CHAPTER 7

Atmospheric Emissions of Arsenic, Cadmium, Lead and Mercury from High Temperature Processes in Power Generation and Industry

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ABSTRACT

High-temperature processes, such as coal and oil combustion in electric power stations and industrial plants, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration, and kiln operations in cement plants, emit several pollutants, especially those being easily volatile. Among the volatile pollutants are As, Cd, Pb and Hg.

In this chapter, atmospheric fluxes of As, Cd, Pb and Hg are calculated for the above-mentioned sources in a quantitative and qualitative sense, and are based on measurements and estimates. The measurements were carried out around coal-fired power plants and copper and lead smelter complexes in Poland during the period 1975–80. Estimates were based on: (1) the chemical composition of source materials, (2) the physical–chemical properties of metals, (3) the technology employed, and (4) the efficiency and type of emission control devices utilized. Non-ferrous metal smelters appear to be a predominant source of the As and Cd emissions. Traffic is a major contributor to Pb emission, however, this source is not considered here. Significant amounts of Pb are also emitted from lead smelters. The most important sources of Hg emission include mining and smelting of non-ferrous metals, burning of fossil fuels (mainly coal), and chloralkali process for production of chlorine and caustic soda.

Combustion temperature in boilers, furnaces, roasters, etc. is the key parameter affecting the amounts of As, Cd, Pb and Hg released into the atmosphere, as well as their chemical form and particle size distribution. The metallic As, Cd and Pb and their oxides and sulphides are commonly found in stack dust. Hg is released mainly in a gaseous form. Mercury associated with aerosol particles normally contributes only marginally to the total atmospheric load. High-temperature processes
produce fine fraction particles with a significant portion of particles below 2 μm in diameter. These particles can penetrate through emission control devices, enter the atmosphere, and travel for long distances. Penetration of As, Cd and Pb through the boilers of two coal-fired power plants in Poland, equipped with electrostatic precipitators of 99.5% efficiency was between 2 to 3%. More than 95% of Hg was released in a vapour phase. Penetration rates 2-3 times lower for the above elements were measured through wet scrubbers.

Atmospheric fluxes of As, Cd, Pb and Hg were calculated on global, regional, and local scales. Estimates in this chapter are then compared with emission surveys by other authors.

Finally, recommendations for further efforts are presented emphasizing the role of emission surveys for planning control strategies to achieve ambient air quality goals. Gaps in the knowledge and uncertainties of emission assessments have been also taken into account.

INTRODUCTION

The processing of mineral resources at high temperatures, such as coal and oil combustion in electric power stations and industrial plants, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration and kiln operations in cement plants result in the release of volatile elements into the atmosphere. Among the volatile pollutants, arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) are widely studied because of the serious health concern associated with them. The emissions of these elements by the above processes alter their biogeochemical cycles in the whole human environment. To assess these perturbations, extensive emission inventories are required. During the last decade the growing interest in this field has been documented in the literature. Emission strengths of As, Cd, Pb and Hg were estimated by several international and national communities and agencies. As an example, the US National Academy of Sciences, the US Environmental Protection Agency, and the National Research Council of Canada have produced emission inventories for all four elements in the USA and Canada (e.g. NAS, 1977; US EPA, 1979; NRCC, 1979). In Europe, special attention has been paid to the anthropogenic fluxes of Cd (e.g. van Enk, 1980; Hutton 1982; OECD, 1984). This does not mean that the evaluation of anthropogenic fluxes of other elements has been neglected. The As, Cd, Pb and Hg emission sources and their strengths were also discussed during several workshops (e.g. Lindqvist et al., 1983; Nriagu, 1984) and by individual authors in scientific papers (e.g. Nriagu, 1979; Lantzy and Mackenzie, 1979; Walsh et al., 1979).

In this chapter, atmospheric fluxes of arsenic, cadmium, lead, and mercury are presented with emphasis on: (1) the chemical composition of source materials, (2) the physical-chemical properties of metals, (3) the technology
employed, and (4) the efficiency and type of emission control devices utilized. Special consideration is given to metal releases from power generation and non-ferrous metal production. The atmospheric transport of As, Cd, Pb and Hg is then discussed considering the information on their chemical nature and tendency to concentrate on fine particles.

