Air Toxics Analysis—Particularly Metals

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ABSTRACT

The objective of this paper is to provide an analysis of particulate metal emissions in the USA. The analysis will identify natural and industrial sources, environmental standards, emission trends, and controls of particulate emissions. Since the majority of airborne metal emissions originate from metal industries and electric utility facilities, environmental and worker assessments of exposures as well as air pollution control research will be presented. The toxicity of ten particulate metals are characterized by inhalation exposure limits, risk-based concentrations, drinking water standards, solid waste toxicity leaching characteristics, and overall environmental hazard ranking system. The most recent biomonitoring studies have provided urinary metal concentrations for assessing background metal exposures of thirteen metals for USA populations. The increasing urinary metal concentrations and potential bioaccumulation of metals such as cadmium, mercury and selenium are discussed. Metal emissions include selenium compounds which are not assessed by OSHA, are found in coal and recycled metal materials. Selenium emissions are now greater than mercury emissions by an order of magnitude in the electric utility industry. Airborne emissions monitoring and exposure assessments of indicator metal particulate compounds are recommended for regulatory compliance and to validate the effectiveness of air pollution control technologies.

INTRODUCTION

Air Toxics Exposures

An August 2007 report from the Center for Disease Control and Prevention (CDC) has summarized the core hazard indicators for potential for exposure to contaminants or hazardous conditions.[1] The top five indicators are air quality related exposures.

- Criteria pollutants in ambient air,
- Hazardous or toxic substances released in ambient air,
- Residence in non-attainment areas for criteria air pollutants,
- Motor vehicle emissions—intervention indicator, and
- Tobacco smoke in homes with children.

In 1997, the Organization for Economic Co-operation and Development (OECD) and the World Health Organization (WHO) European Centre for Environment and Health (ECEH) organized a Workshop on Environmental and Environmental Health Information to Support National Environmental Action Programs and National Environmental Health Action Plans.[2,3] These reports indicate that data quality is a common but difficult issue. When considering data relating to exposure the hierarchy of value in decreasing relevance is:

- measurements of internal dose in target organism,
- measurement of personal exposures,

- ambient environmental concentrations
- emission data.

Hazardous air pollutants (HAPs) or air toxics are considered to cause serious health effects including cancer, damage to the immune system, as well as neurological, reproductive, developmental, respiratory and other health problems. The three sources of air pollution in the USA include area or natural sources (25%), major industrial point sources (25%), and all mobile sources (50%). Deposition of air toxics onto soils or surface waters may lead to biomagnification through the food chain causing fish ingestion exposures and advisories, particularly to metal compounds such as mercury and selenium. This report describes the state of airborne metal particulates with respect to sources, databases, toxicity, biomonitoring, occupational exposures, ecosystem evaluations, and air pollution control technologies. A hazard evaluation system is presented which utilizes toxicity and persistence information for ten metal compounds.

METHODS

Air Toxics Databases

For compiling the major and area air toxics sources, USEPA relies on ninety percent state-reported emissions, maximum achievable control technology (MACT) data, the toxics release inventory (TRI) database, and national estimates. Of the 579 chemicals listed on EPA Toxic Release Inventory, about 9% of the chemicals are measured. About thirty of the 189 HAPs have health effects data. Of the thirty-three major HAPs, thirteen metal compounds are monitored by the USEPA TRI database.[4,5]

Despite increases in population, vehicle miles traveled, and increased electric energy consumption, the USA concentrations of air toxics have decreased about 30% from 1990 to 1999 with further decreases of 75% (four air toxics) predicted by 2020. The 2003 USEPA urban hazardous air pollution monitoring data indicated less than 41% of the samples were above the analytical method detection and about 95% of the cancer and noncancer risks were attributed to ten hazardous air pollutants. The EPA air toxics data quality is reported to have high confidence for analytical measurements of seven compounds including acetaldehyde, benzene, formaldehyde, lead, manganese, methylene chloride and nickel. The median ambient air concentrations of these chemicals were above the method detection limit. The majority of urban air toxics were either not detectable, present at low concentrations, and health risks were dominated by a few indicator compounds such as volatile organic compounds and particulate matter.[6,7,8,9]

Therefore, air quality monitoring sampling and analysis can be simplified by selecting surrogate or indicator compounds such as particulate matter, which is also representative of potential metal contaminant levels. Technological advances in real time optical light-scattering particulate concentration monitors and continuous laser-based particle analyses have simplified worker and public air quality monitoring. If ambient air metal analysis is needed, the analytes list includes about 15 metals which are collected on a glass fiber filter and analyzed by inductively coupled argon plasma spectroscopy or graphite furnace atomic adsorption.[10]

RESULTS

Sources of Particulate Metal Emissions

The four major industrial sources of total metal emissions as reported by EPA Toxic Release Inventory (EPA TRI, 2002-2005) include the electric power industry (SIC 4911), the primary metals industry (SIC 33XX), hazardous waste disposal facilities (SIC 4953, 7389) and metal mining operations (SIC 10) as depicted in Table 1 and Figure 1. The total metal releases (18 metals) in 2005 was about 1.2 million tons. The individual releases of arsenic, cadmium, lead, mercury and selenium are reported in

