Sources, Transport and Alterations of Metal Compounds: An Overview. I. Arsenic, Beryllium, Cadmium, Chromium, and Nickel

by Lawrence Fishbein*

An overview is presented of the current state of knowledge of the salient aspects of the sources, transport, and alterations of arsenic, beryllium, cadmium, chromium, and nickel. This information is considered vital for a better assessment of the scope of potential human hazard to these ubiquitous toxicants and their compounds. Stress is focused on both natural and industrial activities, particularly on the latter's projected trends. Increasing use patterns per se of most of these metals, as well as aspects of waste disposal and the anticipated increased combustion of fossil fuels for power generation and space heating (particularly in the United States), are major causes of potential health concern. Additionally, attention is drawn to the need for increased research to fill the gaps in our knowledge in these vital areas, all in the hope of permitting a more facile identification and quantification of the potential hazard to exposure to these agents.

Introduction and General Considerations

It is generally acknowledged that one of the most dangerous and pernicious forms of pollution arises from the potential mobilization of a spectrum of toxic trace metals and metalloids in our environment (1-10). Among the most important elements in this regard are arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, and selenium.

The primary objective of this overview is to highlight germane aspects of the more recent knowledge of the environmental sources and sinks, transport and alterations of As, Be, Cd, Cr, and Ni. (A subsequent analogous treatment will focus on Hg and Pb.) This information is considered vital for the better assessment of the scope of potential human hazard (1-10).

We recognize that significant amounts of metals, singly or in combination, are introduced into the environment from both natural and anthropogenic sources. The latter include fossil fuel combustion and vehicle exhausts, incineration, metalliferous mining and smelting, agricultural chemicals, inorganic fertilizers, and liquid and solid wastes from animals and humans. These manmade sources can result in relatively large amounts of toxic elements to the working, immediate residential, and general environment.

It is abundantly clear that the contamination of the environment may also occur naturally via volcanic and thermal spring activity, erosion or seepage from metal-rich superficial deposits in mineralized zones, or from deeper underground contain ore deposits.

In a rigorous elaboration of the exposure levels of metals it is of primary importance to distinguish the chemical forms present and concentrations ordinarily found in the environment as well as introduced by man and mechanisms that affect their cycle. In the case of several of the metals of concern (e.g.,...
arsenic, mercury, lead) the chemistry of these elements provides for several molecular forms to exist in both air and water, in addition to compounds found in the biosphere.

In view of the acknowledged toxic nature of the metals and metalloids it becomes extremely important to know their sources and fate in the environment and hence mechanisms involved in their transport and transformation from one form to another are viewed as integral with respect to environmental pollution. In this view, special note is made to the recent handbook by Friberg et al. (2). Recent general reviews which are particularly germane are those of Summer and Silver (4) and Saxena (5) which addressed the environmental transformation of alkylated and inorganic forms of a number of metals and metalloids, while those of Lantzzy and Mackenzie (6), Wagenet et al. (7), Anderson (8), Gibbs (9), and Van Hook (10) addressed the global cycles and assessment of man's impact, models of the environmental transport of heavy metals, movement of metallic contaminants through ground water flow systems, mechanisms of trace metal transport in rivers, and transport and transportation pathways of hazardous chemicals from solid waste disposal, respectively.

It is well established that many trace elements are mobilized in association with airborne particles derived from high-temperature combustion sources, e.g., fossil-fueled power plants, blast furnaces, metallurgical smelters, municipal incinerators and vehicles (11-13). Biological, chemical, and physical effects of airborne metals are a direct function of particle size, concentration, and composition. It should be stressed that the major parameter governing the significance of natural and anthropogenic emissions of environmentally and toxicologically important metals is particle size (11-13). Hence, metals associated with fine particulates larger than 3 μ aerodynamic equivalent diameter are minimally respirable and uncollective in atmospheric interactions and have a short air residence time (11, 12).

Many elements, notably Pb, Cd, Zn, Cr, V, Ni, Mn, and Cu are found at the highest concentrations in the smallest particles collected from ambient air (11-13).

A particularly useful recent report of Lee and Duffield (12) reviewed the major sources in the U.S. of 17 environmentally important metals (As, Be, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, Sn, Ti, V, and Zn) with emphasis on five particulate emission sources. Initially, it should be noted that it is extremely difficult to unambiguously ascertain what proportion of the anthropogenic and natural particulate emissions are composed of the environmentally important elements.

