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Project Summary

Trace Metals and Stationary Conventional Combustion Processes

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A search of United States literature was performed to identify published information on trace elements and Stationary Conventional Combustion Processes (SCCP). The search was initially computerized with later cross-referencing from identified reports. A summary of the information found in the articles, with specific references, comprises the report.

To assess the existing situation, the report summarizes what has been published about ambient trace elements in air, water, and soils. A survey, reporting the trace element concentration in combustible fuels, identifies coal as the fuel of most concern; generally, trace element levels in coal are similar to their crustal abundances. Conventional combustion technology is reviewed. The trace element flows and partitioning around various types of boilers and pollution control devices are discussed both generally and specifically; data from cited studies are reported. In addition to coal, data are presented for oil, municipal refuse, and wood. Emissions to air, water, and soil, including trace element leaching studies, are covered.

The health and environmental effects of trace elements are documented. Where possible, specific contributions from SCCPs are assessed. Environmental transport systems and special problems associated with radioactive elements are covered. Following is a comprehensive summary of the project objectives and findings as they relate to the impact and control of SCCPs.

Introduction

The shift in principal feedstocks for electrical power generation from natural gas and fuel oil to coal has stimulated concern about trace element emissions. Some of the trace elements present in the effluent streams from a typical coal-fired plant can reach toxic levels. Because the background levels for most trace elements in the atmosphere and natural waters are low, emissions from SCCPs may be the dominant contributing factor to their degradation.

The Conventional Combustion Environmental Assessment (CCEA) program charted by EPA in 1977 was created to assess the environmental and human health impacts of conventional combustion and to study and recommend methods for controlling adverse effects. The purpose of this study is to review the literature concerning trace element emissions from SCCPs as a first step in assessing the environmental and human health impacts from SCCPs and potential control measures.

Included in the SCCP category for this analysis are utility, industrial, commercial, and residential combustion sources. Emissions from the combustion of coal, oil, natural gas, wood, and refuse were considered for each combustion source. However, the primary source of SCCP trace element emissions comes from the combustion of coal in electric utility boilers. As a result, the most intensive area of research deals with emissions from coal-fired power plants. Over 90% of the articles identified in this work concerned coal-fired power plants. Unfortunately, few data on other fuels and combustion processes were available.

A comprehensive, computer-assisted literature search of databases extending as far back as 1970 identified about 20,000 citations in the US literature and covered all phases of public and private research. The number was reduced to about 1,000 relevant articles after an extensive review. Other articles not identified in the computerized search were added later. These citations form a bibliography, which is presented as a companion document to the literature review.

Ambient Trace Metal Concentrations

The National Air Surveillance Network (NASN) was set up in 1957 to monitor criteria pollutants [sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HC), and total suspended particulates (TSP)] primarily in urban areas. Since 1975 trace element analyses of particulate samples have been performed at about 400 NASN stations. These data are compiled in the Storage and Retrieval of Aerometric Data (SAROAD) system, which is part of the National Aerometric Data Bank (NADB). Although this data is published irregularly, current data can be retrieved by computer. Various states, regional EPA offices, and researchers also have collected trace element data. However, much of those data are unpublished and can be very limited both spatially and temporally. Average ambient air concentrations of several trace elements (Be, Cd, Cr, Co, Fe, Pb, Mn, Ni, Ti, V, and Zn) for urban and rural locations are presented in Table 1 and are compared with estimated permissible concentrations (EPC).

Trace Metal Concentrations in Fuel

Trace elements, inherent in all fossil fuels, are mobilized through the combustion process. Because of the very low levels found in natural gas, trace element emissions from the combustion of gas have received little attention. Trace element emissions from the combustion of wood also have received little attention, mainly because the organic pollutants have been of greater concern. Conversely, emissions from oil and coal combustion are of major concern, with the bulk of the literature devoted to emissions from coal combustion. The combustion of municipal refuse as a fuel supplement in fossil fuel plants is also of concern. Researchers have found that concentrations of several toxic trace elements in refuse are much higher than those observed in coal.

Representative concentrations of several major and minor elements in coal, paper products, and the combustible fraction of urban refuse are presented in Table 2. Trace element content in coal ash, approximate detection limits for each element, frequency of detection, and elemental abundances in the earth's crust are given in Table 3. Often elemental concentrations in coal ash are used to characterize the coal. These values, however, are usually inaccurate for the more volatile elements such as Hg and Se because greater than 90% of these two elements leave the stack in a gaseous state.

Trace elements in the fossil fuels are mobilized during the combustion process. Some elements can be volatilized during combustion and escape control devices. Others may be concentrated on fly ash and collected, while some elements condense out on very small particles that also can pass through control devices. The species of the trace element in coal, whether organic or inorganic (sulfides, aluminosilicates, carbonates, or quartz), has an effect on how the trace element will be distributed in wastestreams and on the particle size distribution. The understanding of this distribution process, however, is incomplete.