Table 1. It is interesting that the ratio of mercury to selenium in coal (about 0.1 ppm and 1.0 ppm respectively) is about the same as the ratio (1:10) of mercury and selenium reportedly released by the electric power industry in 2005 (Table 1). The total emissions of mercury and selenium are compared in Figure 2 which illustrates that selenium emissions are five to ten times greater than the mercury emissions for electric utilities and primary metal industries. About fifty percent of the total metal emissions were reported by metal mining operations, representing primarily the naturally occurring minerals in the ore bodies contained onsite.[11]

The major source of airborne metal emissions is the metals industry (35%) which includes primary and secondary metal operations such as recycling facilities (Figure 3) and primarily originate from point sources (68%). The electric utility industry consistently contributes about 30% of the total airborne metal releases which are also point source emissions (98%). [11]

Stack testing implementation data indicate that in 2003, about 9500 stack tests were reported and about 5% failed compliance with emission limits. USEPA Region 4 states conducted 40% of the stack tests, five states reported less than 20 tests and two states reported no stack tests. The point source or stack gas sampling and analytical methods for airborne particulates can be found in USEPA 40 CFR Part 60, Appendix A, Test Methods 1-5. [4,5]

The emissions factor is an attempt to relate the quantity of a pollutant released to the atmosphere with an activity associated with the pollutant's release and are long-term averages for all facilities in the source category. The reference source for major source categories is EPA AP-42, Compilation of Air Pollutant Emission Factors, Section 12 Metal Processing. The emission factors are rated according to the quality and quantity of emission data generated by source categories utilizing the maximum achievable control technology, ratings are from A to E which is the worst-case, most uncertain database information. [12,13,14]

The majority of the emission factors for primary aluminum production, mini-mills, secondary aluminum production, and gray iron foundries are rated poorly, especially particulate emissions which also represent the metal contaminants. Secondary metal plant emissions have been found to include HAPs such as antimony, cobalt, selenium, cadmium, and arsenic, but specific emission factors for these HAPs have not been recommended due to lack of information. The USEPA issued a final rule to reduce hazardous air pollutants emitted from secondary aluminum production plants (40 CFR Part 63, March, 2000). The rule is anticipated to reduce air toxics emissions 12,000 tons per year, representing about 1.0% of total 2005 metal releases. [12,13,14] National emission standards for hazardous air pollutants for iron and steel foundries (EPA 40 CFR Part 63, August 29, 2003) have also been promulgated. Site specific environmental monitoring data for industries releasing metals and quantifiable data validating compliance with hazardous air pollution standards is generally not accessible for public review.

Health Based Metal Concentrations

The health hazard properties of ten metal compounds with respect to inhalation exposure limits, toxicity, hazardous air pollutant rankings, risk based concentrations, hazardous waste classifications, drinking water standards, biological exposure indices, and analytical detection limits are presented in Table 2. The airborne exposures to particulate metals are ranked in order of most stringent worker exposure limits according to Occupational Health and Safety Administration (OSHA) eight hour permissible exposure limits (PEL). Biological exposures indices for recommended urinary metal concentrations are available for nine of the ten metals. The carcinogenic metals include arsenic, beryllium, cadmium, and nickel compounds.[15,16, 17,18,19]

Classification of metal containing wastes, sludges, slags, or residues as hazardous solid wastes is mandated by the USEPA Toxicity Characteristic Leaching Procedure (TCLP) method which estimates the metal compounds leaching characteristics for protection of ground and surface water. The health based concentrations in Table 2 includes eight metals which do have TCLP limits, the most stringent limits in order of decreasing toxicity include beryllium, mercury, selenium and cadmium.[20]

The Indiana Relative Chemical Hazard Scores (1-100) ranks total environmental hazard scores by incorporating acute and chronic human health based risk levels as well as aquatic toxicity limits. The toxicity information includes worker exposure limits for inhalation, oral dietary intake limits, recommended maximum daily intake levels, no observable effect levels for toxic responses, non-carcinogenic hazard quotients, cancer potency values, mammalian oral lethal doses (LD50%), lethal concentration (LC50%) data for aquatic life, acute/chronic water quality limits, and hazardous waste disposal limits. The hazard rankings for ten metals representing metal toxicity and environmental persistence are presented in Figure 4.

Occupational Exposures to Metal Particulates

Occupational inhalation exposure limits for ten metal compounds that are generally considered to be protective of most workers for eight hours are represented in Table 2. Occupational exposure limits do not reflect multiple exposures, health effects to sensitive populations, or chronic low level exposures to airborne pollutants. Worker inhalation health based exposure limits are generally several orders of magnitude greater than ambient air or risk based standards for public health protection. The total particulate exposure standard for risk based chronic exposures according to USEPA (0.15 mg/m^3) is two orders of magnitude less than the OSHA permissible exposure limit (15 mg/m^3). The relative differences in exposure standards between USEPA and OSHA are similar for respirable particulates and lead. The application of safety and uncertainty factors to occupational exposure limits result in risk based concentrations and ambient air quality standards which are more conservative. Five of the ten metals (Table 2) have analytical detection levels greater than the USEPA risk based concentrations, which therefore could not be validated as quantifiable risks.

