composed of lime or limestone slurried with water that can be used in a regenerable process or in a nonregenerable process. Both processes produce a calcium sludge effluent that must be disposed of properly. The sludge can be stored in a settling pond or dewatered to take up less space in a landfill.⁵⁷ In addition to removing sulfur oxides, regenerable processes generate a usable product from the sludge, such as gypsum, which can be used in the manufacture of wallboard.

In a dry FGD system, the flue gas is contacted with an alkaline material to produce a dry waste product for disposal. The alkaline material can be added either in the fuel prior to combustion, through dry injection into the flue gas, or as an alkaline slurry.⁵⁸ For example, SDAs inject a lime/limestone alkaline slurry into the flue gas stream. The reagent droplets absorb SO₂ while simultaneously being dried. In all these methods, the resulting dried reagent and fly ash are then captured by an FF or ESP and, thus, do not represent an additional liquid or solid waste problem except that the sorbent may contaminate salable fly ash.

The use of all forms of carbon adsorption have the potential to add additional PM loading to existing PM controls. Also, the spent AC either has to be disposed of as an additional solid waste or regenerated and reused. Studies on other industries indicate that the adsorbed HAP (e.g., mercury, dioxin) does not have a tendency to leach out of the AC.

Section 3001 (b)(3)(c) of the Resource Conservation and Recovery Act (RCRA) required that the EPA determine, based on the results of a study required by section 8002(n) of RCRA, whether RCRA subtitle C regulation of fossil fuel combustion wastes is warranted. On August 9, 1993, the Agency determined that regulation of four large-volume waste streams resulting from fossil fuel combustion (specifically, coal combustion in utility steam-generating units) was inappropriate. These waste streams are fly ash, bottom ash, boiler slag, and flue gas emission control waste. However, any change in the characteristics of these wastes resulting from actions taken to specifically control HAPs could necessitate a review of that decision by the Agency.⁵⁹

Changes in all elements of the alternative controls, from conservation to technology improvements, can reduce the amount of waste produced by the utility industry.

13.6 AVAILABLE CONTROL TECHNOLOGY AND STRATEGIES FOR MERCURY CONTROL

Typical mercury removal efficiencies for conventional emission controls are discussed in section 13.3. Conventional controls are generally inconsistent in their effectiveness, and range from 0 to more than 83 percent removal (based on emissions testing at full-scale utility boilers).

Strategies for further reducing mercury emissions from electric power generation include demand reduction to decrease overall fossil fuel use, use of other forms of generation (e.g., nuclear power, biomass), switching to fuels having less mercury (e.g., natural gas), improving the mercury removal efficiency of conventional controls, and adding controls that remove mercury more effectively than conventional controls. The mercury content in utility flue gas ranges from 0.2 $\mu\text{g}/\text{dry standard cubic meter}$ ($\mu\text{g}/\text{dscm}$) to 25 $\mu\text{g}/\text{dscm}$ at 7 percent oxygen and standard conditions of 20° C and 1 atmosphere, while utility flue gas flow rates may range from 10,000 to 4,000,000 dscm/min.⁶⁰ Thus, at utility plants, any strategy for mercury control must consider adequately treating large volumes of gas in order to remove relatively small concentrations of mercury as well as addressing any resulting impacts on power plant equipment operations (such as particulate control devices) and on waste disposal issues.

There has been some evidence that a higher carbon content in fly ash may lead to lower levels of stack mercury emissions, with the hypothesis being that the mercury is adsorbed by the carbon in the flue gases. There is other evidence that the chloride content of the coal impacts on the form and suitability of mercury removal by conventional control systems. This evidence has led to research on improving mercury removal from utility flue gas streams.

This section briefly reviews one pre-combustion technology (coal cleaning) and three classes of post-combustion technologies (enhancement of existing APCDs, carbon injection, and novel techniques). Additional information may be found in Appendix I.

13.6.1 Pre-Combustion Strategies

As mentioned in section 13.1.2, conventional coal cleaning may be effective for reducing mercury concentrations only in specific coals and, at this time, cannot be considered a mercury control technique for all coals.⁶³ Advanced coal cleaning techniques are being

investigated for improved mercury removal potential. Like conventional cleaning techniques, the advanced cleaning techniques cannot be considered a mercury control technique for all coals at this time.

Advanced coal cleaning methods such as selective agglomeration and column froth flotation have the potential to increase the amount of mercury removed by conventional cleaning alone. Bench-scale studies indicate that the combination of conventional and advanced coal cleaning techniques removed from 40 to 82 percent of the mercury contained in eight samples of raw coal.^{61,62}

Advanced cleaning methods, such as column froth flotation, are starting to emerge. Microcel™ is a type of column froth flotation available through ICF Kaiser and Control International. The company is the exclusive licensee for the technology in the coal fields east of the Mississippi River and has sold units for commercial operation in Virginia, West Virginia, and Kentucky. Ken-Flote™ is another type of column froth flotation cell.

13.6.2 Post-Combustion Strategies

13.6.2.1 Impact of Fuels and Temperature on Mercury Emissions
Fuels and the temperature of the flue gas can have a significant impact on the quantity of mercury emissions in the flue gas from a boiler and on the ability of control systems to remove the mercury.

13.6.2.1.1 Fuels and Mercury Speciation. Mercury is contained in the coal and oil fuels burned in utility boilers. During combustion, mercury readily volatilizes from the fuel and is found predominantly in the vapor phase in the flue gas⁶³ in one of three forms: (1) elemental, (2) ionic, or (3) organic.

In the early 1990s, test methods were developed to quantify the species of mercury present in utility flue gas. Since that time, more accurate speciation test methods (e.g., Ontario Hydro, EPA draft 101B) have been developed. Mercury speciation testing indicates that the distribution of ionic mercury, most likely mercuric chloride (HgCl_2), and elemental mercury each varied in the sampled coal-fired utility flue gas.