**EMISSIONS OF As, Cd, Pb AND Hg DURING COAL AND OIL COMBUSTION**

Coal and oil are the main fossil fuels used to produce electricity. Apart from many unquestionable advantages, such as the relatively low cost of energy generation and easy availability of the fuel required, coal- and oil-power plants are known to create serious environmental hazards due to the emission of such pollutants as arsenic, cadmium, lead and mercury.

The trace element behaviour during combustion of fuels depends mainly on: (1) affinity of elements for pure coal and mineral matter, (2) physical-chemical properties of elements and their concentrations in coal and oil, and (3) combustion conditions. Kuhn et al. (1980), in their thorough review of the abundance of trace and minor elements in organic and mineral fractions of coal, found As, Cd, Pb and Hg as the sulphide-forming elements. They concluded that information on the affinity of trace elements for pure coal and mineral matter could be used, in conjunction with concentrations, for determining the chemical forms of elements, for estimating the theoretical percentage of an element that can be removed by coal cleaning, and for predicting material balances in the coal products and wastes. The needed information on trace element concentrations in coal has been collected by this author (Pacyna, 1986a). The As, Cd, Pb and Hg concentrations in coals, taken from this review, are presented in Table 7.1, together with the metal concentrations in crude oils. As can be seen, there are large differences between metal concentrations in coals from several producing fields of the world. As a result, it is difficult to generalize on impurities in coal. However, the literature (Gluskoter et al., 1977; US EPA, 1980; Pacyna, 1980) suggests that lignite and sub-bituminous coals are less contaminated by these metals than medium-, low-, and high-volatility bituminous coals. As an example, coal from the Western Basin in the United States is much less contaminated than the coals from Eastern and Illinois basins. In Europe, German brown coal (lignite) seems to be cleaner than bituminous and sub-bituminous coals from Czechoslovakia and Poland (Pacyna, 1980; Heinrichs, 1982). On the other hand, the production of a certain amount of energy (i.e. electricity) requires a lignite charge almost two times as high as that of bituminous coal (Dvorak and Lewis, 1978), resulting in enhanced emissions of As, Cd, Pb and Hg.
During combustion, the volatile species in the coal evaporate in the boiler and recondense as submicrometre aerosol particles, or on the surfaces of ash particles as the flue gas cools in the convective sections. The concentrations of arsenic, cadmium and lead increase markedly with decreasing particle size from bottom ash through fly ash from control devices to stack fly ash (stack dust) emitted into the atmosphere. Apparently, more than 90% of mercury in coal is released as vapor (Billings et al., 1973; Kaakinen et al., 1975; Pacyna, 1980). Combustion temperature in the boiler is one of the key parameters affecting the amounts of metals released. The higher the temperature in a boiler, the larger the discharges of volatile elements. Thus, larger amounts of As, Cd and Pb are emitted into the atmosphere from conventionally-fired boiler systems (e.g. stoker-boiler or cyclone-boiler) burning fuel at temperatures higher than 1650 K, as compared with fluidized-bed systems with temperatures between 1100 and 1200 K. The latter systems are now being employed in electric utilities together with cyclone furnaces. The stoker-type boiler is the dominant unit used in industrial plants and in atypically small (<40 MW) power plants. The type of fly ash control system and its efficiency also influence the As, Cd and Pb emissions. Electrostatic precipitators (ESP), wet scrubbers, mechanical collectors and fabric ‘bag-house’ filters are the most commonly used systems. The two former are installed in coal-fired power plants. Generally, a venturi wet scrubber system is more efficient in removing As, Cd and Pb from a flue gas stream than electrostatic precipitators. Ondov et al. (1979) have studied the penetration of several elements contained in particles from coal-fired plants equipped with both control systems. They calculated the following values for penetration through ESP: 4.3–11.5% for As, 3.3–8.8% for Cd and 2.2–5.5% for Pb. The arsenic penetration through a venturi wet scrubber ranged from 2.5–7.5%. No information was presented for cadmium and lead.