A representative measurement of occupational exposures is to biologically monitor the blood, urine, hair, nails, and other tissues of the target population. The recommended biological exposure limits for urinary concentrations of metals are found in Table 2. Biological monitoring of Taiwan steel production workers indicated the urinary concentrations of selenium, arsenic and beryllium significantly exceeded the controls. The report suggests the need for improvement of environmental conditions in the workplace through better ventilation and industrial hygiene practices during the production of aluminum, iron, and steel.[21]

Primary aluminum production exposures include: alumina dust, particulate and gaseous fluorides, carbon monoxide, sulfur dioxide, polycyclic aromatic hydrocarbons, heat stress, magnetic fields, vibration and shift work. Coke oven workers are exposed to a range of particulates, gases, and vapors probably unequaled in any other industrial setting. It is estimated that one-quarter of the total weight of coal is evolved as gases and vapors in the coking processes and that over 2000 different chemical species may be formed. Excess lung cancers in coke oven workers employed for more than five years is believed to be correlated with the concentration of coke oven particulate emissions identified as the benzene soluble fraction (BSF). The BSF fraction of particulate emissions which includes several carcinogens can be applied as the indicator measurement for assessing multiple inhalation hazards.[22]

Occupational exposures to workers handling, burning, and land filling refuse were monitored at three municipal landfill sites, a refuse transfer station and a refuse derived fuel plant. Overexposures to lead and cadmium dusts were reported, especially for workers cleaning the boiler room. Another 2002 study of boiler maintenance workers monitored particulate matter less than 2.5 micrometer diameter (PM2.5) with associated chromium copper, manganese, nickel and lead compounds. Workers were reported to have increases in autonomic cardiac dysfunction.[23]

The particulate and gaseous emissions when welding aluminum alloys was evaluated and high levels of particulates were considered to be greater than 20 mg/m^3. Alloys containing elements with lower melting and boiling points or elements that are more reactive would be expected to produce higher concentrations of particulate matter. Manganese, zinc, and copper would be more likely to volatilize and contribute to the particulate matter. The percent reduction in particulates outside versus inside the welding helmet ranged from about 50 to 99%.[24]

A recent National Institute of Occupational Safety and Health (NIOSH) study evaluated hexavalent chromium inhalation exposures in thirty sectors of operations such as material handling, welding, painting, electroplating, and cement manufacturing. The concentrations of hexavalent chromium ranged from 3 to 55 ug/m^3 and the worst case exposures were workers applying atomized chromium alloys to recoat heat exchange tubes. One third of the industrial operations had no information with respect to chromium exposures and controls.[25]

Another survey of 45 industry sectors examined the chemical handling and use of lead containing materials from 2003 to 2007. The results indicated that 46% of the industries had been OSHA inspected, 17% were cited for violation of the general industry lead standards, and 25% of the industries had not performed air monitoring in the last three years. Substandard industrial hygiene practices for controlling lead exposures were observed in about quarter of the industries. The OSHA statistics for monitoring metal exposures in the metals industry (SIC 33XX) were evaluated over the past five years. The number of monitoring tests per year for foundries, secondary non ferrous facilities and aluminum rolling facilities were 284, 130, and 1.5 per year, respectively. About one OSHA inspection monitoring test is performed per day for the metals industry sector, primarily in foundries. Selenium was not an OSHA reported metal hazard.[26]

The majority of events leading to occupational injuries are contact with equipment or being struck by an object. Overexertion accounts for about 25% of the injuries while overexposures to hazardous substances are less than 5% of the total 1.54 million occupational injuries in 2002. Hazard communication violations continue to be a leading cause of OSHA citations every year, which implies a lack of workplace health and safety training. Monitoring workplace exposures has been documented to be effective in reducing injury rates.[27]

Biological Exposure Monitoring

To link contaminants in the environment with adverse health effects, biological exposure indices or internal exposure levels in human tissues and fluids is considered an accurate measure. Ecosystem bioaccumulation studies addressing metals are abundant, especially with respect to monitoring lichen concentrations of copper, chromium, lead, and nickel.[28]

Human blood lead levels monitored since 1976, has been a successful biological monitoring program used to identify at-risk populations, evaluate regulatory actions, improve exposure estimation models, and identify sources of preventable exposures. Removing lead from gasoline has resulted in decreased urban lead concentrations and has been validated by decreasing blood lead levels in children . The 2005 *"Third National Report on Human Exposure to Environmental Chemicals"* summarizes the biomonitoring measurements providing exposure information to evaluate the potential for adverse health effects. This report presents exposure data for 148 environmental chemicals over the period from 1999 to 2002 for the civilian USA population. For most of the chemicals, more research is needed to determine whether exposure levels reported are valid health concerns.[1]

The *Third Report* reported urinary measurements for ten metals which are illustrated in Figure 5. Recent research studies have shown that urine cadmium levels as low as 1 ug/gram creatinine in people may be associated with subtle kidney injury and increased risk for low bone-mineral density. The *Third Report* shows that about 5% of U.S. population aged twenty years and older had urinary cadmium levels at or near those levels. Cigarette smoking is the most likely source for higher cadmium levels. Metal health hazards with no biomonitoring data include arsenic, copper, chromium, nickel, and selenium.