It is broadly acknowledged that stationary sources are the principal contributors of most environmentally important metals in air (11-15). Table 1 depicts the annual air emissions of 17 metals from stationary sources (12, 15) in the U.S. through the period 1969-1971 and projected through 1983 based on production estimates and assuming no changes in processes or control technology. Comparatively low emissions (150-900 tons/year) of the highly toxic metals Be, Se, and Hg were reported for the 1969-1971 period, while quantities of Cd, Ni, Pb, and Cr ranged from 3,000 to 12,000 tons/year during the same period. The significant projection increases for 1983 of all of the environmentally important metals should also be noted (12, 15). The trend for the immediate future appears to be of greater exposure to these metals not only as a result of generally increased usage patterns but also because of prospective enhanced use of fossil fuels for space heating and electricity generation (whether from conventional coal-fired power plants or new coal technologies such as in-situ gasification, coal pyrolysis, chemical pre-cleaning, etc.).

A measure of the enhanced projected coal utilization can be gleaned from a consideration of the U.S. production of electrical power alone. For example, in 1973 coal use for electrical power generation in the U.S. produced 3.6 million tons of fly ash, 22.6% of the total U.S. particulate emissions (16). With the addition of 241 new coal-fired power plants, coal consumption by U.S. electric utilities is expected to

| Pollutants, tons/year | 1969-1971 | 1978 | 1983 |
|----------------------|----------|------|------|
| Metal                | Average  | Projection | Projection |
| As                   | 9,000    | 12,750 | 16,900 |
| Be                   | 150      | 200   | 260   |
| Cd                   | 3,000    | 4,090 | 5,050 |
| Cr                   | 12,000   | 14,980 | 17,800 |
| Cu                   | 13,500   | 20,680 | 24,070 |
| Fe                   | Unknown  | Unknown | Unknown |
| Hg                   | 800      | 1,160 | 1,560 |
| Mg                   | Unknown  | Unknown | Unknown |
| Mn                   | 19,000   | 25,840 | 31,720 |
| Ni                   | 6,000    | 10,940 | 17,500 |
| Pb                   | 9,300    | 11,840 | 14,370 |
| Sb                   | 350      | 460   | 550   |
| Se                   | 900      | 1,240 | 1,560 |
| Sn                   | Unknown  | Unknown | Unknown |
| Ti                   | 88,000   | Unknown | Unknown |
| V                    | 18,000   | 37,240 | 56,370 |
| Zn                   | 151,000  | 216,700 | 273,000 |

* Data of Flinn and Reimers (15) and Lee and Duffield (12).
expand from 446 million tons in 1976 to more than 840 million tons in 1985 (17), further increasing the amount of fly ash emitted to the atmosphere with concomitant toxic metals.

Table 2 lists the major stationary emission sources for Be, Cd, Cr, Cu, Mn, Ni, Pb, Ti, and V from smelter metallurgical processing and coal and oil combustion. Coal and oil combustion are important contributors of Be, Ni, and V and smelters/metallurgical processes are predominant sources of airborne Cd, Cr, Cu, and Mn. Emissions from incineration, it should be noted, are greatly dependent on the composition of the waste material burned (12, 18, 19).

Many of the metals of higher concentration observed in incinerator atmospheric emissions, e.g., Ag, Cr, Pb, Sn, and Zn, are metals that are used in surface coatings, galvanizing solders, and similar surface applications where high temperatures could cause flaking and volatilization from bulk metal scrap (19). These metals are derived from the noncombustible components of refuse as well as from the combustibles in municipal incinerator emissions (20).