Preliminary test results suggest that the chloride concentration in the coal and the type of coal (e.g., bituminous, subbituminous, or lignite) may be associated with a particular speciation of mercury in the flue gas, but more data are needed to verify these associations. Specifically, higher concentrations of ionic mercury were associated with tested coals containing high chloride concentrations (0.1 to 0.3 weight percent),⁶⁴⁻⁶⁶ while 149° C (300° F) flue gas from tested

subbituminous coals appeared to contain approximately ten times the percentage of elemental mercury as compared with flue gas from tested bituminous coals.⁶⁷⁻⁶⁹ The variability in the speciation of vapor-phase mercury in coal-fired flue gas may explain the variation in mercury removal that is seen with existing control devices.⁷⁰

The association between fuel chloride content and the concentration of ionic mercury in the flue gas may also apply to fuel oil, but this association has not been examined. Analysis of two samples of flue gas suggests that mercury is predominantly in the elemental form when the fuel is oil.

It is important to understand mercury speciation because it will indicate potential ways to reduce mercury emissions. For example, the ionic mercury form (i.e., Hg^{++}) is water soluble. Wet scrubbing of the flue gas may result in increased ionic mercury removal.

The scrubbing affinity for ionic mercury has been observed in pilot-scale studies. Preliminary results from tests of pilot-scale wet and dry scrubbers indicate that at least 90 percent of the ionic mercury was captured, while the removal of elemental mercury ranged from 0 to approximately 70 percent.^{65,66,71-73} These preliminary test results suggest that a scrubbing system will have a low mercury removal efficiency if it treats flue gas from a boiler that fires subbituminous coal (containing relatively more elemental mercury) and a high mercury removal efficiency if it treats flue gas from a boiler that fires bituminous coal (containing relatively more ionic mercury).⁷⁴ Full-scale studies are needed to verify these observations.

Speciation of mercury is important in planning control strategies but is still under investigation. The speciation information is also needed to understand what is emitted from utility stacks, how it is affected by atmospheric chemistry, and the subsequent deposition of mercury.

13.6.2.1.2 Temperature. Utility flue gas typically has a temperature range of 121° to 177° C (250° to 350° F) after leaving an air preheater, which is a heat exchanger commonly used to heat incoming combustion air.⁶⁰ Mercury is found predominantly in the vapor phase in utility flue gas.⁶³ If the vapor-phase mercury was condensed onto PM, the PM could be removed with existing PM control devices. Theoretically, cooler temperatures will give relatively more mercury condensation onto PM⁶³ and, subsequently, increased mercury removal with existing PM control devices.

There is limited, preliminary evidence for the temperature dependence of mercury removal in a pilot-scale FF study. The pilot

study suggests that mercury removal efficiencies apparently increased from 27 percent to 51 percent as the temperature of the flue gas decreased from 107° C (225° F) to 96° C (205° F).⁷⁵

13.6.2.2 Effectiveness of Mercury Capture Effectiveness of Existing Pollution Control Technology. Typical mercury removal efficiencies for conventional emission controls are discussed in section 13.3. Since conventional controls are generally inconsistent in their effectiveness, with a range from 0 to more than 83 percent removal (based on emissions testing at full-scale utility boilers), conventional controls cannot be considered a mercury control strategy for all electric utility plants at this time. Due to the limited effectiveness of conventional controls, research continues on ways to improve mercury capture by conventional emission control devices, sorbent injection, and the development of novel techniques. In order to develop low cost post-combustion mercury strategies for full-scale utility operation, fundamental research must continue on the chemistry and interactions of flue gas constituents, fly ash, and mercury-species encountered at various flue gas conditions across the utility industry.

The following sections briefly describe research on enhancing mercury removal with existing control technologies, activated carbon injection, and development of novel mercury control technologies.

13.6.2.3 Enhancement of Existing Control Devices.

13.6.2.3.1 Enhanced Particulate Control. Several approaches to improving the capture of fine particles and mercury with existing control devices are being investigated. Studies are underway on enhancing particulate control with a new Asea Brown Boveri (ABB) precharger, a wet ESP, flue gas cooling and humidification, and an advanced power supply (the ABB Switched Integrated Rectifier). Flue gas cooling and humidification tests are currently in progress. This approach shows promise in improving the collection of particulate-bound mercury, and may also cause vapor-phase mercury to condense on particulate matter and be captured in the ESP.⁷⁶ Research is also underway on optimizing the mercury removal capability of conventional pollution control technologies.⁷⁷

13.6.2.3.2 Enhanced Wet Scrubbers. Several approaches to improving the capture of total and elemental mercury are being investigated. These include optimizing the liquid-to-gas ratio, wet FGD tower design, and improved elemental mercury removal with scrubbing liquid additives and catalysts. Brief descriptions of these approaches follow.

Liquid-to-gas ratio. The liquid-to-gas (L/G) ratio of a wet FGD system is dictated by the desired removal efficiency of SO₂ and impacts the removal efficiency of oxidized mercury. In general, high efficiency (95 percent SO₂ removal) systems are designed with L/G ratios of 120 gal/1000 acf to 150 gal/1000 acf. In two separate pilot-scale studies, increasing the L/G ratio from approximately 40 gal/1000 acf to approximately 125 gal/1000 acf increased the removal efficiency of oxidized mercury from 90 percent to 99 percent.^{73,78} Test data suggest that increasing the L/G ratio did not affect the removal efficiency of elemental mercury, which was close to zero percent.⁷⁹

Wet FGD tower design. Most of the existing U.S. wet FGD systems have open spray tower or tray tower designs.⁸⁰ Recent research has shown that tray tower designs are more effective in removing oxidized mercury from boiler flue gas than tower designs. In one study of wet FGD systems, where the composition of the flue gas was mostly oxidized mercury, the tray tower design removed from 85 to 95 percent of the total mercury, whereas the open spray tower design removed from 70 to 85 percent of the total mercury.⁸¹

Improved elemental mercury removal. Since two studies noted higher concentrations of elemental mercury in the outlet of a wet FGD system compared to the inlet concentrations of elemental mercury,^{82,83} research is in progress on ways to convert and capture elemental mercury. Research currently is investigating scrubbing liquid additives and catalysts to convert elemental to ionic mercury.