Pollution controls and public health efforts to reduce the number of children with elevated blood lead levels in the general population continue to be successful, except for special populations of children. No safe blood lead level in children has been identified, so continued controls of environmental lead exposures are recommended.

In 1999, blood mercury levels in children were about 25% of levels in women of childbearing age (0.0012 mg/L). Mercury concentration in hair can be used as an indicator of mercury concentration in the blood, with a ratio of blood to hair of 1:250. Most of the mercury in blood comes from the consumption of fish or shell fish which accumulate methyl mercury from water and soil. Data from the *Third Report* show that all women of childbearing age had levels below 58 ug per liter (ug/L), a concentration associated with neurodevelopmental effects in the fetus. However, about 6% women of childbearing age had levels within a factor of 10 of those associated with adverse effects. Transboundary migration of mercury has been evaluated since China has an estimated 2,000 coal combustion facilities emitting about 600 tons of mercury into the air annually, accounting for nearly a quarter of the world's non-natural emissions. Estimates are that about a third of the atmospheric mercury is from natural sources including volcanic eruptions and evaporation.[29]

The second meeting of International Society of Environmental Bioindicators gathered human health, wildlife, and molecularly focused researchers to evaluate the status of mercury bioindicators. The recommendations included the evaluation of co-contaminated residues in tissues such as selenium, as the toxicity is related to the mercury to selenium ratio. [30]

Medical geology, the study of the impacts of geological materials and processes on animal and human health, is a dynamic emerging discipline bringing together the geosciences, biomedical, and public health communities to solve a wide range of environmental health problems. The review examines both deficiency and toxicity of trace element exposure. Goiter is discussed, as is deficiency of selenium in the soil as the cause of juvenile cardiomyopathy and muscular abnormalities. High concentrations of arsenic in the groundwater but also coal combustion of mineralized coal with high arsenic concentrations in Asia, Africa, Europe, North and South America, are causing arsenic poisoning. Dental and skeletal fluorosis also impacts the health of millions of people around the world and like arsenic, is due to naturally high concentrations in water and to a lesser extent, coal combustion. Other medical geology issues described include geophagia, exposure to radon, and ingestion of high concentrations of organic compounds in drinking water. [31,32]

The role of selenium in reducing bioaccumulation of mercury in fish has been reported and inverse relationships between fish tissue mercury and the abundance of selenium present in the ecosystem have been noted. Selenium supplementation of lake waters in Sweden resulted in a 75%-85% reduction in mercury levels of fish over a 3 year period, and loss of selenium can have the opposite effect. When selenium-rich discharges of fly ash to an artificial lake were removed, researchers noted a steady increase in mercury concentrations. Studies such as these indicate the importance of selenium dependent mercury retirement in aquatic ecosystems, possibly through formation of insoluble mercury-selenium complexes that deposit in sediments. Several studies of the relationships between Hg and Se are currently ongoing in Canada and elsewhere in the world.[33]

The bioaccumulation of metal compounds in the lipophilic flesh of fish has been surveyed by the USEPA. The target analytes selected were based on their occurrence in fish and shellfish detected in regional or national fish monitoring programs, their persistence in the environment (half-life >30 days), their potential for bioaccumulation (BCF values >300) and their oral toxicity to humans. Metal target analytes for fish sampling programs include inorganic arsenic, cadmium, methyl mercury, selenium and tributyltin. The USEPA has established fish consumption advisory screening values 0.40 ppm and 0.049 ppm for methyl mercury for recreational (17.5 grams/day) and subsistence fishers (142.4 grams/day), respectively. The screening value is the concentration of chemical in the fish tissue that is of potential public health concern, based on both carcinogenic and non carcinogenic effects. The FDA action level is 1.0 ppm mercury. Mercury was detected at 92% of the 374 sites surveyed by the USEPA in 1992, with higher mean tissue concentrations in the predator fish than in the bottom feeders, especially in freshwater fish samples from the Northeast. [34]

California, Colorado, North Carolina, Texas, and Utah have 11 advisories in effect for selenium in fish as of 1998. Selenium concentrations of about 2.0 ppm were detected in pike fillets, due to exposures from selenium compounds leaching from a coal fly ash disposal area. Selenium should be included in all state fish and shellfish monitoring programs in areas where it occurs in geologic formations (western and southwestern USA states) and near oil or coal combustion sites. USEPA also has recommended water quality concentrations of 20 ppm and about 3.0 ppm selenium as a screening value for "green waterways" for safe consumption of fish by recreational fishers and subsistence fishers, respectively. [34]

DISCUSSION

Particulate Emission Controls

To comply with National Emissions Standards for Hazardous Air Pollutants, coal fired power plants have applied MACT technologies which include scrubbers, baghouse collectors, and electrostatic precipitators to control total particulates and associated metal emissions. The additive effect of air pollution controls is reflected in the particulate mercury emission control efficiencies presented in Table 4. Removal efficiency of selenium and arsenic are considered highly variable for both electrostatic precipitators and baghouse controls. They are volatile metals and are enriched on the particulates. Additive air pollution control technologies may apply to other particulate metal contaminants but for metals other than mercury have not been reported by industry or regulatory sources. [33,35]