Oil-fired power plants are also important sources of As, Cd, Pb and Hg emissions into the atmosphere. During refining of oil, these metals concentrate in the heavy distillate residuals, such as residual fuel oils, asphalts, and in the liquid and solid waste streams. The limited information available indicates that probably 30% of the metals in crude oil are retained in residual fuel oil and asphalt (Smith et al., 1975). The amounts of As, Cd, Pb and Hg discharged during combustion of residual fuel oil in power plants and
industrial boilers depend mainly on their concentrations in crude oils (Table 7.1), the efficiency of combustion, and the build-up of boiler deposits. Generally, the most contaminated crude oils are those from the Middle East and Venezuela (Pacyna, 1982), while crude oils from the Far East (Singapore, Indonesia), Africa (Algeria, Gabon, Nigeria) and North America seem to be lowest in impurities. Poor mixing in a boiler, low flame temperatures, and short residence time in the combustion zone result in larger particles with a higher content of combustible matter and higher particulate loadings. Considering boiler design, the As, Cd and Pb emission rates from two commonly used types of boilers, tangential and horizontal, working under similar conditions, are comparable. Oil-fired boilers do not require fly ash removal equipment and, under such circumstances, the emissions of elements are comparable with the emissions from a coal-fired unit of better than 99% collection efficiency. Generally, the stack dust loadings for industrial oil combustion units are higher than those for electricity generating plants.

The above information has been used to calculate the trace element emissions from coal and oil combustion in Europe (Pacyna, 1983). Emission factors have been estimated for each European country separately. The differences were very significant: from 15.4 μg As/MJ for hard coal-power plants in West Germany to 95.5 μg As/MJ for lignite-power plants in Poland, and from 8.8 μg As/MJ for Switzerland to 58.1 μg As/MJ for Denmark in the case of oil-fired power plants (Pacyna, 1982). Similar differences in emission factors were estimated for lead, cadmium and mercury emitted from coal and oil combustion for electric utility, industrial, commercial and residential

<table>
<thead>
<tr>
<th>Source</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coal combustion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>power plants</td>
<td>205</td>
<td>64</td>
<td>733</td>
<td>85.5</td>
</tr>
<tr>
<td>industry</td>
<td>240</td>
<td>77</td>
<td>870</td>
<td>135.0*</td>
</tr>
<tr>
<td>commercial and residential</td>
<td>16</td>
<td>5</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>units</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oil combustion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>power plants</td>
<td>79</td>
<td>37</td>
<td>450</td>
<td>v.l.</td>
</tr>
<tr>
<td>industry and commercial</td>
<td>138</td>
<td>73</td>
<td>709</td>
<td>v.l.</td>
</tr>
<tr>
<td>and residential units</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>678</td>
<td>256</td>
<td>2835</td>
<td>221</td>
</tr>
</tbody>
</table>

* Industry + commercial and residential units.
v.l. — very low.
furnaces. The emissions of As, Cd, Pb and Hg for Europe are presented in Table 7.2. The Hg emissions in Table 7.2 include both the metal releases in the vapor phase and as particles. Oil firing contributes insignificantly to the mercury emissions from fossil fuel combustion. The metal emissions due to burning of fossil fuels in the United States were the following: 497 tons of Cd in 1979 (US EPA, 1981), 120 tons of Hg in 1975 (Watson, 1979), and 650 tons of As in 1974 (NAS, 1977). Fuel combustion includes not only stationary combustion but also mobile sources, particularly gasoline combustion engines. The fate of lead in gasoline has been studied extensively, and is not reviewed here in detail. For statistical purposes only, the author's calculations of Pb emissions from gasoline combustion in Europe give a value of 74 300 tons in 1979, compared with 128 000 tons in the United States in 1975 (US EPA, 1977).

**NON-FERROUS METAL PRODUCTION AS A SOURCE OF ATMOSPHERIC As, Cd, Pb AND Hg**

A major source of arsenic and cadmium and an important source of lead and mercury is smelting and refining of non-ferrous metals. Both primary processing from mineral concentrates and secondary processing from scrap and residual materials are considered. The first process in non-ferrous metal production is mining and beneficiation of sulphide ores. Most of the ores are extracted by underground mining methods, but open-pit mining is also used. The exploitation of lead-zinc ores is particularly important due to their contamination by Cd and As. The latter element is also enriched in copper-nickel ores. The concentrations of Cd and As in non-ferrous metal ores vary widely from one field to another. As an example, Wedepohl (1969) gives the arsenic concentration range from 10 to 10 000 µg/gm.