Table 1. *Average atmospheric metal concentrations in U.S., 1966-1967*

	Urban				*Non-urban*				
Element	*Most common value detected (µg/m³)*	*Range (µg/m³)*	*Detection limit (µg/m³)*	*% below detection limit*	*Most common value detected (µg/m³)*	*Range (µg/m³)*	*Detection limit (µg/m³)*	*% below detection limit*	*Estimated permissible concentration (EPC) (µg/m³)*
Be	*0.0003*	*0-0.0007*	*0.0002*	*85*	*0.00007*	*0-0.0004*	*0.0007*	*95*	*0.01+*
Cd	*0.01*	*0-0.09*	*0.01*	*73*	*0.004*	*0-0.03*	*0.004*	*93*	*0.12*
Cr	*0.006*	*0-0.1*	*0.006*	*62*	*0.003*	*0-0.03*	*0.002*	*70*	*0.12*
Co	*0.006*	*0-0.045*	*0.006*	*99*	—	—	*0.002*	*99.5*	*0.12*
Fe	*1.5*	*0.1-6.1*	*0.2*	*3*	*0.2*	*0.02-1.5*	*0.05*	*17*	—
Pb	*0.8*	*0.1-5.0*	*0.1*	*1*	*0.08*	*0.03-0.8*	*0.03*	*28*	*0.36*
Mn	*0.03*	*0-0.81*	*0.01*	*6*	*0.01*	*0.002-0.07*	*0.004*	*21*	*12.0*
Ni	*0.01*	*0-0.187*	*0.006*	*30*	*0.002*	*0-0.03*	*0.002*	*36*	*0.24*
Ti	*0.02*	*0-0.13*	*0.001*	*51*	*0.002*	*0-0.03*	*0.003*	*28*	*14*
V	*0.02*	*0-0.905*	*0.003*	*40*	*0.003*	*0-0.01*	*0.001*	*55*	*1.2*
Zn	*0.5*	*0-1.7*	*0.1*	*60*	*0.1*	*0-0.6*	*0.04*	*56*	*9.5*

Table 2. *Concentrations of elements in coal, paper products, and the combustible fraction of urban refuse (typical values in parentheses)*

Major elements (conc. in pct)	Urban refuse	Selected paper products	Magazines	Coal
Aluminum	0.3-1.6 (1.1)	0.1-3.0 (1.0)	1.0-6.0	09000.1-2.0 (0.14)
Calcium	0.23-1.0 (0.5)	0.04-2.7 (0.5)	0.04-1.1	0.007-0.50 (0.03)
Chlorine	0.3-1.5 (0.4)	0.05-2.5 (0.1)	—	0-0.1 (0.01)
Iron	0.05-0.7 (0.2)	0.01-0.06 (0.03)	0.04-0.5	0.01-1.0 (0.1)
Magnesium	0.05-0.8 (0.1)	0.002-0.2 (0.05)	0.005-0.3	0.01-0.4 (0.02)
Phosphorus	0.001-0.7 (0.1)	—	—	<0.03
Potassium	0.03-0.2 (0.07)	0.01-0.10 (0.03)	0.01-0.03	0.01-0.60 (0.2)
Silicon	1-10 (4)	—	—	0.08-4.1 (0.2)
Sodium	0.15-0.9 (0.5)	0.01-3.3 (0.3)	0.01-0.1	0.01-0.35 (0.2)
Sulfur	0.1-0.3 (0.2)	<3	—	1-2.5 (1.2)
Titanium	0.07-1.7 (0.2)	0.01-1.7 (1.0)	0.3-1.8	0.003-0.18 (0.006)
Zinc	0.04-0.8 (0.1)	0.005-0.02 (0.008)	0.001-0.04	0.001-0.10 (0.003)
Minor elements (conc. in ppm)				
Rare earths	—	<600	—	<50
Antimony	20-80 (45)	0.02-250 (3)	—	1-1800 (20)
Arsenic	<3	0.001-9	—	1-70 (45)
Barium	35-100 (50)	1-10,200 (1)	1-300	20-1600 (80)
Beryllium	<2	<4	<2	0.4-90 (25)
Bismuth	3-45 (22)	—	<15	0.02-3 (0.2)
Boron	5-70 (15)	0.1-20 (1)	—	1-270 (100)
Cadmium	3-70 (15)	0.01-19 (0.3)	0-2	0.2-5 (0.5)
Cesium	<20	<35 (6)	—	0.1-9 (0.3)
Chromium	10-175 (30)	0.4-330 (20)	70-260	0.3-400 (1)
Cobalt	2-17 (5)	1-4	10-20	0.3-135 (25)
Copper	30-450 (195)	0.04-100 (12)	4-100	1-180 (7)
Germanium	<6	<15	—	0.03-1000 (45)
Gold	<2	0.01-90 (0.03)	—	0.02-0.5 (0.1)
Lead	110-1300 (230)	0.3-250 (10)	20-1400	1-100 (7)
Lithium	2-10 (3)	2-200 (10)	5-15	1-165 (20)
Manganese	50-480 (85)	0.5-500 (25)	1-50	20-240 (25)
Mercury	—	0.1-90 (0.3)	—	0.07-0.6 (0.15)
Molybdenum	10-30 (20)	3-330	—	1-20 (5)
Nickel	4-50 (15)	1-100 (5)	10-20	3-900 (65)
Niobium	<6	<15	—	3-40 (4)
Platinum	<10	<35	—	<0.06
Rubidium	<6	9-60	—	1-450 (25)
Scandium	—	1-18 (1)	—	0-36 (6)
Silver	0.1-16 (2)	0.03-6 (0.2)	<7	0.01-8 (0.2)
Strontium	20-70 (50)	5-100 (30)	5-40	15-1000 (135)
Tantalum	<4	0.15-200 (3)	—	<1 (6)
Tin	20-95 (50)	0.1-20 (2)	<30	1-50 (20)
Tungsten	<30	<70	—	0.5-40 (20)
Vanadium	5-70 (15)	0.1-20 (10)	—	2-80 (20)
Zirconium	1-70 (10)	0.05-25 (5)	—	25-450 (70)