According to USEPA database information, air emission standards applied to electric utilities have succeeded in reducing air contaminants associated with coal combustion and further reductions are predicted by 2018. Air toxic field measurements at more than 50 power plants, performed by Electric Power Research Institute (EPRI), found emissions of particulate trace metals in coal are a function of total particulate emissions as well as initial trace metal concentration. For volatile elements such as chlorine and selenium, average removal efficiencies depend on the availability of flue gas desulphurization technologies. Mercury removal estimates were developed for various control technology categories and with coal's chloride content the key dependent variable. Average emission factors for organic compounds proved suitable.[33,35] By 2020, more than half of the USA coal fired power plant generating capacity is projected to be equipped with selective catalytic reduction and flue gas desulfurization technologies.[36]

Case Study-Secondary Aluminum Facility Hazardous Wastes

A case study of environmental management of selenium at three USA aluminum facilities indicated uncontrolled reduction furnace particulates emissions had measurable quantities of selenium. Additionally, hazardous waste was generated due to baghouse dust contaminated with selenium from secondary aluminum rotary furnaces. The selenium metal releases reported are not representative of the number of operating facilities or of the increased use of selenium-containing manganese (0.15%). It is estimated 85% of the manganese alloy (99.7% electrolytic manganese) used in the world today contains selenium at concentrations up to 1500 ppm. The primary and secondary processing of aluminum and steel will generate selenium waste products.[37] Only about one third of the primary metals industry is reporting selenium emissions.[11] Many USA industries have experienced and managed environmental impacts due to selenium as illustrated in Table 4.[38, 39, 40, 41,42] Managing the environmentally friendly content of products introduced to metal processing operations may reduce future waste management concerns, as illustrated with selenium containing manganese alloys.

Recycling Metal Materials

Waste emissions are also being controlled by environmentally friendly practices such as recycling. According to the United Nations Environmental Programme (UNEP), about 50 million tons of electronic devices are recycled every year, including about 500 million cell phones and 700 million computers. As the cut-off grade of metals such as nickel and copper in ores is decreasing to less than one percent, the metal content is of electronics is significantly greater (forty times) than the metal content in mined ore bodies. Additionally, the environmental impacts of initial metal mining operations are eliminated. According to the Bureau of International Recycling, the energy saved by recycling lead, steel, copper, and aluminum is 65%, 74%, 85%, and 95% respectively, as compared to primary production. Power consumption conservation and energy saved translates into reduced environmental emissions. The recycling rates for lead, magnesium, nickel and zinc have increased, but aluminum, copper, tin, and titanium recycling rates decreased from 1999 to 2003.[43]

CONCLUSIONS

The major industrial sources of total metal emissions include the metals industry, the electric power industry, hazardous waste disposal facilities, and metal mining operations. The primary sources of airborne metal emissions are the metals industry and coal fired power plants. Secondary metal plant emissions have been found to include air toxics such as antimony, cobalt, selenium, cadmium, and arsenic, but specific emission factors for these air toxics have not been recommended due to lack of information. Environmental database reporting for metal compounds has poor confidence ratings due to lack of site specific air monitoring data.

However, the air pollution control technologies implemented by the electric power industry have proven effective for particulate and trace metal removal. Air emission research for coal fired power plants is likely applicable to the metal industry plants for evaluating particulate metal removal efficiencies. Selenium is a major component of coal as well as recycled metal materials and manganese alloys. The environmental impacts of selenium contaminates have been well documented by many USA industries in various ecosystems. Airborne industrial selenium emissions are increasing, are five to ten times greater than mercury emissions and are primarily from controllable point sources.

Environmental exposures to metal compounds have been assessed by monitoring occupational inhalation exposures, biological monitoring of worker and public exposures, bioaccumulation in plants, fish, and soils, biodegradation, and water quality concentrations. Urinary concentrations of mercury and lead in the general population are decreasing, but cadmium levels are increasing due to smoking. Health-based standards are generally not representative of chronic inhalation exposures to low levels of pollutants but existing biomonitoring data for metals provides substantial data to evaluate human exposures and health effects.

Health risks are generally controllable risks. Most deaths are due to lifestyles and habits which contribute to cardiovascular diseases, not environmental exposures. Most occupational injuries are due to impacts with vehicles or objects, not respiratory exposures. Air quality management policies for locally impacted populations should minimize human activities which consume energy and therefore generate airborne wastes. Recycling metal materials should be maximized since power consumption and particulate metal emissions are both minimized. Air toxic emissions are now shared emissions as indicated by global mercury measurements from uncontrolled coal combustion, but air pollution control technologies have proven effective.

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KEY WORDS

Particulate Metals, Emission Inventories, Health-Based Risk Concentrations, Biological Exposure Indices, Hazardous Solid Wastes, Air Pollution Controls, Air Monitoring, Emission Factors, Indicator Metals, Mercury, Selenium.

TABLES

Table 1. Total metal emissions 2005 USEPA TRI (million pounds).

METALS	ALL Industries	Electric Utilities	Primary Metals	RCRA	Metal Mining
Arsenic	185	6.45	5.25	1.77	172
Cadmium	3.33	No Data	1.14	1.56	0.52
Lead	470	8.27	34.0	19.7	394
Mercury	4.40	0.15	0.03	0.44	3.67
Selenium	3.47 (~1 700 tons)	1.25	0.43	1.13	0.46
TOTAL (18 Metals)	2,310 (~1.2 million tons)	384 17% Total	470 20% Total	168 7.3% Total	1,160 50% Total

Table 2. Health-based metal concentrations.