Primary metal production converts the concentrated ore into metal by several processes. Roasting of ore concentrates and low grade ore enrichment, the initial steps in smelters, are common in copper, nickel, lead, zinc and cadmium production. The processes occur at about 1500 K, and volatile elements, such as arsenic, cadmium and mercury, are partly removed from the concentrates, and remain in the flue gases. As much as 95% of arsenic contained in copper ores may be driven off in the gases; however, 50% is more typical. Most of this is recycled. All the mercury in a smelter will vaporize early in the process and enter the gas stream, which is usually passed through an acid plant to remove mercury.

The next process, smelting, can be either thermal (in horizontal or vertical retort) or electrolytic extraction. The old, pyrometallurgical zinc plants employing thermal smelting are a major cadmium emission source. Hutton (1982), studying cadmium behaviour in the environment, suggests metal emission factors from 10–100 gm Cd/ton, in pyrometallurgical zinc produc-
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...tion, to 0.20 gm Cd/ton in the electrolytic process. At present, five of 18 primary zinc plants within the European Community use thermal facilities while two pyrometallurgic plants operate in the United States. All the primary zinc in Canada is produced by the electrolytic process. In 1977 the thermal process in horizontal retorts was used in three countries: Mexico, Poland and the USSR. As in zinc smelting, the thermal process in copper and lead production results in cadmium emissions. Based on the literature reviewed by Hutton (1982), the Cd emissions from primary copper and lead production are lower than the Cd emission from pyrometallurgic zinc plants.

Smelting and converting in copper–nickel smelters are important sources of As emissions. Behaviour of the metal depends primarily upon the process itself. Several smelting technologies are currently used in the copper–nickel industry, including reverberatory smelting, flush smelting (two processes are currently in commercial use: the INCO process and the OUTOKUMPU process), and the Noranda and Mitsubishi Continuous Copper Smelting Process. About 90% of copper is presently being produced by these processes. The rest comes from hydrometallurgical techniques. Smelting technology has been widely reviewed in the literature (e.g. Environment Canada, 1982). Reimers et al. (1977) concluded that the portion of arsenic volatilized during the smelting operation ranges from 20% of the arsenic input for the reverberatory furnace to 85% for the Noranda reactor for making high grade matte. The effluent gases include also about 85% of the lead input in the copper–nickel ores and 80% of the cadmium input. Most of the metal is usually recycled in flue dusts, but the remainder is emitted into the atmosphere. Lead is produced in a similar way to zinc through processes such as roasting, sintering, smelting and refining. Most of the airborne trace element emissions in lead ore processing are due to the roasting operations. Reduction in the blast furnaces is also a source of air pollution by trace elements. The emission rates of As, Cd, Pb and Hg from primary non-ferrous metal production are highly sensitive to differences in the efficiency of control devices. High-efficiency control devices are often employed in smelters. Emissions from roaster facilities, as well as from sintering processes, are mainly controlled with fabric filters and electrostatic precipitators.

The share of non-ferrous metals produced by secondary processing in the total metal production varies from 20% for zinc and nickel to 37% for lead and 38% for copper (Barbour et al., 1978). Besides, many ‘primary’ lead plants are fed with a mixed charge of roasted ores and scrap materials (Hutton, 1982). The chemical composition of input scrap and the type and efficiency of control devices are two factors which affect the Cd and Pb emissions most from this source.

To assess quantitatively atmospheric fluxes of As, Cd, Pb from non-ferrous metal production, the metal emission factors have been calculated for the above-mentioned processes, and used to estimate the metal releases...
in Europe in 1979. The results are listed in Table 7.3. Similar inventories have been prepared for the US emissions, indicating releases of about 1000 tons/year for Cd (several US EPA reports), 70 tons/year for Hg (Watson, 1979), and 4800 tons/year for As from copper smelting only (NAS, 1977).