Several scrubbing liquid additives that combine strong oxidizing properties with relatively high vapor pressures are being investigated as techniques to enhance the capture of mercury in a wet scrubber. Of three halogen (i.e., chlorine, bromine, and iodine) solutions tested to date, the chlorine solution appears to remove the most elemental mercury in the presence of SO₂ and NO. Further testing of these and possibly other oxidizing reagents is planned.⁸⁴

Due to a much higher solubility compared to elemental mercury, oxidized mercury is readily removed in a wet scrubber. Investigations are underway on the conversion of vapor-phase elemental mercury to more soluble Hg⁺⁺ in bench and pilot-scale studies. The effect of flue gas temperature and residence time on the oxidation potential of a number of catalysts and coal-based fly ashes is being studied. To date, pilot-scale tests of three iron-based catalysts, a carbon, a bituminous, and lignite fly ash have shown the carbon-based catalyst to be the most effective in converting elemental mercury to Hg⁺⁺. Further testing of the carbon catalysts is planned.⁸⁵

13.6.2.4 Activated Carbon Injection. Activated carbon (AC) injection is considered a potential control technology for mercury

emitted from electric utilities, since a form of this technology has been successfully demonstrated on medical waste incinerators and municipal waste combustors.⁸⁶⁻⁸⁹

The level of mercury control that might be achieved with AC injection into utility flue gas may depend upon flue gas characteristics such as temperature, chloride content (in the fuel), mercury content (in the flue gas), and the volume of flue gas. As shown in Table 13-14, these properties distinctly differ from those in MWC flue gas. In particular, mercury concentrations in MWC flue gas streams may be up to several orders of magnitude greater than those seen in utility flue gas streams.

Due to the differences between the flue gas characteristics at MWCs and utility units, the application of AC injection to utility flue gas has not been directly scaled from the application at MWCs. At utility plants, the small concentrations of mercury are contained in a large volume of flue gas, and large amounts of AC may be needed to provide adequate contact between the carbon particles and mercury. Pilot-scale studies of AC injection on utility flue gas have been conducted, but full-scale testing is needed to determine the feasibility of using AC at utility plants.

13.6.2.4.1 Factors Affecting Mercury Removal Efficiency.

Preliminary data from various pilot- and bench-scale studies suggest that factors besides the optimum amount of AC that is injected may affect mercury removal. These factors are temperature, the speciation of the vapor-phase mercury and type of activated carbon⁶⁷ injected into the flue gas, and flue gas composition.

Temperature. A pilot-scale study of AC injection upstream of an FF suggests that mercury removal efficiencies and the required amount of AC injection were apparently temperature dependent.⁷⁵ In reducing the temperature from approximately 116°C (240°F) to approximately 93°C (200°F), the mercury removal increased from approximately 80 percent (with an injection rate of approximately 3,500 µg carbon/µg of inlet mercury) to approximately 98 percent (with an injection rate of approximately 155 µg carbon/µg of inlet mercury). (The high mercury removal percentages suggest that flue gas contained mostly ionic mercury.)

These test results suggest that more mercury is removed and less carbon is needed at lower flue gas temperatures. However, it may not be possible to lower the flue gas temperature sufficiently at a given utility plant because utility plants typically operate with a stack gas temperature between 121° and 177° C (250° and 351° F) upstream of any PM control device to avoid acid condensation and, consequently, equipment corrosion. The stack gas temperature may be lowered below

Table 13-14. Comparison of Typical Uncontrolled Flue Gas Parameters at Utilities and MWCs^a

Uncontrolled flue gas parameters	Coal-fired utility boiler ^{60,90}	Oil-fired utility boiler ^{91,92}	MWC ^b ^{93,94}
Temperature (°C)	121 - 177	121 - 177	177 - 299
Mercury content (μg/dscm)	1 - 25	0.2 - 2	400 - 1,400
Chloride content (μg/dscm)	1,000 - 140,000	1,000 - 3,000	200,000 - 400,000
Flow rate (dscm/min)	11,000 - 4,000,000	10,000 - 2,000,000	80,000 - 200,000

MWC = municipal waste combustion

^a Standard conditions are 0° C and 1 atmosphere.

^b Moisture content in the MWC flue gas was assumed to be 13.2 percent.

96° C (205° F) and still avoid acid condensation, provided low-sulfur coals (less than about 1 weight percent sulfur) are burned.⁹⁵ If the utility burns low-sulfur coal and uses an ESP for PM control, the flue gas will probably require conditioning to reduce the high resistivity of the fly ash since high resistivity makes the fly ash hard to collect in an ESP.

Speciation of mercury. The effectiveness of AC injection in recovering different forms of mercury is still under investigation. The available data indicate iodide- and sulfur-impregnated AC are needed for significant elemental mercury removal.

Studies without AC injection at a pilot-scale SDA/ESP system in Denmark and a full- and pilot-scale SDA/FF system indicated that essentially all of the ionic mercury was removed (with greater than 97 percent removal efficiencies) while essentially none of the elemental mercury was removed (with 0 to approximately 3 percent removal efficiencies).⁶⁵ Studies indicated that the removal of elemental mercury was increased to approximately 50 percent with AC injection ahead of the SDA/ESP and SDA/FF and to approximately 93 percent with injection of iodide- and sulfur-impregnated AC ahead of two pilot-scale test systems (a SDA/FF system and the University of North Dakota Energy and Environmental Research Center (UNDEERC) system consisting of a boiler and baghouse).^{65,96} Pilot-scale testing at the UNDEERC system indicated that the percent-removal of elemental mercury with lignite-based AC was temperature dependent.⁹⁷

Since mercury speciation affects total mercury removal from utility flue gas with AC injection and because the speciation of

mercury is not understood at this time, more data are needed to establish the factors that affect, and to characterize, mercury speciation in utility flue gas.