Table 3. · *Average trace element content in ash of coal from three areas, as weight percent*[a]

Element	Crustal abundance	Approximate lower limit of detection	Eastern province: Frequency of detection %	Eastern province: Average trace element content of ash	Interior province: Frequency of detection %	Interior province: Average trace element content of ash	Western states: Frequency of detection %	Western states: Average trace element content of ash
Barium	0.0425	0.002	100	0.0876	100	0.0399	100	0.1467
Beryllium	0.00028	0.0001	100	0.0012	100	0.0014	100	0.0006
Boron	0.0010	0.002	100	0.0265	100	0.0731	100	0.0529
Chromium	0.0100	0.0001	100	0.0230	100	0.0224	100	0.0066
Cobalt	0.0025	0.0020	100	0.0184	98	0.0193	98	0.0097
Copper	0.0055	0.0001	100	0.0128	100	0.0089	100	0.0047
Gallium	0.0015	0.0002	100	0.0071	100	0.0039	100	0.0033
Germanium	0.00015	0.0003	99	0.0048	100	0.0104	95	0.0017
Lanthanum	0.0030	0.01	92	0.0145	86	0.0131	81	0.0128
Lead	0.0013	0.0001	100	0.0055	100	0.0131	100	0.0029
Lithium	0.0020	0.0001	100	0.0584	100	0.0235	100	0.0168
Manganese	0.0950	0.0001	100	0.0260	100	0.0325	100	0.0212
Molybdenum	0.00015	0.0001	99	0.0082	99	0.0073	100	0.0020
Nickel	0.0075	0.0001	100	0.0209	100	0.0262	100	0.0054
Scandium	0.0022	0.002	100	0.0089	100	0.0069	97	0.0052
Strontium	0.0375	0.001	100	0.1052	100	0.0658	100	0.1456
Tin	0.0002	0.0001	100	0.0019	99	0.0019	100	0.0017
Vanadium	0.0135	0.0001	100	0.0336	100	0.0325	100	0.0152
Ytterbium	0.00034	0.0001	100	0.0007	100	0.0005	100	0.0003
Yttrium	0.0033	0.001	100	0.0142	100	0.0118	100	0.0076
Zinc	0.0070	0.005	98	0.0230	100	0.0743	93	0.0258
Zirconium	0.0165	0.005	100	0.0704	100	0.0825	100	0.0850
Arsenic	0.00018	0.005	67	0.0159 (0.0107)	41	0.0119 (0.0049)	16	0.0073 (0.0012)
Bismuth	0.00002	0.0001	82	0.0002 (0.0002)	77	0.0001 (0.0001)	83	0.0001 (0.0001)
Cerium	0.0060	0.02	31	0.0238 (0.0074)	11	0.0214 (0.0024)	13	0.0238 (0.0031)
Neodynium	0.0028	0.01	29	0.0213 (0.0062)	10	0.0183 (0.0018)	15	0.0295 (0.0044)
Niobium (columbium)	0.0020	0.001	73	0.0053 (0.0039)	88	0.0055 (0.0048)	85	0.0053 (0.0045)
Rubidium	0.0090	0.001	97	0.0239 (0.0232)	100	0.0276 (0.0276)	58	0.0064 (0.0037)
Thallium	0.00005	0.0005	43	0.0019 (0.0008)	49	0.0008 (0.0004)	9	0.0005 (0.00005)
Average trace element, % of ash				0.6651		0.6568		0.6466
Average ash, % of dry coal				9.3		10.5		9.8
Average trace element, % of dry coal				0.0618		0.0690		0.0634
Number of samples				600		123		104

[a] Average calculated for number of samples in which element was detected, except that averages in parentheses were calculated for all of the samples tested using zero for element contents below limit of detection.

Control Technologies

Fuels normally used in SCCPs include coal, oil, natural gas, refuse, and wood. However, the bulk of the literature on trace element control technologies deals with coal-fired power plants.