<table>
<thead>
<tr>
<th>Source</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary non-ferrous metal production</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper-nickel</td>
<td>4500</td>
<td>600</td>
<td>9250</td>
<td>61</td>
</tr>
<tr>
<td>zinc-cadmium</td>
<td>900</td>
<td>1050</td>
<td>7880</td>
<td>13</td>
</tr>
<tr>
<td>lead</td>
<td>300</td>
<td>8</td>
<td>10450</td>
<td>3</td>
</tr>
<tr>
<td>Secondary non-ferrous metal production</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper</td>
<td>v.l.</td>
<td></td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>lead</td>
<td>v.l.</td>
<td></td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Mining</td>
<td>v.l.</td>
<td></td>
<td>1090</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>5700</td>
<td>1658</td>
<td>29125</td>
<td>77</td>
</tr>
</tbody>
</table>

* Data include both pyrometallurgical and hydrometallurgical processes.
  v.l.—very low.

OTHER ANTHROPOGENIC SOURCES OF As, Cd, Pb AND Hg EMISSIONS

Other anthropogenic sources releasing arsenic, cadmium, lead, and mercury include high-temperature processes in steel and iron manufacturing, municipal and sewage sludge incineration, and cement production, as well as industrial application of the metals. Recently, the trace element emissions from the above sources have been analysed in detail (Pacyna, 1986a). Briefly, the cadmium and lead emissions from steel works depend significantly on the type of technology used. Electric arc and basic oxygen furnaces are much safer than older open-hearth ones.

Large quantities of coke are produced for use in the iron and steel industries, but the release of metals from this process is considered when analysing coal combustion for industrial purposes.

Only limited information is available on trace element emissions from refuse incineration. As, Cd, Pb and Hg emissions are mainly affected by the chemical composition of the refuse input, the incinerator chamber design (combustion temperature), and the efficiency of control devices (if any).
The high-temperature kiln operations in cement plants emit several trace elements, among them Pb and Cd.

Industrial applications of As, Cd, Pb and Hg often involve their discharges as air pollutants. Arsenic is used in agriculture (herbicides, insecticides, feed additives), in glass manufacturing, and in wood preservatives. Approximately 10% of the As used to produce pesticides may be volatilized to the atmosphere by aerobic and anaerobic microbial activity. An important source of arsenic emissions is the cotton ginning process, removing the seeds from raw cotton. Cadmium is used in the plating of iron, steel, and other metals, as pigments for glass and paint, and in insecticide production. The metal is also used to produce nickel-cadmium batteries. The chloralkali industry is the largest consumer of mercury, followed by the electrical and paint industries, agriculture, dentistry and the chemical industry. Industrial applications of lead include lead alkyl manufacture, storage battery production, and production of can solder.

Table 7.4 shows atmospheric fluxes of As, Cd, Pb and Hg from the above sources in Europe in 1979 (Pacyna, 1983). The metal emissions from relevant sources in the United States are as follows: 1100 tons As/year (NAS, 1977), 135 tons Cd/year (US EPA, 1979), 40 tons Hg/year (Watson, 1979), and 10130 tons Pb/year (US EPA, 1977).

<table>
<thead>
<tr>
<th>Source</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron, steel, and ferro-alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>manufacturing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refuse incineration</td>
<td>10</td>
<td>85</td>
<td>800</td>
<td>20</td>
</tr>
<tr>
<td>Cement production</td>
<td>15</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial application of metals</td>
<td>140*</td>
<td>20</td>
<td>2000</td>
<td>20</td>
</tr>
<tr>
<td>Total</td>
<td>150</td>
<td>180</td>
<td>18210</td>
<td>40</td>
</tr>
</tbody>
</table>

* Without pesticide production.

It should be noted that for some sources, as well as for certain countries in Europe, the information necessary for calculations of trace element emissions was difficult to obtain or was simply lacking. The uncertainties included data on: (1) metal concentrations in fuels and other raw materials, (2) industrial technologies, and (3) the efficiencies of control devices used. A simple trajectory model has been used to verify the above estimates for As, Cd and Pb emissions from anthropogenic sources in Europe. The metal concentrations calculated by the model were compared with measured daily
ambient concentrations at Birkenes in Southern Norway. The measured concentrations exceeded the calculated by 24, 34 and 38% for Pb, As, and Cd, respectively, thus in reasonable agreement.