Flue gas composition. Flue gas components such as sulfur oxides, water, and chlorine compounds can affect the mercury removal efficiency of carbon. A recent bench-scale study investigated the effects of SO₂ and HCl on the adsorption of elemental mercury and mercuric chloride (HgCl₂) by a lignite-based activated carbon.⁹⁸ Removing SO₂ from the flue gas increased the equilibrium adsorption capacity for elemental mercury by a factor of about 5.5 compared to 3.5 for mercuric chloride. Removing HCl from the flue gas did not affect the equilibrium adsorption capacity of the carbon for mercuric chloride; however, it did prevent the carbon from adsorbing elemental mercury. With no HCl in the gas, the carbon adsorption capacity for mercuric chloride was larger than that for elemental mercury. Other carbons may not be affected by the presence of HCl and SO₂ if the mercury adsorption mechanism is different.

Research continues on the chemistry and interactions of flue gas, fly ash, and mercury species. This fundamental research is needed at various flue gas conditions encountered across the utility industry in order to develop low cost mercury strategies for full-scale utility operation. Thus, while AC injection shows promise as a mercury control technology, more data and research are needed to understand the factors that affect mercury removal.

13.6.2.5 Emerging Technologies for Controlling Mercury Emissions from Utilities. Research continues on developing potential technologies for mercury emission reduction from utility plants. This research is aimed at either the addition of some type of sorbent technology or novel technology for mercury control. Emerging technologies are described below.

13.6.2.5.1 Sorbent technology. Although AC injection has been shown to be a promising technology, research with impregnated ACs, sodium sulfide (Na₂S) injection, and an AC circulating fluidized bed suggest that greater mercury removal is possible.

Sulfur-impregnated carbon. In sulfur-impregnated AC injection, the carbon-bound sulfur reacts with mercury to form mercuric sulfide (HgS) on the carbon and the carbon is removed by a PM control device. In a pilot-scale study, sulfur-impregnated carbon increased mercury removal to 80 percent, an increase of 25 percent over results achieved with an equal amount of nonimpregnated AC.⁶⁵

Iodide-impregnated carbon. With iodide-impregnated AC injection, the carbon-bound iodide reacts with mercury to form mercuric iodide

(HgI_2) on the carbon and the carbon is removed by a PM control device. In pilot-scale studies, iodide-impregnated carbon achieved approximately 99 percent mercury removal.^{65,99}

While all testing to date has shown that iodide-impregnated AC injection has a substantial effect on the mercury removal capability of AC, further testing has shown that, under certain conditions (with certain coal types and at temperatures of 177°C [350°F] and higher), a portion of the captured mercury (postulated to be mercuric iodide) may be revolatilized as oxidized mercury.¹⁰⁰

Chloride-impregnated carbon. Chloride-impregnated AC injection has been tested only on MWCs in Europe. The chloride reacts with mercury to form HgCl_2 on the carbon and the carbon is removed by a PM control device. European MWC experiments have shown that impregnating AC with chloride salts increases the adsorptive capacity of the AC 300-fold.¹⁰⁸ Although the amount is small, chloride-impregnated AC injection would introduce additional chlorine (a HAP) into the flue gas stream.

Sorbalit. Another potential method of improving mercury collection efficiency is to combine calcium hydroxide (lime, $\text{Ca}(\text{OH})_2$) with AC. This reagent, consisting of approximately 95 to 97 percent lime and 3 to 5 percent AC, is known under the product name Sorbalit.⁹³ Sorbalit has only been tested on European MWCs and MWIs.

Sulfur-, iodide-, chloride salt-, and $\text{Ca}(\text{OH})_2$ -impregnated ACs show promise for increasing the mercury removal efficiency, but further testing is needed. The cost of these modified carbons can be as much as 20 times higher than that of unmodified AC.¹⁰¹

Other sorbents. Numerous studies are underway to develop other sorbents as economical alternatives to activated carbon.^{102,103} Some of the sorbents under investigation include volcanic pumice, sulfur- and iodide-impregnated carbons, several proprietary sorbents, high-carbon fly ash, Darco FGD (an activated carbon derived from lignite), an activated carbon prepared from a bituminous coal, steam-activated lignite, thermal-activated bituminous coal, chemical-activated hardwood, iodine impregnated steam-activated coconut shell, and sulfur-impregnated steam-activated bituminous coal.¹⁰⁴

Sorbent Technologies is marketing a sorbent called Mercsorbent.¹⁰⁵ The company claims that the sorbent is effective in removing elemental mercury at high temperatures typical of utility flue gas, and is unaffected by common co-existing flue gases, such as SO_2 , HCl , and H_2O . Mercsorbent can be used for sorbent injection or it can be used as a coating on an FF. A bench-scale duct-injection system at Sorbent Technologies facilities is now being used to test Mercsorbent with this

approach. The company is also scheduled to demonstrate the sorbent at the refuse incinerator in Fort Dix, New Jersey; prior compliance sampling at this facility suggests that a significant amount of its mercury is in the elemental form. A coal-fired boiler or slipstream is also being sought for a test of the new sorbent material.

Sodium sulfide injection. Mercury reduction has been achieved at MWCs through injection of Na_2S solution into the flue gas prior to the acid gas control device. The resulting solid, HgS , can be collected by an FF.¹⁰⁶ There are several potential limitations to Na_2S injection. These include reaction of Na_2S with calcium in the sorbent (as found in Sorbalit) to form calcium sulfide (CaS); reduction of the amount of sulfur available to react with mercury (CaS can also cause scaling of the sorbent feed line); corrosion of ductwork (Na_2S is a corrosive material); clogging and plugging of the screw conveyor due to solidification of Na_2S ; and sludge formation due to the presence of inorganic salts in the mixing water.¹⁰⁷ At present, full-scale operational injection of Na_2S has been done only in MWCs. No plans have been announced to test this technology on utility units.

Carbon with circulating fluidized beds (CFBs). Another potential process for the reduction of mercury emissions is the use of AC in a CFB.⁶³ In a CFB, the AC is continuously fed to the reactor, where it is mixed with the flue gas at a relatively high velocity, separated in the subsequent FF, and recycled to the reactor. A small part of the used AC is withdrawn from the process and replaced by fresh material.¹⁰⁸

The main advantages of CFBs over fixed carbon beds are the increased flue gas-to-carbon contact area and the smaller overall pressure drop. No pilot or full-scale utility boiler testing has yet been performed with this system although it has been used in Germany for MWC operation.