Trace metals are discharged into utility plant wastestreams during the following processing steps:

- Coal storage and preparation
- Raw water treating
- Ash handling and disposal
- Combustion process
- Metal cleaning
- Cooling system
- Floor and yard drain
- Air pollution control.

The wastestream most subject to analysis and control, and also of the greatest environmental concern, is flue gas from coal-fired utility boilers. The level of a trace element in the flue gas usually depends on its volatility. In general, the greater a trace element's volatility at the combustion temperature, the higher its concentration in the flue gas. Conversely, the lower its volatility, the greater the element's inclusion with the bottom ash. Because of the enrichment of many trace elements on small particles, controlling trace element emission is tantamount to controlling fine particles. Unfortunately, these fine particles escape conventional collection devices most easily, have the greatest atmospheric residence times, and are most easily deposited in the respiratory system.

Four technologies have been used for particle control in power plant boilers and include:

- Dry mechanical separators (cyclones)
- Electrostatic precipitators (ESP)
- Wet scrubbers
- Baghouses.

Although none of these methods were designed specifically to control trace element emissions, substantial reductions in emissions for most elements are achieved because of the close association between trace elements and particulates. Typical trace element collection efficiencies for each of the four control technologies, as determined from actual operating data, are presented in Table 4.

The ash and sludge generated by the control processes present a disposal problem. The trace element content of these wastes is significant, but there are adequate technologies for safe disposal of the materials. Certainly, the trace elements are more manageable and less mobile in the condensed wastestreams than in the atmospheric emissions and therefore of less potential environmental impact. Leaching of the solid ash and ash pond overflow are the main problems associated with their disposal.

Trace Element Emissions From Stationary Conventional Combustion Processes

Trace elements enter the combustion process with the fuel and are returned to the environment with effluent gases or with the solid wastes. Most trace elements discharged during the combustion process leave as a solid waste. The disposal of this solid waste at land fills is potentially hazardous because trace elements may be mobilized through leaching, contaminating the surrounding soil and groundwater. Therefore, it is important not only to consider the trace element content of the solid wastes but also its leaching characteristics.

Major aqueous streams leaving the combustion process are often associated with ashes or other solids containing ash. Aqueous effluent streams, which often contain trace elements leached from ashes, include ash sluice water, ash pond liquor, and liquor associated with flue gas desulfurization scrubbers. Coal ashes and sludges from throwaway flue gas desulfurization systems have been found to be potentially the most hazardous solid (and liquid) wastes discharged by the utilities.

Maximum trace element concentrations permitted for primary and secondary drinking water supplies and for water used continuously for irrigation are presented in Table 5. In addition, Table 5 also lists trace element concentrations in four waters collected from coal-fired power plants. These data illustrate reported concentrations, not necessarily typical or worst-case situations.

Concentrations that exceed at least one set of standards are in bold. These leachates do not necessarily pose an environmental hazard. The magnitude of the hazard will be determined by several site-specific factors such as amount of dilution before the leachate enters a water supply, sorption by soils, and bioaccumulation.

Trace elements discharged to the atmosphere are usually associated with particulates suspended in the effluent gas. A few trace elements (As, F, Hg, and Se) may be volatilized and leave in the vapor state. Much of the atmospheric emission data available in the literature concerns emissions from coal-fired power plants. In most studies, trace element emissions have been measured at operating power plants under conditions prevailing at the plant at the time of sampling. This method of collecting data makes it difficult to compare results from different studies or power plants. Large variations in trace element emission rates exist even when normalized to the heating value of the coal. Trace element emissions data for four coal-fired power plants are presented in Table 6, and although not typical or worst-case values, they illustrate the variability in reported emissions.

Part of the observed variations can be related to differences in total particulate emissions from the plant. But other factors appear to significantly influence the actual trace element emissions from a given power plant. Some of these include trace element content of the coal, the boiler configuration, and the type of particle control device used.