![Bar chart](image)

**Figure 7.1** Total atmospheric emissions of As, Cd, Hg, and Pb in Europe, USA, USSR, and from natural sources

It is of interest to compare the anthropogenic emissions of the As, Cd, Pb and Hg to the metal releases from natural sources, shown in Figure 7.1. The trace metal emissions from sources in the Soviet Union have been estimated at the Norwegian Institute for Air Research (NILU, 1984). The data for natural sources in Figure 7.1 are taken from a literature review by Pacyna (1986b), except for the Hg emissions, given by NAS (1978). The natural emissions of arsenic and mercury contribute very significantly to the total releases of the metals. The latter element is discharged mainly from natural sources, such as volatilization of gaseous mercury from soils and vegetation, as well as from the ocean and other water bodies. The predominant source of

* It should be noted that the mercury study groups suggest a global ratio of from 2:1 to 4:1 for natural versus anthropogenic contributions of Hg (Editors).
natural As and Cd appears to be volcanoes, whereas for Pb it is windblown dust. The natural Cd and Pb contributions to the total emissions of the metals seem to be less significant than the contribution for As and Hg, but cannot be neglected. Generally, very little is known about the magnitude of natural fluxes of Cd and Pb, or about the species involved.

The total anthropogenic emissions of the elements in Europe, USA and USSR, are broken up in source categories in Figure 7.2. The largest amounts of As, Cd and Pb are emitted in all these areas from non-ferrous metal smelters (excluding Pb from gasoline combustion), while fossil fuel combustion seems to be the most important anthropogenic source of mercury. Thus, the high-temperature processes emit a major part of As, Cd, Pb and Hg into the atmosphere. The magnitude of the metal fluxes is important information in the assessment of their potential threat to human health. However, the environmental behaviour and toxicity of an element are also dependent on its chemical speciation and the tendency to concentrate in fine particles. In high-temperature processes these two factors are closely related to the combustion temperature and volatility of the metal.

![Graph showing atmospheric emissions of As, Cd, Hg, and Pb from fossil fuel combustion, non-ferrous metal production, other anthropogenic sources, and gasoline combustion in Europe, USA, and USSR.]

**Figure 7.2** Atmospheric emissions of As, Cd, Hg, and Pb from fossil fuel combustion (I), non-ferrous metal production (II), other anthropogenic sources (III), and gasoline combustion (IV) in Europe, USA, and USSR

**CHEMICAL SPECIATION OF As, Cd, Pb AND Hg FROM HIGH-TEMPERATURE PROCESSES**

There is a very limited information in the literature on the chemical speciation of metals emitted into the atmosphere. Based on the results from the EPA's National Air Sampling Network, it can be suggested that for arsenic
inorganic forms dominate in the air over emission areas. Major chemical species of arsenic and of the other elements discussed which evolve during high-temperature processes are presented in Table 7.5. Trivalent arsenic is the most common form of the metal. Air samples containing arsenic, of either smelter or coal-fired power plant origin, consist largely of trivalent arsenic in both vapour and particulate states. This is very important, because, as a general rule, inorganic arsenicals exhibit greater toxicity than organic arsenicals, and the trivalent state more so than the other states. Methylated forms of arsenic are probably of minor significance.

Table 7.5 Major chemical species evolved during fossil fuel combustion and industrial processes

<table>
<thead>
<tr>
<th>Process</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal combustion</td>
<td>As(O), As₂O₃</td>
<td>Cd(O), CdO</td>
<td>PbCl₂, PbO,</td>
<td>Gaseous Hg,</td>
</tr>
<tr>
<td></td>
<td>As₂S₃</td>
<td>CdS</td>
<td>PbS, Pb</td>
<td></td>
</tr>
<tr>
<td>Oil combustion</td>
<td>As(O), As₂O₃</td>
<td>Cd(O), CdO</td>
<td>PbO</td>
<td>Gaseous Hg</td>
</tr>
<tr>
<td></td>
<td>CdS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-ferrous metal</td>
<td>As₂O₃</td>
<td>CdO, CdS</td>
<td>PbO, PbSO₄,</td>
<td>Gaseous Hg</td>
</tr>
<tr>
<td>production</td>
<td></td>
<td></td>
<td>PbO, PbSO₄</td>
<td></td>
</tr>
<tr>
<td>Iron and steel</td>
<td></td>
<td>CdO</td>
<td>PbO</td>
<td></td>
</tr>
<tr>
<td>manufacturing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refuse incineration</td>
<td>As(O), As₂O₃, AsCl₃</td>
<td>Cd(O), CdO, CdCl₂</td>
<td>PbO, PbO, PbCl₂</td>
<td>Gaseous Hg</td>
</tr>
</tbody>
</table>