In the United States, Environmental Elements Corporation is developing a CFB that promotes agglomeration of fine particulate matter, allowing for its capture in an ESP. In addition, activated carbon is added to the fluid bed to adsorb mercury vapor. High residence time, due to the recirculation of the particles, allows for effective utilization of the carbon. Water sprayed within the circulating bed further promotes the removal of mercury. Results from bench-scale testing indicate that mercury was significantly reduced when passed through the fluidized bed of fly ash and activated carbon. Based on these tests, a carbon-to-mercury usage was determined for the system that compares favorably with other sorbent-based mercury control techniques. There are plans to install a pilot unit and test at Public Service Electric and Gas's Mercer Station.¹⁰⁹

13.6.2.5.2 Novel technologies. Additional potential processes for controlling mercury emissions include advanced coal cleaning, a condensing heat exchanger, gold sorbent technology, other sorbent injection processes, a corona reactor, and mercury amalgamation. These technologies are briefly described below.

Condensing heat exchanger. Based on condensing heat exchanger technology, McDermott Technology (formerly Babcock & Wilcox) is developing an integrated flue gas treatment system for recovering waste heat and removing SO₂, SO₃, particles, and trace elements from coal combustion flue gas. The condensing heat exchanger is a two-pass, counter-flow shell and tube heat exchanger. The hot flue gas enters the top and flows downward through the first cooling stage, across a horizontal transition region, then upward through the second cooling stage. An alkali reagent is sprayed from the top of the second stage to aid in the removal of SO₂. Testing of the technology is being conducted at McDermott Technology's research facility in Alliance, Ohio. Preliminary results indicate that total mercury removal across both stages of the condensing heat exchanger is about 62 percent when firing a blend of Ohio coals. Additional testing is planned on two other bituminous coals.¹¹⁰

Gold sorbent technology. ADA Technologies has begun development and testing of a process, called Mercur-RE, for the removal and recovery of vapor-phase mercury from coal-fired utility boilers. The process takes mercury from flue gases and produces liquid, elemental mercury with no secondary wastes. Noble metals are used to adsorb mercury at typical flue gas temperatures. The mercury is then thermally desorbed.

Preliminary results from laboratory tests indicate that a gold-coated monolith captured virtually all of the elemental mercury injected into a simulated flue gas. Pressure drop through the monolith was low, which is critical to full-scale use. Further testing of the gold monoliths will include repeated sorption and desorption cycles. This phase will be followed by testing on a pilot-scale coal combustion flue gas at Consol's research facility in Library, Pennsylvania.¹¹¹

Sorbent injection processes. The Enhanced Limestone Injection Dry Scrubbing (E-LIDS™) process combines furnace limestone injection with dry scrubbing to achieve high efficiency SO₂, particulate, and trace element emissions control. Dry, pulverized limestone is injected into the upper furnace region of the boiler. The limestone is calcined to lime and a portion of the sorbent reacts with SO₂ in the flue gas. The flue gas passes through a particulate matter collector ahead of the dry scrubber to remove some of the solids from the gas

stream. The solids are mixed with material collected in a baghouse to produce the SO₂ scrubbing reagent for the spray dryer.

Application of the E-LIDS™ system, when firing an Ohio bituminous coal in the Clean Environment Development Facility (CEDF) at the Alliance Research Center of McDermott Technology, Incorporated, has shown efficient emissions control performance. Sulfur dioxide emissions generated from firing the nominal 3-percent sulfur coal were reduced by more than 99 percent to less than 0.10 lbs SO₂/10⁶ Btu. Total mercury emissions were reduced from an uncontrolled level of 17.6 μg/dscm to less than 0.2 μg/dscm for an average total removal efficiency of greater than 98 percent. The measured performance confirmed earlier results obtained in the 5 x 10⁶ Btu/hr small boiler simulator (SBS) facility. Mercury measurements upstream of the dry scrubber indicated that both the limestone injection and operation of the spray dryer/baghouse system at close to the saturation temperature contributed to the observed total mercury emissions reduction. The furnace limestone injection alone reduced mercury emissions to an average of 3.1 μg/dscm.¹¹²

Corona reactor. Environmental Elements Corporation is developing a process for mercury control through DOE's Small Business Innovative Research program. The first concept utilizes an intense corona discharge to convert Hg⁰ to mercuric oxide. The process also produces SO₃ to serve as a conditioner for high-resistivity fly ash. A corona discharge in coal combustion flue gas will produce oxidizing radicals, such as OH and atomic oxygen. Bench-scale results indicate that the corona reactor, operating at relatively low power levels and short residence time, yielded high elemental mercury vapor oxidation. The mercuric oxide, in the form of solid particles, was removed using conventional particulate control technology. The corona reactor may also convert mercuric chloride to mercuric oxide, allowing for its capture as well. The system is currently being tested on a slipstream at Alabama Power's Plant Miller.¹¹³

Mercury amalgamation. There are plans to investigate the interaction of mercury with metals such as zinc, silver, tin, and cadmium. Mercury has been shown to amalgamate with certain metals. Both experimental and modeling efforts are planned to determine the suitability of metals for the capture of mercury.¹¹⁴

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14.0 SUMMARY OF RESULTS, TECHNICAL FINDINGS, AND RESEARCH NEEDS

The following summary of results, technical findings, and research needs is based on this study and the currently available scientific data.

14.1 INDUSTRY GROWTH AND HAP EMISSIONS

1. Utility units emit a significant number of the 189 HAPs included on the section 112(b) list, although in most cases they are responsible for very small percentages of total anthropogenic emissions. Coal-fired units emit the largest number of utility-originated HAPs. Coal-, oil-, and gas-fired utilities emit a mix of HAPs, including organics (e.g., polycyclic aromatic hydrocarbons, dioxins) and heavy metals (e.g., arsenic, lead, cadmium, chromium, nickel, mercury). Utilities are responsible for approximately 34 percent of the United States anthropogenic airborne emissions of mercury but no more than 4 percent of other measured HAPs.
2. Under the assumptions made in this Report, HAP emissions are predicted to increase during the period 1990-2010. Over this period, utility coal consumption is estimated to increase by approximately 29 percent, oil consumption is estimated to decrease by approximately 48 percent, and natural gas consumption is expected to increase by about 61 percent. Coal combustion accounts for the increase in HAP emissions.
3. Actions anticipated to be taken by the utility industry to comply with other provisions of the Act (e.g., acid rain, NAAQS revisions) or with other initiatives (e.g., electricity restructuring, global warming abatement) may impact HAP emissions.
4. The emission test program provided valid and representative results for the purpose of this study. The utility industry is composed of a wide variety of units employing a mix of fuel types, burner types, boiler types, and control device configurations. The HAP emission test data were obtained by a variety of organizations using common test and analytical protocols. The EPA helped to establish these protocols.