Table 4. *Trace element removal efficiencies of various control technologies*

Trace elements	Cyclone separator*	Electrostatic precipitator	Venturi scrubber	SO_2 Scrubber* Coal-fired boiler	SO_2 Scrubber* Oil-fired boiler	Baghouse
	Average Trace Element Removal Efficiencies (%)					
Aluminum	66.0	99.2	99.6	99.0	92.0	~100
Antimony	7.4	91.2	97.4	99.0	91.0	ND
Arsenic	75.3	95.3	94.2	97.0	81.0	ND
Barium	95.4	98.5	99.3	ND	ND	ND
Beryllium	84.3	98.4	99.2	98.0	ND	ND
Boron	31.4	94.7	93.6*	88.0	93.0	ND
Bromine	ND	99.8*	ND	ND	ND	ND
Cadmium	44.0	95.6	92.3	99.0	77.0	ND
Calcium	54.8	99.1	99.4	99.0	83.0	~100
Cerium	ND	99.1	>99.9*	ND	ND	ND
Cesium	ND	98.9	>99.9*	ND	ND	ND
Chlorine	8.7	4.5*	98.4*	ND	ND	ND
Chromium	27.7	95.1	92.5	95.0	90.0	ND
Cobalt	45.1	98.3	98.4*	99.0	89.0	ND
Copper	56.8	99.2	99.3*	99.0	99.0	~100*
Fluorine	25.3	52.3*	98.0*	ND	ND	ND
Gallium	ND	97.8	99.5*	ND	ND	ND
Iron	54.2	99.1	>99.5*	99.0	95.0	~99.9*
Lead	30.0	95.5	98.0*	99.0	94.0	~100
Lanthanum	ND	99.0	>99.9*	ND	ND	ND
Magnesium	61.0	99.4	99.2	99.0	91.0	ND
Manganese	66.8	99.0	99.4	98.0	87.0	ND
Mercury	3.2	0.0*	12.6*	55.0	87.0	ND
Molybdenum	24.9	92.1	75.6	99.0	89.0	ND
Neodynium	ND	58.7*	99.9*	ND	ND	ND
Nickel	18.6	52.5	95.0*	95.0	83.0	~100
Potassium	ND	99.2	>99.9*	ND	ND	ND
Rubidium	ND	97.0	ND	ND	ND	ND
Scandium	ND	99.0	>99.9*	ND	ND	ND
Selenium	33.1	86.0	91.4	87.0	97.0	ND
Silver	79.6	98.7*	94.8*	ND	ND	ND
Strontium	ND	100.0*	99.8*	99.0	98.0	ND
Thorium	ND	99.0	>99.9*	ND	ND	ND
Titanium	74.4	98.9	99.8	ND	ND	~100
Tungsten	ND	92.8*	97.4*	ND	ND	ND
Uranium	60.6	97.7	97.8	ND	ND	ND
Vanadium	36.2	96.8	98.1	70.0	98.0	ND
Zinc	39.4	97.0	98.4	98.0	90.0	~100
Zirconium	ND	58.6*	>99.9*	99.0	94.0	ND
Total ash	65.0	98.8	98.0	ND	ND	ND

ND - No data available.
* - Does not represent an average value, since only one data point was available.

Table 5. *Water quality standards for trace element concentrations in water supplies and trace element concentrations in some water associated with coal-fired power plants**

	Drinking water standards (mg/l)	Continuous irrigation standards (mg/l)	Ash pond effluent (mg/l)	Bottom ash sluice water station III (mg/l)	Plant D (mg/l)	Plant C (mg/l)
Arsenic	0.01	1.0	**0.027**	0.0087	**0.03**	**0.013**
Barium	1.0	—	—	<0.5	0.2	0.2
Beryllium	—	0.10	<0.0002	0.0017	<0.01	<0.01
Boron	—	0.75	**12**	0.25	—	—
Cadmium	0.01	0.01	0.001	0.0011	0.001	0.005
Chlorine	250	—	—	16	—	—
Chromium	0.05	0.10	0.002	<0.053	0.004	0.005
Cobalt	—	0.05	—	0.0041	—	—
Copper	1	0.2	0.003	0.014	0.01	0.03
Fluorine	2.4	1.0	**16**	0.25	—	—
Iron	0.3	5.0	—	**2.1**	—	—
Lead	0.05	5.0	—	0.024	0.01	0.02
Manganese	0.05	0.2	—	**0.055**	0.03	**0.22**
Mercury	0.002	—	—	<0.0005	0.0002	**0.015**
Molybdenum	—	0.01	**0.170**	**0.016**	—	—
Nickel	—	0.2	—	0.0014	0.05	<0.05
Selenium	0.01	0.02	**0.057**	0.0011	**0.065**	**0.014**
Silver	0.05	—	—	<0.00003	<0.01	0.01
Vanadium	—	0.10	**0.130**	<0.005	—	—
Zinc	5	2.0	0.440	0.013	0.03	0.12
Total dissolved solids	500	5000	—	—	151	363
pH	6.5–8.5	4.5–9.0	—	—	8.6	7.1

*Values in bold exceed either the drinking water or continuous irrigation standard.

Table 6. *Atmospheric emissions of trace elements from coal-fired power plants with different types of particle control devices (grams element emitted per 10^{12} joules in the coal)**

Element	Cold-side electrostatic precipitators	Hot-side electrostatic precipitators	Wet scrubber	Cyclones
Arsenic	5	0.08	5.24	120
Barium	8	<26	97.9	<680
Beryllium	—	0.43	—	3
Boron	—	94	—	6600
Cadmium	0.6	<0.2	—	6.8
Chromium	8	60	13.4	430
Cobalt	0.5	1.5	0.165	30
Copper	2	2.8	11.6	210
Iron	2000	980	239	31,000
Lead	5	6.2	—	37
Manganese	5	19	23.0	710
Mercury	3 (gas)	1.7	—	10
Molybdenum	—	3.2	2.07	340
Nickel	2	30	13.3	319
Selenium	10**, 0.8	13	12.9	35
Silver	—	0.04	—	<0.4
Vanadium	10	26	9.39	290
Zinc	50	8.7	5.83	350

* These numbers represent the hourly emission rate of each element from a plant with approximately 140 MW capacity.