Lantzy and Mackenzie (6) in a recent comprehensive survey present global data for sources of atmospheric input for 20 trace metals and assessed the relative importance of natural and anthropogenic sources. In addition, the authors developed a mathematical model to calculate enrichment factors which were then compared to the observed factors (6). Interference factors were calculated as (total anthropogenic emissions/total natural emissions) × 100. For lithophic metals such as Fe and Mn, interference factors are found to be small, while the atmophlic metals such as As, Se, and Hg exhibit large interference factors. Additionally, a significant degree of correlation is suggested to exist between interference factors and enrichment factors, where enrichment factor is defined as the metal/Al ratio in atmospheric particulates divided by the metal/Al ratio in soils. Enrichment factors for many of the trace metals were found to be of the same order of magnitude at high latitudes in both the Northern and Southern hemispheres and are larger at high latitude than at mid-latitude. Table 3 illustrates the magnitude of fluxes (in units of 10⁵ g/year) derived from several natural and anthropogenic processes for 20 trace metals. The industrial emissions flux is calculated for the mass of material annually emitted to the atmosphere from industrial activities, 200 × 10¹² g (21, 22) and the concentration of metals in urban particulates (Table 4). Metal concentrations in urban particulates from the U.S. and Europe have been found to be remarkably similar (23-26) suggesting that on a global basis the complex and varied industrial activities of different industrial nations tend to lead to atmospheric emissions of similar composition (6).

As suggested by Lantzy and Mackenzie (6), one method for assessing the importance of the anthropogenic flux for any metal is given by the interference factor (IF) as shown in Table 3. A value of 100% indicates that the anthropogenic flux equals the total natural flux. As shown in Table 3, that for Al, Ti, Sn, Fe, Mn, and Co, the anthropogenic flux is less than the natural flux, while for Cr, V, and Ni the anthropogenic flux is only slightly greater than the natural flux. In contrast, for Sn, Cu, Cd, Zn, As, Se, Sb, Mo, Ag, Hg, and Pb, IF values are considerably greater than 100%. Hence, for these metals the anthropogenic flux is much greater than the natural flux.

While the major focus on environmental sources of hazardous metals thus far has been on anthropogenic sources and their impact on atmospheric transport and pollution, we should additionally recognize the potential impact of transport and transportation pathways of these elements from solid waste (including sewage sludge) disposal in both terrestrial river and oceanic environments (10, 28-40) and the consequences of biological concentration factors in aquatic and terrestrial environments for trace elements that may occur in hazardous wastes (10). Significant transport of trace metals by particulates is found in most rivers of the world (40). Solid surfaces are believed to control trace metal concentrations and account for the observed undersaturation of metals in oxidizing environments (40). The importance of solid surfaces to the transport, control, and biological availability of trace metals requires an understanding of sorption-desorption mechanisms (38).

The heavy metals present in raw sewage arise
from a number of sources. Many industrial effluents contain appreciable concentrations of metals (27, 28), and domestic sewage is also an important source (31). Where urban storm-water enters the sewage works for treatment, this contributes a number of metals, especially lead (32). Industrial use of heavy metals frequently results in the production of contaminated waste waters. While methods of metal removal exist, except for large industrial units, they are seldom economically viable and are thus little used (33). Hence, these waste waters are frequently discharged to surface waters either directly or via a sewage treatment works. During the processes of sewage treatment, the heavy metals are concentrated in the sludges produced (27, 28, 34, 35).

The presence of heavy metals in sewage sludges has been associated with adverse effects upon crop yield and an increase in the uptake of heavy metals by crops grown on land repeatedly treated with heavy-metal contaminated sewage sludge. The safety with respect to animal and human health of crop-land application is currently the subject of considerable research activity (36, 42, 43).

Figure 1 depicts the major physical and biological transport pathways of hazardous chemicals derived from solid waste disposal as delineated by Van Hook (10). After substances enter the environment, they may be diluted, concentrated, or transformed by a variety of chemical, physical, and biological processes. Although the specific parameters associated with interfacial processes may vary among terrestrial, fresh water, and marine ecosystems, the basic features of the interfaces are similar (10). Interactions occurring at interfaces mediate the ability of ecosystems to absorb contaminants and simultaneously control their biological activity (10).

Factors which govern the biological concentration of chemicals include the amount and chemical and physical form of the agent in the diet or surrounding environment which determine its biological availability, the quantity of contaminated food which is consumed, the degree of assimilation and the extent of retention in the organism's tissues (10). Table 5 illustrates biological concentration factors in aquatic and terrestrial environments for As, Cd, Hg, Pb, and Zn that may occur in hazardous wastes (10). The biological concentration factors may vary over many orders of magnitude (10⁻³ to 10⁵) in aquatic and terrestrial environments (44-46). Additional recent comparative studies on trace level in the marine environment and biota have also been reported (47-51).
Table 4. Concentrations of trace metals in various materials.a