METALS (10)	As	Be	Cd	Cu	Cr	Pd	Hg	Ni	Se	Zn
OSHA PEL RANK (mg/m3) CANCER	3 0.01 X	1 0.002 X	2 0.005 X	6 0.10	8 0.50	5 0.05	6 0.10	4 0.015 X	7 0.20	9 5.0 Dust
USEPA Ambient Air Risk-Based Conc. (mg/m3)	4.1E-7	7.5E-7	9.9E-7	1.5E-1	5.5	3.7E-7 Tetra-ethylPb	3.1E-4	7.3E-2	1.8E-2	1.1
USEPA Hazardous Air Pollutant RANK Total = 189 HAPS Detection Limit (mg/m3) High Analytical Confidence	17 3.1E-3	56 8.0E-5	13 3.0E-5		5 2.0E-4	42 8.0E-4 X	4 4.9E-4	36 3.0E-5 X	126 4.0E-5	
IFC Metal Mining Standards (mg/m3)	0.002			0.10		0.05	0.05		0.20	
USEPA Hazardous Solid Waste TCLP (mg/L)	5.0	0.007	1.0		5.0	5.0	0.2	70.0	1.0	
EPA Drinking Water MCL (mg/L)	0.05	0.004	0.005	1.0	0.1	0.015	0.002		0.05	5.0
Biological Exposure Indices Taiwan Steel Worker Overexposures	35 ug/L Urine	2 ug/g creat. Urine	5 ug/g creat. Urine	50 ug/g creat. Urine	25 ug/L Urine	30 ug/100 ml Blood	35 ug/g creat. Urine	2 ug/g creat. Urine	25 ug/g creat. Urine	
Total Chemical Hazard Score (1-100 IRCHS)	40.4	39.7	32.9	29.4	32.7	33.3	28.7	32.1	21.6	10.6
Ecosystem Bioaccumulation Lichen Studies (120)	X			X	X	X	X	X	X	

Table 3. Particulate mercury emission controls based on coal fired power plants.

Dependent on Coal Type	% MERCURY Capture
Particulate Matter	
Electrostatic Precipitator: Cold-Side (ESP:CS)	2-63%
Electrostatic Precipitator: Hot-Side	27-48%
Fabric Filter (FF)	87-93%
Particulate Matter/SO2	
ESP:CS + Wet Flue-Gas Desulfurization (FGD)	56-74%
FF + Wet FGD	89%
Particulate Matter/SO2/NOX	
Selective Catalytic Reduction + ESP:CS + Wet FGD	>90%
Selective Catalytic Reduction + Spray Dryer + FF	47-99%

Table 4. Industrial impacts in USA due to selenium contaminants.

SELENIUM Contaminant of Concern	Ground Water Impacts	Surface Water Impacts	USEPA Fish Advisories	Bird Impacts	Mammal Impacts	Hazardous Waste Impacts
Coal Fly Ash Disposal	X	X	X	X		X
Oil Refinery Wastewater		X	X	X		X
Copper Mining Wetlands	X	X	X	X		X
Phosphate Waste Shale Disposal	X	X	X	X	X	
Gold Mining Heap Leach	X	X	X			
Aluminum Recycling Facility						X
USA Five States 1993/1998			X			

FIGURES

Figure 1. Industry total metal releases (USEPA TRI).