** Selenium was analyzed by two methods. Gas chromatography-microwave emissions spectroscopy gave a value of 10 grams selenium per 10^{12} joules. Neutron activation analysis gave a value of 0.8.

Health and Environmental Effects of Trace Elements

Emissions from coal-fired power plants represent a significant percentage of the anthropogenic contribution for some trace elements, many of which are potentially harmful to materials and biological systems. It is the emission of these toxic trace elements into the atmosphere that is of greatest concern.

Relationships between particulate air pollution episodes from industrial boilers burning coal and increased community mortality and morbidity due to pulmonary diseases are well documented in the literature. Trace elements present on particles have been suggested as the causal agents of increased mortality associated with such episodes.

It is estimated that 50 to 90 % of human cancers are caused by carcinogens in the environment. Trace elements emitted from SCCPs constitute a significant fraction of the total mass of carcinogens released to the environment. Several elements (As, Be, Cd, Cr, Co, Hg, and Ni) are known to be carcinogens. All of these elements and Pb are oncogenic (tumor-producing) as well. In addition, Ba, Cd, Pb, Li, Hg, and Se are all considered teratogenic (inducing structural and/or functional deviation in an embryo during its development, resulting in congenital birth defects). Several laboratory studies also have shown the mutagenic properties of fly ash extracts. Apparently some trace elements present in these extracts are capable of causing changes in the DNA of tested bacteria.

As previously mentioned, small particulates (<15 μm in diameter) are of particular importance. Not only are they enriched in many of the toxic trace elements, but they easily penetrate and are deposited deep within the respiratory tract. The retention of particulate matter in the lung also increases sharply with decreasing particle size.

To date, most efforts toward establishing safe ambient trace element concentrations have extrapolated from occupational health standards and threshold limit value (TLV) data to estimate permissible concentrations in the environment. The validity of this approach has been questioned because some elements, specifically carcinogens, do not have TLV values, individual element standards ignore the consequence of synergisms among trace elements or other pollutants, and no definitive correlation between acute toxicity laboratory studies on test animals and long-term, low level toxicity effects on humans has been established. Thus, it is difficult to specify safe ambient levels for trace elements, and current estimates may be expected to change as a better understanding of this entire discipline evolves.

Material transfer of trace elements from solid waste to various ecological compartments is very difficult to quantify. The exact nature of the transfer process depends on several site-specific factors including:

- The type and thickness of any clay or plastic pond liners
- The permeability, cation exchange, and porosity (mobilization-attenuation characteristics) of the soil for specific elements
- Soil and pond liquor pH
- Trace element concentration
- The proximity of the disposal site to the groundwater table and/or surface water.

Ash disposal pond drainage systems have been studied to assess the impact of trace element concentrations on aquatic biota. Studies to date have indicated that species diversity may be repressed in such a contaminated environment. Indigenous species seem to possess an inherited or acquired resistance to the toxic effects of high concentrations of trace elements, and cycling of trace elements released from the ash pond between biological trophic levels occurs. Planktonic crustaceans appear to be more sensitive to certain pollutants than either phytoplankton, aquatic macrophytes, or fish. Bioaccumulation potential is highest in benthic and invertebrate organisms.

The major impact of trace elements emitted from coal-fired plants is elevated concentrations in surface soils and vegetation. Several studies have correlated trace element concentration in soils and vegetation with distance and direction of prevailing winds for a particular emission source. However, similar studies have not been able to detect increased trace metal concentrations near coal-fired plants. Site-specific factors, such as the trace element content of parent soil material, have complicated efforts to monitor trace metal emissions and their impacts on terrestrial ecosystems.

Radiological Emissions from Stationary Conventional Combustion Systems

Radiological emissions from fossil fuels are not usually of much concern. Several isolated coals do contain high enough uranium levels to make the recovery from coal ash profitable. More generally, coal contains about 1 part per million (ppm) of U and 2 ppm of Th, both long-lived radionuclides. Other radioactive species reported include P, Pb, Ra, and Rn. Total radioactivity is typically 3 to 5 picocuries per gram (pCi/g) for western coals and 1 to 3 pCi/g for eastern coals. These elements, except Ra, which is a gas, are concentrated ten-fold in the ash. Typical emission levels for a 1,000 MW power plant burning sub-bituminous coal are about 1 curie per year and that mostly from a short-lived Ra isomer. No other fuel sources are of concern except radiological incinerators, which require special attention.

The primary potential health hazard is caused from ingestion of plants or animals raised near the power plant. Only the most severe assumptions cause models to predict exposure levels considered unsafe, and then only for accumulation levels in bones. No radiation regulations currently pertain to coal-fired plants and may not be soon forthcoming because effects of chronic, long-term exposure to low levels of radiation from coal burning are unknown.