| Element | Soils | Andesites | Oil | Coal | Urban particulates, ng/m³ |
|---------|-------|-----------|-----|------|--------------------------|
| Al      | 71,300| 88,500    | 0.5 | 10,000| 2,007                    |
| Ti      | 4,600 | 8,000     | 0.1 | 500   | 181                      |
| Sm      | 6.4   | 6.2       | 1.6 | -     | 0.35                     |
| Fe      | 38,000| 58,500    | 2.5 | 10,000| 3,710                    |
| Mn      | 850   | 1,200     | 0.1 | 50    | 149                      |
| Co      | 8     | 20        | 0.2 | 5     | 1.19                     |
| Cr      | 100   | 56        | 0.3 | 18    | 31.7                     |
| V       | 100   | 100       | 50  | -     | 50                       |
| Ni      | 40    | 55        | 0.1 | 15    | 30                       |
| Sn      | 10    | 1.6       | 0.01| -     | 20                       |
| Cu      | 20    | 62        | 0.14| 15    | 110                      |
| Cd      | 0.5   | 0.29      | 0.01| 0.5   | 2                        |
| Zn      | 50    | 72        | 0.25| 50    | 359                      |
| As      | 5     | 1.8       | 0.01| -     | 48                       |
| Se      | 0.6   | 0.69      | 0.17| 3     | 2.3                      |
| Sb      | 1.9   | 0.2       | 0.01| 6.4   | 8.8                      |
| Mo      | 2     | 0.9       | 10  | 5     | 5                        |
| Ag      | 0.1   | 0.087     | 0.0001| 0.5  | 1.7                      |
| Hg      | 0.05  | 0.075     | 0.022| 2    | 2.3                      |
| Pb      | 10    | 5.8       | 136 | 25    | 790                      |

a Adapted from data of Lantzy and MacKenzie (6).

A useful compendium is that of IRPTC (50) concerning Mediterranean Data Profiles for As, Ca, Cr, Hg, Pb, and Se.

Arsenic

Recent germane publications bearing on sources, transport, and alterations of arsenic published as part of the Proceedings of the International Conference on Environmental Arsenic, Fort Lauderdale, Fla., October 5-8, 1976 include: industrial contribution of As to the environment (52); emissions in Sweden and their reductions (53); occurrence and transformation in the marine environment (54); environmental mobility (55); biomethylation and demethylation (56); fate in different environmental substrates (57); occurrence and distribution in soils and plants (58) and implications of inorganic/organic interconversion on fluxes of As in marine food webs.

Table 5. Biological concentration factors in aquatic and terrestrial environments for trace elements that may occur in hazardous wastes.a

| Biological concentration factorb | Aquatic | Terrestrial |
|--------------------------------|---------|-------------|
|                                | As  | Cd | Hg | Pb | Zn | Soil | Plants | Invertebrates | Mammals | Birds |
| Water                          | 1  | 1  | 1  | 1  | 1  | 1    | 1000   | 1000          | 1000    | 1000  |
| Plants                         | 170| 1000 | 1000 | 200 | 1000 | 1000 |
| Invertebrates                  | 330| 2000 | 10000 | 100 | 10000 | 10000 |
| Fish                           | 330| 200 | 1000 | 300 | 10000 | 10000 |
| Soil                           | 1  | 1  | 1  | 1  | 1  | 1    | 1000   | 1000          | 1000    | 1000  |
| Plants                         | 0.01| 0.3 | 0.4 | 0.07 | 0.4 | 0.001|
| Invertebrates                  | 0.01| 17  | 0.02 | 8   | 0.001| 0.6  |
| Mammals                        | 0.001| 0.008 | 0.001| 0.6 | 0.001| 0.6  |
| Birds                          | 0.001| 50  | 0.001| 0.6 | 0.001| 0.6  |

a Data of Van Hook (10).
b Ratio of concentration in organism to concentration in substrate.

August 1981
Averages report on type transport range weathering total as above ppm (60) and is crust. As Arsenopyrite is abundant and hence is considered scarce, it is nevertheless a major constituent of 245 mineral species (60). Arsenopyrite is the most common of the As containing minerals. The amounts of arsenic in soils and water depend largely on the geologic inputs from mineral weathering processes (57, 59, 60, 67, 68). GESAMP (49) estimates that about 72,000 tons/year of arsenic as arsensinous oxide is weathered from the earth's crust. The average As content in soil is about 5-6 ppm (60) and is probably in the form available for biotransformation and plant uptake (57). Arsenic resides in water are generally low (57, 59, 60, 67, 70). Concentrations of As in seawater generally range from 1-8 ppb and in sediments at 2-20 ppm (67). That these levels are biologically significant is indicated by the generally higher levels of As in marine foods compared with terrestrial foods (59).