14.2 INHALATION RISK ASSESSMENT

5. For the vast majority of the more than 196 million persons living within 50 km of any utility unit, the lifetime cancer risk due to inhalation exposure to HAP emissions is likely to be less than 1×10^{-6} .

6. Out of 426 coal-fired plants, EPA's modeling indicates that only 2 coal-fired plants pose high-end excess lifetime cancer risks greater than 1×10^{-6} due to inhalation exposure to HAP emissions. For no plant does the inhalation MIR exceed 4×10^{-6} . More than 50 percent of the inhalation cancer risk is attributable to arsenic. The average inhalation MIR across all plants is estimated to be roughly 1/10th to 1/100 as large as the highest inhalation MIR. Central tendency inhalation risks for all exposed individuals are predicted to be approximately one to three orders of magnitude lower than the highest inhalation MIR. The population cancer incidence due to inhalation exposure to coal-fired utility HAP emissions, considering the results of both the local and long-range transport modeling, is estimated to be no greater than 1.3 cases per year nationwide.
7. For the year 2010, the cancer MIRs from coal-fired utilities are not expected to be significantly different. However, due to uncertainties about future demand, industry operations, government regulation, etc., the EPA has low confidence in this projection.
8. Out of 137 oil-fired plants, EPA's modeling indicates that only 11 oil-fired plants pose high-end excess lifetime cancer risks greater than 1×10^{-6} due to inhalation exposure to HAP emissions. For no plant does the inhalation MIR exceed 6×10^{-5} . More than 50 percent of the inhalation cancer risk is attributable to nickel and the assumption that nickel emissions are 50 percent as carcinogenic as nickel subsulfide. The average inhalation MIR across all plants is estimated to be roughly 1/10th to 1/100th as large as the highest inhalation MIR. Central tendency inhalation risks for all exposed individuals are predicted to be roughly two to three orders of magnitude lower than the highest inhalation MIR. Population cancer incidence due to inhalation exposure to oil-fired utility HAP emissions (considering local and long-range transport) is estimated to be no greater than 0.5 cases per year nationwide.
9. For the year 2010, the cancer MIRs from oil-fired utilities are predicted to be approximately 30 to 50 percent lower than the 1990 estimates. The EPA has good confidence in this projection because of the well-established trend of declining oil use by utilities.
10. Based on the quantitative parameter uncertainty analysis conducted for the inhalation risk assessment, the EPA estimates that the high-end inhalation risk estimates presented in this report are conservative (i.e., more likely to be overestimating rather than underestimating the true MIR). The quantitative variability and uncertainty of many

of the input parameters such as emission estimates, stack height, breathing rates, and exposure duration were considered in the uncertainty analysis. This resulted in an estimated range and distribution of potential risks due to inhalation exposure only. The median ("central tendency estimate") inhalation MIR estimates are predicted to be roughly 2 to 10 times lower than the high-end MIR estimates. However, there are limitations to the uncertainty analysis and limitations in available data and the range of uncertainty is, most likely, larger than estimated by this study.

11. The risk estimates contain additional uncertainties that are not represented in the quantitative uncertainty analysis. The impact of using different high-to-low dose extrapolation models was not quantitatively assessed in this study. In addition, there are other factors, such as variation in population sensitivity (e.g., sensitive subpopulations), residence time, activity patterns, and other uncertainties and variabilities, that were not quantitatively assessed.
12. With regard to noncancer effects, the highest hazard quotient for any HAP, considering both short- and long-term exposures, is approximately 0.1 for HCl from coal-fired utilities. That is, the highest exposure concentration for HCl was estimated to be 10 times lower than the Inhalation Reference Concentration (RfC) for HCl. The highest hazard index for all HAPs is about 0.2.

14.3 MERCURY

13. Mercury cycles in the environment as a result of natural and human (anthropogenic) activities. Most of the mercury in the atmosphere is elemental mercury vapor, which circulates in the atmosphere for up to a year, and hence can be widely dispersed and transported thousands of miles from sources of emissions. Even after it deposits, mercury commonly is emitted back to the atmosphere to be re-deposited elsewhere. The modeling of long-range transport of mercury suggests that about one-third of United States utility emissions is deposited within the lower 48 States. The remaining two-thirds are transported outside of United States borders where it diffuses into the global reservoir. Finally, predictions of the ISC3 and RELMAP models indicate that most of the mercury emitted by utilities is transported further than 50 km from the emission source.
14. The analysis of mercury fate and transport completed for this study, as well as the analyses completed in the EPA's 1997 Mercury Study Report to Congress, in conjunction with available scientific knowledge, supports a plausible link between mercury emissions from anthropogenic combustion and

industrial sources and mercury concentrations in air, soil, water and sediments. The critical variables contributing to this linkage are these:

- the species of mercury that are emitted from the sources, with Hg^0 mostly contributing to concentrations in ambient air and Hg^{2+} mostly contributing to concentrations in soil, water, and sediments;
- the overall amount of mercury emitted from a combustion source;
- the watershed soil loss rates, including reduction and erosion;
- the water body loss rates, including outflow, reduction, and settling; and
- the climate conditions.