Accuracy of Data and Analytical Techniques

To assess the accuracy of trace metal measurements, a program involving round-robin analyses of the same samples was conducted. These samples were typical of those taken from SCCPs. The results of a coal and fly ash analysis by several different methods are presented in Tables 7 and 8. It can be seen from an examination of these tables that the volatile trace elements, such as As, Cd, Cl, F, Hg, and Se, show the least consistent results. However, relatively new analytical techniques for instrumental, multi-element analysis are simplifying and increasing the speed of analysis with a resulting increase in the reliability of the data.

Regulations

With the exception of Pb, no specific regulations exist for trace element emissions. However, atmospheric trace element emissions are associated with particulate matter, except for a few volatile elements, and therefore are indirectly regulated by standards governing particulate emissions.

National Ambient Air Quality Standards (NAAQS) are limits that have been established for ambient air. The primary NAAQS, adequate to protect the public health, became effective in 1975; the secondary NAAQS, designed to ensure the public welfare, will go into effect within a "reasonable period of time." These standards for particles are given in Table 9. Similar standards exist for all criteria pollutants, and each state or region has the option to set more stringent standards.

Table 7. Coal analysis for trace elements—comparison of methods

Analytical method	*SSMS* [a]	*SSMS* [a]	*SSMS* [a]	*OES* [b]	*OES* [b]	*NAA* [c] *ppm (by weight)*	*NAA* [c]	*NAA* [c]	*NAA* [c]	*NAA* [c]	*AAS*
Hg	<2	<2	<0.10	NA	NA	<0.2	NA	<0.02	0.03	NA	0.051+
Be	0.4	NA	0.4	<1	<0.1	NA	NA	NA	NA	NA	NA
Cd	6	<1	0.7	<30	<10	NA	<3	<40	NA	NA	NA
As	2	2	0.25	<100	<50	<1	1.4	1.6	NA	<1	NA
V	10	NA	7.7	10	10	7.0	5.5	7	NA	6.0	NA
Mn	20	3	1.9	10	20	7.6	4.8	6.7	NA	5.0	NA
Ni	<40	4	6.0	<10	<20	NA	NA	<20	NA	NA	NA
Sb	0.6	NA	0.04	<30	<10	0.14	0.2	0.4	NA	NA	NA
Cr	<30	7	12	<10	<30	3.4	5.0	4.8	NA	NA	NA
Zn	<100	5	6.6	<100	<50	NA	NA	<100	NA	NA	NA
Cu	10	9	4.5	10	10	NA	NA	<0.4	NA	NA	NA
Pb	<4	4	1.8	<30	<10	NA	NA	NA	NA	NA	NA
Se	<15	<8	0.1	NA	NA	1.0	5.0	2.0	1.5	NA	NA
B	15	5	14	10	7	NA	NA	NA	NA	NA	NA
F	<2	4	60	NA	NA	NA	NA	NA	NA	NA	NA
Li	0.3	NA	2.8	<300	10	NA	NA	NA	NA	NA	NA
Ag	<2	NA	<0.1	<1	<1	NA	NA	<2	NA	NA	NA
Sn	3	NA	0.19	<30	<10	NA	NA	NA	NA	NA	NA
Fe	2000	2000	1800	2000	3000	2400	2700	3140	NA	8000	NA
Sr	100	50	46	<30	NA	160	NA	120	NA	80	NA
Na	600	100	660	300	500	800	870	840	NA	800	NA
K	100	50	200	150	20	NA	2200	280	NA	100	NA
Ca	10000	10000	5800	8000	10000	NA	5500	7070	NA	NA	NA
Si	6000	10000	10000	3000	20000	NA	NA	NA	NA	NA	NA
Mg	2000	700	2000	600	100	2600	NA	920	NA	1000	NA
Ba	400	30	110	500	200	NA	220	430	NA	<2.0	NA

Key: NAA, neutron activation analysis; SSMS, spark source mass spectrometry; OES, optical emission spectrometry; AAS, atomic absorption spectrometry; NA, no analysis.

a - analysis on sample direct
b - DC are on sample direct
c - instrumental NAA
+ - dissolution followed by flameless AAS

In addition to the NAAQS regulations, implementation plans have been established by states for all existing stationary sources. The USEPA has also set New Source Performance Standards for various industries.

Two elements, Be and Hg, have been singled out as potentially toxic in amounts sometimes found in the atmosphere. Standards have been proposed for each element and emissions per source should be less than 10 grams per day (g/da) for Be and 2,268 g/da for Hg. In 1978 lead was classified as a criteria pollutant by the USEPA with a NAAQS of 1.6 $\mu g/m^3$ to be achieved by 1982.

In summary, trace element emissions are not directly regulated or controlled. But control of particulate matter, with which the trace elements are intimately associated, is well established and more stringent standards are evolving. As better analytical techniques allow for an improved assessment of the environmental situation and newer technologies permit a greater degree of control, regulations will likely be promulgated that relate emission rate to particle size; specific elements may be regulated as is now the case with Pb.