Cadmium and its oxide are the predominant chemical forms of the metal emitted from all the sources considered in this chapter. These two forms seem to be the most toxic cadmium speciations, together with cadmium chloride (found in releases from refuse incineration). With respect to the chemical forms of lead from sources considered here, it can be suggested that inorganic forms are the most widely released, particularly lead oxide and lead chloride. The mercury from industries and power plants is emitted primarily as mercury vapour. This vapor consists mainly of elemental mercury and dimethyl mercury. It is difficult to say which volatile compound dominates the discharge process. Mercury species other than elemental Hg and (CH₃)₂Hg can also contribute. Seiler (in Lindqvist et al., 1983) suggests that most mercury is emitted as dimethyl mercury with a relatively fast degradation to elemental mercury taking place in the air. Brosset (1981) concludes that Hg(O) is mobilized to the atmosphere where it is subjected to atmospheric oxidation processes to yield water soluble forms, subsequently scavenged by wet or dry deposition.

Considering the volatility of As, Cd, Pb and Hg compounds in Table 7.5, elemental arsenic (As(O)), As₂O₃, AsCl₃, elemental Cd (Cd(O)), and
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CdCl₂ are volatile, PbCl₂ is intermediate, and CdO, elemental lead (Pb(O)) and PbO are non-volatile (Gerstle and Albrinck, 1982). The volatile species would be in the vapor state during the high-temperature processes, whereas the non-volatile compounds would continue to be emitted largely as fly ash, even at the higher temperature.

ATMOSPHERIC TRANSPORT

Volatile elements evaporated in a furnace condense on small particles in the flue gas stream. The relationship between volatile metal concentration and particle size during high-temperature processes has already been mentioned, when discussing emission from coal combustion. The condensation of trace elements continues in the atmosphere. The outermost layer on the surface of emitted ashes is often composed of H₂SO₄, which permits surface condensation of several elements including As, Cd, Pb and partly Hg. The condensation takes place preferentially on fine particles in the 0.1 to 1.0 μm diameter range. Additionally, the presence of sulphuric acid on some particle surfaces may give rise to post-combustion crystal formation of metal and/or ammonium sulphates, but how this affects the physico-chemical form of trace elements has not been studied. Small particles from high-temperature processes are very easily transported by air masses over long distances. Gaseous mercury behaves in a similar manner to As, Cd and Pb on fine particles. The concentrations of As, Cd and Pb on the larger particles will be low and decrease rapidly with distance from a power plant or smelter. The results from several studies seem to indicate that at a distance of 30 km from the high-temperature source the As, Cd and Pb concentrations reach the background level (e.g. Rozenshtein, 1970; Yankel et al., 1977; Glowiak et al., 1977; Pacyna, 1980). Lead concentrations around power plants, smelters or other industrial plants are often enhanced by emissions from gasoline combustion. Several studies in the surroundings of copper and lead smelters in Poland (Glowiak et al., 1977; Kubacka et al., 1977; Pacyna et al., 1981) have been carried out to assess the ‘local deposition’ of trace elements. It was found that about 11% of the mass of trace element is deposited in the same area as it is released. Pacyna et al. (1984) have studied long range transport of several trace elements in Europe. Based on the literature sources (OECD, 1979), they have inferred local deposition to be 5% of the emissions.

A major portion of the arsenic, cadmium, and lead emissions from high temperature sources with tall stacks is, however, transported over long distances. The behaviour of these elements during transport depends on their physical-chemical properties, the particle size-distribution, and meteorological conditions, such as the rate of turbulent vertical air exchange and wind speed. The two former parameters seem to dominate the long range-
transport of As, Cd and Pb. According to the literature review by Davidson and Osborn (1984), lead is generally associated with submicrometre particles, while cadmium size distribution contains submicrometre as well as supermicrometre aerosol. Rahn (1976) has compiled information on massmedian diameters of As, Cd, Pb, Hg and other trace elements, shown in Figure 7.3. The residence time of As, Cd, and Pb in the atmosphere was found to be about 7 days. This time is sufficient for transport over thousands of kilometres.