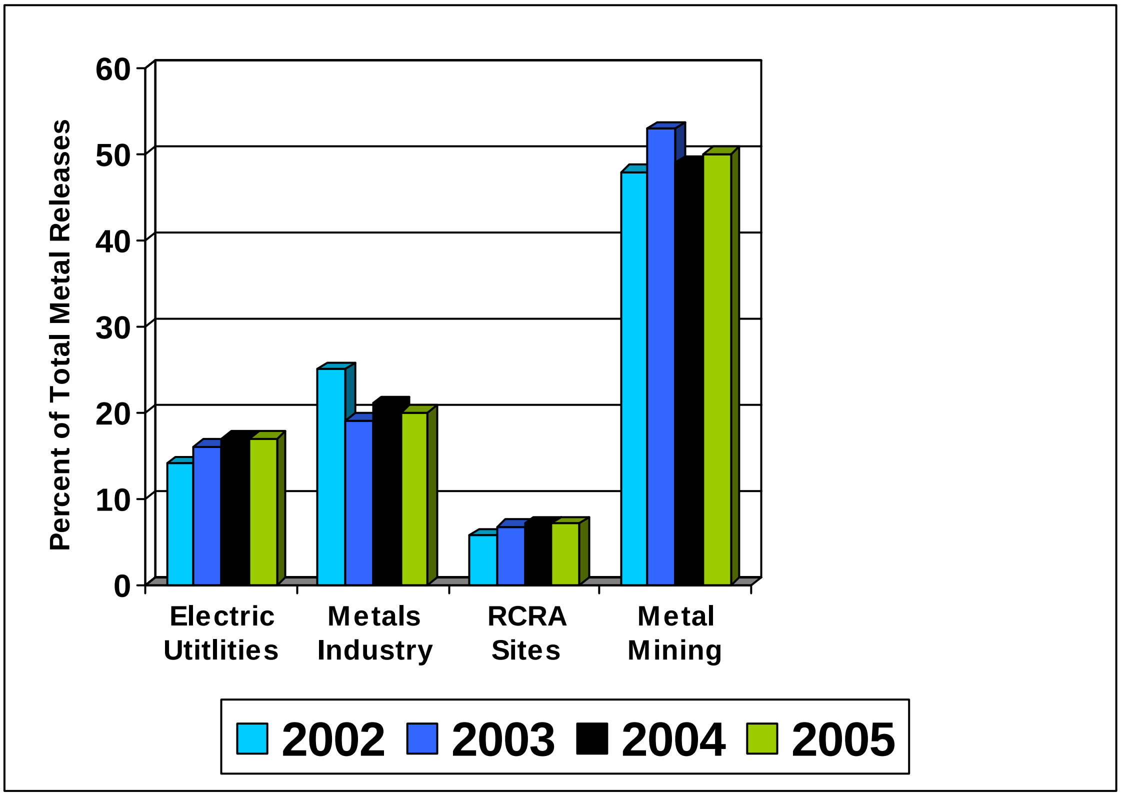

Figure 2. Industry trends in total mercury and selenium releases (USEPA TRI).

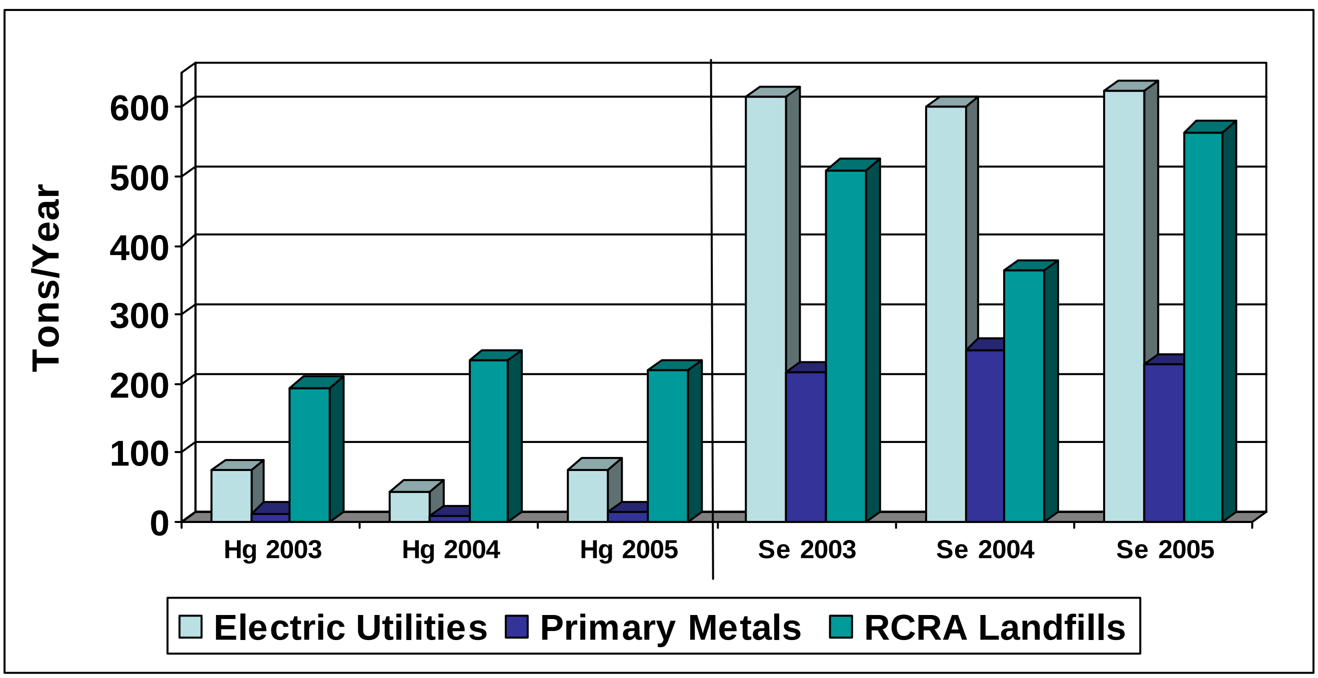

Figure 3. Industry airborne metal releases (USEPA TRI).