In addition, the analysis of mercury fate and transport supports a plausible link between mercury emissions from anthropogenic combustion and industrial sources and methylmercury concentrations in freshwater fish. However, these fish methylmercury concentrations also result from existing background concentrations of mercury (which may consist of mercury from natural sources, as well as mercury which has been re-emitted from the oceans or soils) and deposition from the global reservoir (which includes mercury emitted by other countries). Given the current scientific understanding of the environmental fate and transport of this element, it is not possible to quantify how much of the methylmercury in fish consumed by the United States population is contributed by current United States emissions relative to other sources of mercury (such as natural sources and re-emissions from the global pool). The critical variables contributing to the plausible link include:

- the species of mercury that are emitted, with emitted divalent mercury mostly depositing into local watershed areas and, to a lesser extent the atmospheric conversion of elemental mercury to divalent species which are deposited over greater distances;
- the overall amount of mercury emitted from a source;
- the watershed soil loss rates, including reduction and erosion;

- the water body loss rates, including outflow, reduction, and settling;
- the extent of mercury methylation in the water body;
- the extent of food web bioaccumulation in the water body; and
- the climate conditions.

From the analysis of deposition and on a comparative basis, the deposition of Hg^{2+} close to an emission source is greater for receptors in elevated terrain (i.e., terrain above the elevation of the stack base) than from receptors located in flat terrain (i.e., terrain below the elevation of the stack base). The critical variables are parameters that influence the plume height, primarily the stack height and stack exit gas velocity.

14.4 DIOXINS AND ARSENIC

15. Based on a screening level multipathway analysis, the highest estimated individual risks due to utility arsenic emissions are predicted to be no higher than 1×10^{-4} and are probably much lower for the vast majority of the exposed population. The increased cancer risks due to multipathway exposures to arsenic emissions, based on screening level model-plant analysis, using hypothetical scenarios, were predicted to range from less than 4×10^{-7} up to 1×10^{-4} . The highest predicted risk (i.e., 1×10^{-4}) was for a hypothetical scenario pica child assumed to be living at the point of maximum deposition, which is considered an upper bound, conservative scenario. When the risk from background exposure (2×10^{-4}) is added to the maximum risk from utility exposure, the risk for the pica child is estimated to be up to 3×10^{-4} . Background exposures were estimated to dominate the exposures and risk. There are substantial uncertainties associated with this screening level arsenic multipathway assessment, and the results do not apply to any specific existing utility plant. Further assessment is needed to more fully evaluate the risks due to arsenic emissions from utilities.
16. Based on a screening level multipathway assessment for dioxins, total modeled lifetime cancer risks related to indirect exposure to dioxins, based on model-plant analyses, are predicted to range from 1×10^{-10} to 2×10^{-4} . The results of the analyses indicate that the exposures and risks due to fish consumption are the highest of all pathways considered. In all scenarios, the noninhalation (e.g., ingestion) exposures were predicted to be at least one order of magnitude larger than the inhalation exposures

and modeled exposures exceed the background exposures for dioxins. There are substantial uncertainties associated with this dioxin screening level multipathway assessment and the results do not apply to any specific existing utility plant. Further assessment is needed to more fully evaluate the risks due to dioxin emissions from utilities.

14.5 RADIONUCLIDE ANALYSIS

17. For the vast majority of the more than 196 million persons living within 50 km of any utility unit, the lifetime fatal cancer risk due to radionuclide emissions is less than 1×10^{-6} .
18. The highest MIR to any individual, within a 50-km radius, resulting from multipathway exposure to radionuclide emissions from utility units is estimated to be up to 3×10^{-5} , and 17 of the 684 plants were estimated to potentially pose an MIR greater than 1×10^{-5} .
19. Based on the multipathway exposure modeling conducted with the CAP-93 model, which estimates exposure within 50 km of each utility unit, the estimated deaths/year resulting from multipathway exposure to radionuclide emissions from utility units is approximately 0.3/year.
20. The quantitative uncertainty analysis performed for the radionuclide analysis indicates that the population risk estimates are central values of the true probability distribution.

14.6 ALTERNATIVE CONTROL STRATEGIES

21. There are a number of alternative control strategies that are effective, based on the data obtained for this report, in controlling some of the HAPs emitted from utility units. These strategies are summarized below.
 - Conversion of coal- and oil-fired units to natural gas firing effectively eliminates emission of HAPs.
 - Conversion of coal-fired units to oil combustion will effect decreases in emissions of some HAPs but could lead to increased emissions of others (e.g., nickel).
 - Because of the wide variability in the trace metal contents of coals, switching from one coal to another will not generally result in consistently reduced overall HAP emissions.
 - Current methods of coal cleaning are able to remove portions of the trace metals contained within the

coal. These emission reductions range from approximately 20 percent for mercury to approximately 50 percent for lead. Advanced coal cleaning technologies show promise in reducing mercury from coal from approximately 30 to greater than 60 percent. Further research is needed in methods of effecting greater trace metal removals during coal cleaning and in assessing the various impacts of these methods.

- Newer forms of fuel combustion (e.g., coal gasification) show promise as being cleaner sources of electricity but available data are limited and further research is needed.
- The impact of combustion controls on HAP emissions is inconclusive given the current level of knowledge. While available data appear to indicate that installation of low-NO_x burners results in a trend toward lower HAP emissions, the trend is neither universal nor uniform.
- Particulate matter control devices (i.e., FFs, ESPs) generally effect good control (i.e., greater than 90 percent removal) of the trace metallic HAPs, with the exception of mercury. Research is underway to further enhance fine particle removal, including trace metallic HAPs, from these control devices. Organic HAPs do not appear to be well controlled by PM control devices but these compounds are generally found near the detection limit. Fabric filters appear to moderately control HCl (i.e., 50 percent removal) but not HF, and ESPs do not generally effect good acid gas HAP control.
- Wet acid gas control devices (e.g., FGDs) by themselves do not uniformly effect good control of the trace metallic HAPs, including mercury. Based on limited data, SDA/FF combinations, however, appear to be as effective as do FFs alone. Research is underway to further enhance the mercury removal capability of FGD systems. Flue gas desulfurization units (as operated on utility units) generally effect good control (i.e., greater than 80 percent) of HCl, but control of HF is not uniform.
- Add-on technologies for the control of mercury have not been demonstrated on utility units in the United States. Pilot-scale work on activated carbon injection indicates that mercury removal is possible but that such removal is inconsistent and variable and that further research is needed.