Trace elements can be removed from the atmosphere by dry deposition (sedimentation, interception, impaction and turbulent diffusion) and by wet (precipitation) deposition (rainout, washout). Dry deposition velocities of trace metals were measured by Cawse (1981) and estimated by Davidson (1980). A value of 0.1 seems to be representative for the mean Cd dry deposition velocity, and 0.2 for lead and arsenic. Generally, deposition models consider dry deposition velocity to be a function of aerosol aerodynamic diameter, state of the atmosphere (the variation of wind speed with height and particularly the turbulence of the atmosphere close to the ground), and surface conditions (type and status of the vegetation, open waters, snow, etc.).

Aerosol solubility is one of the key parameters for the wet precipitation process. However, the concentration of pollutants in precipitation is the result of several complex processes both within and below clouds, and uncertainties still remain as to a detailed description of the scavenging efficiency
of precipitation. Generally arsenic and cadmium were found to be ‘soluble’ in the sense that these two elements are likely to be transported over significant distances dissolved in natural waters (Asami et al., 1984). Lindberg and Harriss (1980) have studied solubility of trace elements in aerosols from a power plant plume. They found that coal combustion sources may be a major contributor of soluble trace elements (including Cd and Pb) to the regional tropospheric aerosol. However, our knowledge of complicated physical and chemical processes leading to wet deposition of trace elements is very incomplete and data of this type are largely absent from the literature.

The relative importance of dry and wet deposition depends on the transport distance from the sources. In a heavily polluted area, the amounts removed by dry deposition seem to be larger than by wet deposition, while in remote areas with much precipitation wet deposition may be at least equally important.

The atmospheric behaviour of mercury appears to be a combination of deposition and resuspension or vaporization (Kothny, 1973). After emission into the atmosphere, a part of mercury can be scavenged by even light precipitation, deposited on land, and re-vaporized within 1–2 days (NRCC, 1979). There is no evidence, however, for Hg re-vaporization over water. Most of the Hg in the atmosphere (in particular the insoluble fraction) is transported over long distances (Lindqvist et al., 1983). The average residence time of this fraction of mercury in the atmosphere is estimated to be more than 1 year. The water-soluble fraction and the fraction associated with particulate matter are readily removed from the atmosphere and have a residence time of perhaps a few days or weeks (Lindqvist et al., 1983). Lindqvist et al. (1983) suggest that dispersion parameters of these fractions of mercury are similar to those of pollutants occurring as soluble gases, or associated with submicrometre-size aerosol particles (e.g. Pb, As and Cd). This results in transport scales of several hundred to a few thousand kilometres for the soluble fraction of mercury. These authors also point out that a significant portion of Hg emissions may be deposited close to point sources.

CONCLUSION

A number of studies and reviews cited in this chapter demonstrate the progress in evaluation of trace element emissions. Emission surveys of As, Cd, Pb and Hg from anthropogenic sources are presented in the literature, with measurements and calculations done either for a certain country or for an individual source. Fuel combustion and metal smelting are the most investigated types of emission sources. However, a number of uncertainties have emerged during these investigations concerning the content of the metals in fuels and other raw materials, the efficiencies of control devices, and the uses of different technologies to produce industrial goods.
Future investigations should improve the accuracy of existing inventories, and extend the list of important sources for processes such as waste incineration, biomass burning, phosphate fertilizers, etc. In practice, to improve the accuracy of emission estimates sensitive analytical methodologies for metal and metalloid specification (chemical form and complexation) in emitted dust samples are required. This is particularly important when considering the fate of atmospheric emissions of the elements discussed with respect to the residence times in the air and scavenging processes during atmospheric transport.

To understand the impact of anthropogenic sources of As, Cd, Pb and Hg and their cycles in the environment, we need to know more accurately natural source strengths. The most extensively studied natural source appears to be volcanic eruptions. Information is very scarce on the As, Cd, Pb and Hg releases from wind-blown dust erosion, forest wild-fires, airborne sea-salt, and biogenic emissions from vegetation.

ACKNOWLEDGEMENTS

The author thanks Dr Val Vitols for helpful discussions.

REFERENCES


NAS (1977). *Arsenic*. National Academy of Science, National Research Council, Committee on Medical and Biological Effects on Environmental Pollutants, Washington, DC.