Conclusions

Many areas were identified in which more research or development seems warranted, these areas include:

- Analysis of present SAROAD information to justify greater data gathering efforts
- Analysis of source emission data
- Research on the mechanism of fly ash formation
- Cost/benefit analysis of various pollution control technologies
- Major element concentration effects on trace element fate
- Association of trace elements in coal (organic vs. inorganic, chalcophile vs. lithophile)
- Reliability of sampling techniques and methods of chemical analysis
- Boiler configuration and temperature profiles in the boiler and particulate control devices
- Quantification of emissions from the combustion of municipal refuse
- Assessment of the leachability of ash from the combustion of municipal refuse

Table 8. *Fly ash analysis for trace elements—comparison of methods* [a]

Analytical method	SSMS [b]	SSMS [b,c]	SSMS [b]	SSMS [b]	OES [d]	OES [c,d]	OES [d]	DRES [e]	DRES [e]	NAA [f]	NAA [f]	NAA [f]	NAA [f]	AAS [f]
Hg	1	0.4	2	0.1	1	1	NA	NA	NA	1	18	0.3	NA	0.21
Be	7	1	5	7	5	4	7	NA	3	NA	NA	NA	NA	NA
Cd	3	6	2	2.3	50	100	NA	NA	NA	NA	NA	90	NA	NA
As	40	100	15	2.8	100	200	50	NA	NA	30	70	54	40	NA
V	250	300	200	290	2000	400	200	NA	180	290	247	382	250	300
Mn	300	150	300	170	500	200	500	NA	NA	317	294	369	250	NA
Ni	100	100	100	45	300	50	300	NA	NA	NA	NA	NA	NA	100
Sb	10	40	NA	5.6	50	100	NA	NA	NA	9.2	7	19	NA	NA
Cr	200	100	100	330	500	100	300	NA	80	108	100	130	NA	150
Zn	200	70	1000	330	100	200	200	NA	350	NA	NA	NA	NA	600
Cu	100	150	200	45	300	200	300	NA	NA	NA	NA	33	NA	90
Fb	200	200	100	180	100	200	200	NA	440	NA	NA	NA	NA	95
Se	10	15	NA	0.77	NA	NA	NA	NA	NA	8.2	40	12	NA	NA
B	500	200	300	190	300	300	500	NA	NA	NA	NA	NA	NA	NA
F	30	10max	100	60	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	20	60	150	190	20	100	300	NA	NA	NA	NA	NA	NA	NA
Ag	1	2	NA	0.04	3	2	1	NA	NA	NA	NA	NA	NA	NA
Sn	6	15	NA	1.9	20	100	NA	NA	NA	NA	NA	NA	NA	NA
Fe	High	High	10%	5.3%	20%	10%	5.0%	10.5%	13%	17.5%	18.3%	18.1%	26%	17.8%
Sr	150	200	200	69	200	200	500	NA	400	520	NA	180	1000	NA
Na	2000	2000	500	6600	3000	4000	3000	1400	NA	2700	2300	2450	3500	2800
K	High	High	1.0%	1.7%	2%	2%	0.5%	NA	NA	NA	1.5%	3.1%	2.5%	2.0%
Ca	High	High	4.0%	1.3%	5%	5%	3.0%	3.7%	3.7%	NA	2.2%	3.9%	NA	4.7%
Si	High	High	10%	major	20%	15%	20%	NA	NA	NA	NA	NA	NA	19.5%
Mg	10000	10000	5000	44000	5000	4000	5000	4000	2200	13700	7000	3000	4000	6000
Ba	200	600	700	110	200	300	500	NA	NA	NA	200	410	400	NA

Key: Analysis Code-NAA, neutron activation analysis; SSMS, spark source mass spectrometry; OEC, optical emission spectrometry; DRES, direct reading emission spectrometry; AAS, atomic absorption spectrometry; NA, no analysis.

a- ppm by weight, higher concentrations are specified as percent (%)
b - analysis on sample direct
c - duplicate sample submitted for SSMS and OES analysis only
d - DC are on sample direct
e - dissolution followed by RF spark analysis
f - instrumental NAA

Table 9. *National Ambient Air Quality Standards*

Pollutant	Averaging time	National Standards: Primary	National Standards: Secondary	Sampling method
Suspended particles	Annual geometric mean	75 μg/m³	60 μg/m³	
	24-hour maximum*	260 μg/m³	150 μg/m³	High-volume

** Not to be exceeded more than once a year.*

- Quantification of emissions from residential combustion, packaged boilers (commercial and institutional), and the combustion of wood as a fuel
- Assessment of the effects of low-level, long-term exposure to trace elements
- Synergistic effects associated with trace element exposure
- More correlative studies to confirm trends in morbidity and mortality related to pollution incidents
- A comprehensive study covering several power plants operating under the same conditions, focusing on accuracy of data, and ensuring uniformity of elements studied and sampling procedures
- Studies regarding the need for and the effect of regulations.

If these points could be addressed in the near future we will be in a better postition to assess the impact of SCCP emissions on human health and the environment.

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The complete report, entitled "Trace Metals and Stationary Conventional Combustion Processes," (Order No. PB 80-216 161; Cost: $32.00, subject to change) will be available only from:
National Technical Information Service
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