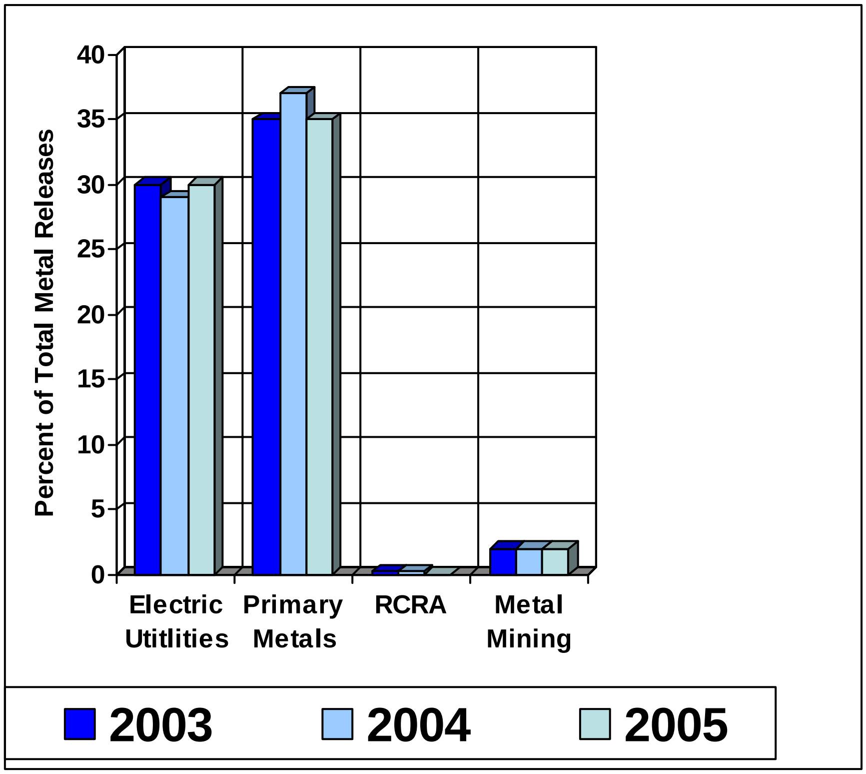

Figure 4. Total environmental hazard scores (Indiana Relative Chemical Hazard Scores 1-100).

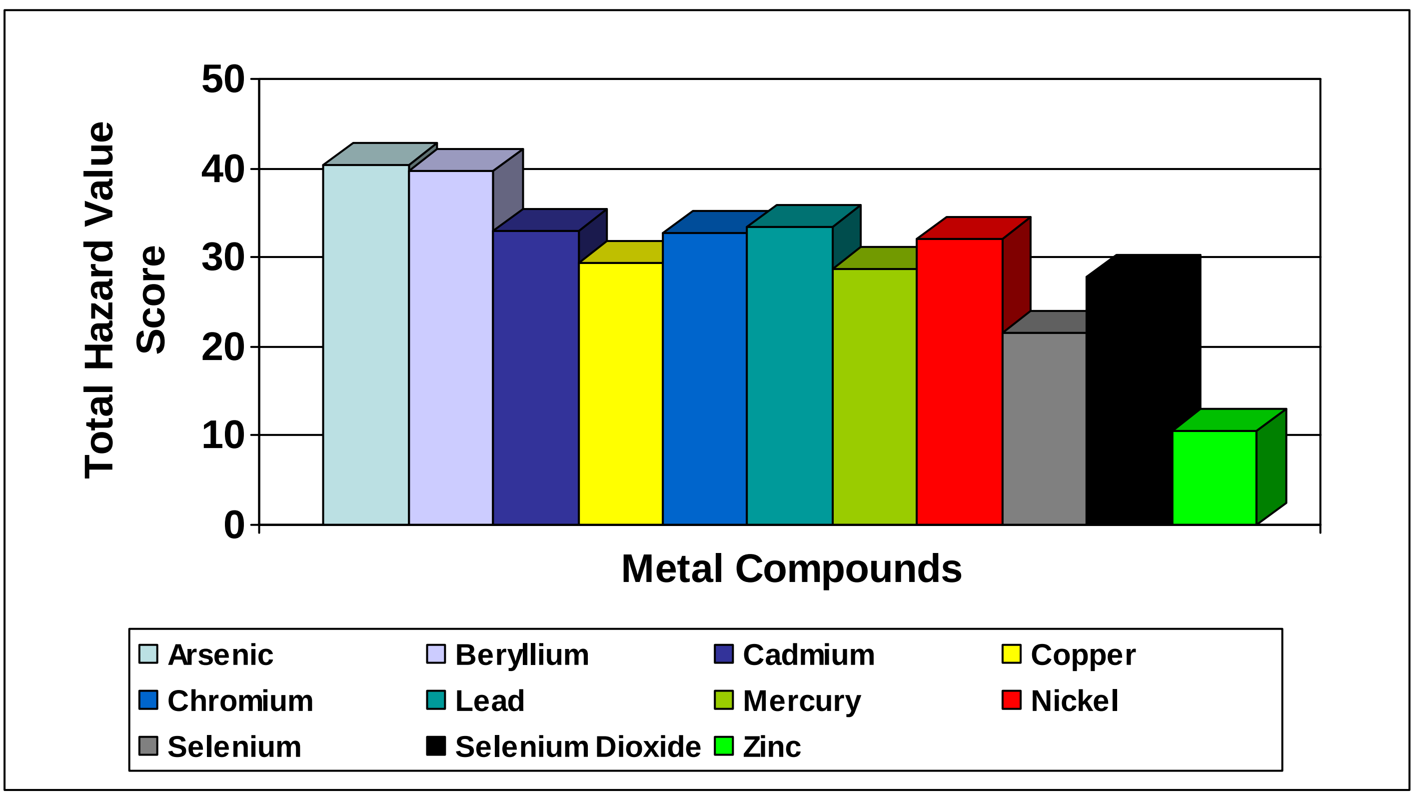

Figure 5. Biological monitoring of metals (CDC Third Report July, 2005).