- Pollution prevention methods (i.e., DSM, energy conservation, repowering for energy efficiency) have the potential to result in reduced HAP emissions. The extent that these methods will be utilized by the industry is not known and, thus, the extent of any emission reductions cannot be forecast at this time.

Each of these alternative control strategies may have significant cost, economic, technical, and research implications before they can be widely utilized in the utility industry.

14.7 AREAS FOR FURTHER RESEARCH AND ANALYSIS

There are numerous uncertainties and data gaps described throughout this report. This section identifies several of the important areas in which further research or scientific and technical work is needed.

14.7.1 Emissions Data for Dioxins

Emissions data for dioxins were available from only eight of the tested utility plants. Therefore, there are greater uncertainties with the dioxin emissions than for many of the other HAPs. All types of utility units were not tested (e.g., there are no data available from coal-fired units with hot-side ESPs).

14.7.2 Speciation of Nickel and Chromium

There are significant uncertainties regarding the forms of nickel being emitted from oil-fired utilities and the health effects associated with those different forms. Therefore, further research and evaluation of the emissions to determine what forms are being emitted and the health effects associated with those different forms would be of value. Further evaluation of chromium speciation is also needed.

14.7.3 Multipathway Risk Assessment

As mentioned previously, further work is needed to study the risks due to multipathway exposure to HAPs that are persistent and bioaccumulate. Arsenic and dioxins are two HAPs identified as priority for further multipathway assessment.

14.7.4 Long-range Transport Exposures

Uncertainties remain regarding long-range transport of HAPs. Further modeling and evaluation could be helpful to assess the impacts of long-range transport of HAPs from utilities.

14.7.5 Mercury Issues

There are numerous areas regarding mercury that may need further research, study, or evaluation. A number of potential areas for further study include the following:

- review the estimates of the levels of exposure to mercury associated with subtle neurological endpoints;

- quantify and/or evaluate the relationship between a change in United States mercury emissions and the resulting change in methylmercury levels in fish;
- evaluate actual consumption patterns and estimates of the methylmercury exposure of the subpopulations of concern;
- gather additional data on the mercury content of various types of coal;
- establish improved methods for measuring mercury concentrations in water;
- study the occupational, dietary, and behavioral factors that affect mercury exposures for people who are determined to be exposed above a threshold of concern;
- study the public health and environmental benefits that would be expected by reducing mercury emissions from utilities;
- evaluate and/or research control technologies or pollution prevention options that are available, or will be available, that could potentially reduce mercury emissions and what are the costs, economic impacts, and feasibility of those options;
- evaluate how other regulations, programs, and activities (e.g., acid rain program, electricity restructuring, NAAQS, climate change) affect mercury emissions;
- gather additional data on mercury emissions (e.g., how much is emitted from various types of utility units, how much is divalent vs elemental mercury, and how do factors such as control device, fuel type, and plant configuration affect emissions and speciation); and
- study how much mercury is emitted from natural sources and past anthropogenic sources.

14.7.6 Projections to the Year 2010

There are significant uncertainties and unknowns in the emissions and risk projections made to the year 2010 (e.g., impact of industry restructuring; impact of State efforts to regulate restructuring; impact of any climate change initiatives). Further research and evaluation in this area is needed.

14.7.7 Ecological Risks

The effects of HAPs on wildlife, endangered species, and terrestrial and aquatic ecosystems were not evaluated in this study. Although not mandated by section 112(n)(1)(A), further evaluation of

ecological risks due to HAP emissions would be needed to fully evaluate the impacts of utility HAP emissions.

14.7.8 Criteria Pollutant and Acid Rain Programs

Further evaluation is needed to assess the impacts of the Acid Rain and Criteria Pollutant programs (e.g., impact of revisions to the PM-fine and ozone NAAQS; impact of Ozone Transport Assessment Group [OTAG] activities) on HAP emissions.

14.7.9 Short-term Emissions

A limited assessment of short-term exposures was completed. However, further evaluation of short-term releases, especially high-end, peak releases, could be useful to fully assess the potential impacts to public health due to emissions of HAPs (particularly HCl and HF) from utilities.

TECHNICAL REPORT DATA

(Please read Instructions on reverse before completing)

1. REPORT NO. EPA-453/R-98-004a,-b		2.	3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units -- Final Report to Congress			5. REPORT DATE February 1998	
			6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S)			8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Emission Standards Division/Air Quality Strategies and Standards Division Office of Air Quality Planning and Standards Research Triangle Park, NC 27711			10. PROGRAM ELEMENT NO.	
			11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS			13. TYPE OF REPORT AND PERIOD COVERED	
			14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES				
16. ABSTRACT This report has been prepared pursuant to section 112(n)(1)(A) of the Clean Air Act, and provides the Congress and the public with information regarding the emissions, fate, and transport of utility HAPs. The primary components of this report are: (1) a description of the industry; (2) an analysis of emissions data; (3) an assessment of hazards and risks due to inhalation exposures to 67 HAPs; (4) assessments of risks due to multipathway (inhalation plus non-inhalation) exposures to four HAPs (radionuclides, mercury, arsenic, and dioxins); and (5) a discussion of alternative control strategies. The assessment for mercury in this report includes a description of emissions, deposition estimates, control technologies, and a dispersion and fate modeling assessment which includes predicted levels of mercury in various media (including soil, water, and freshwater fish) based on modeling from four representative utility plants using hypothetical scenarios. The EPA has not evaluated human or wildlife exposures to mercury emissions from utilities in this report. With regard to non-inhalation exposures (e.g., ingestion) to other HAPs, this report presents a limited qualitative discussion of arsenic, cadmium, dioxins, and lead.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group
Air Pollution Atmospheric Dispersion Modeling Electric Utility Steam Generating Units Hazardous Air Pollutants/Air Toxics		Air Pollution Control		
18. DISTRIBUTION STATEMENT Release Unlimited		19. SECURITY CLASS (Report) Unclassified		21. 787
		20. SECURITY CLASS (Page) Unclassified		22. PRICE