Inorganic arsenic can exist in several oxidation states and forms in water, depending on the pH and Eh of the water (63). It has been estimated that the total arsenic moved to the oceans is $30 \times 10^6$ kg/year (63). Arsenate in both fresh and salt water is metabolized to methylated compounds; mono-, di-, and trimethylarsonic acids have been isolated from both sources. Data on arsenic levels in ground waters are considered, in the main, inadequate (60).

The amounts of arsenic in indigenous plants and animals largely reflect species differences. It should be noted that some species of marine plants, such as algae and seaweed, and marine organisms, such as crustaceans and some fish, often contain naturally high concentrations of arsenic (60). The levels of As found in marine animals exceed those found in their surroundings (59, 67). For example, pelagic fish range from 0.3 to 3 ppm and bottom-feeders from 1.4 to 55 ppm. These levels are higher than the averages of seawater and sediments, respectively.

Although bioaccumulation of arsenic must thus occur, biomagnification through the food chain has not been considered to be a general phenomenon (59, 60, 67, 69).

Anthropogenic sources of arsenic are generally by-products of the smelting of non-ferrous metals, primarily copper and to a lesser extent lead, zinc and gold (52, 53, 60). Figure 2 illustrates sources of arsenicals by country and type of material in 1973 (60). The world production is about 50,000 tons/year as arsenic trioxide. The United States consumes about half the total world production and it produces for its own use about half of what it consumes (52). The production in the U.S. is only at the Asarco smelter in Tacoma, Washington where the current production rates are approximately 1,000 tons of arsenic as the trioxide per month (52). The remainder of the U.S. supply (about 12,000 tons/year) comes from Mexico, Sweden and France. Approximately 97% of the arsenic produced enter end-product manufacture in the form of white arsenic while the remaining 3% as metal for metallurgical additives and special lead and copper alloys (60).

The largest application for arsenic is for agricultural uses (herbicides, insecticides, desiccants, feed additives) and wood preservatives accounting for about 81% of the total consumption in the U.S. in 1973. Arsenic trioxide has been used principally for the production of arsenical pesticides (e.g., lead arsenate, calcium arsenate, sodium arsenite, and organic arsenicals). The newer major organic arsenical pesticides include three herbicides [monosodium methane arsionate (MSMA), disodium methane arsionate (DMSA), and cacodylic acid] and four feed additives that are substituted phenyl arsanic acids. The use of arsenic derivatives as wood preservatives is small compared to pentachlorophenol and creosote. However, the use of chromated copper arsenate has increased three fold in the U.S. during the period 1968-1973. Pentavalent arsenic compounds (zinc and chromium arsenate) are used alone or in admixture for this application (60).

The relatively minor use applications of arsenic include: as an additive in metallurgical applications, glass production, as a catalyst in manufacturing processes and in medicine (in the treatment of tropical diseases such as amoebic dysentery, African sleeping sickness and in veterinary medicine for treatment of parasitic diseases) (60). The flow of arsenic in Sweden was recently reported by Lindau (53). The total amount of arsenic in products produced in Sweden is about 11,000 tons/year of which 95% was exported. The figures can be compared with the U.S. consumption of As2O3 which was about 32,000 tons in 1974 and the world...
production which is about 50,000 tons/year. In Sweden the main products are metallic arsenic, arsenic trioxide, arsenic acid, and arsenic wood preservatives. Products with smaller amounts of arsenic are fertilizers, aluminum sulfate, and calcium phosphates (53).

Figure 3 illustrates inputs into the environment and a redistribution of arsenic in the terrestrial ecosystem (60). Although arsenic is ubiquitous in nature as noted above (inputs from volcanic action, decay of plant matter and weathering of minerals within the soil), it may enter the biosphere through unintended contamination from industrial activity or through desired uses (e.g., combustion of fossil fuels).
fertilizers, smelting of ores, and use of fertilizers and pesticides, feed additives, medicinals, etc.). The largest sink for man-made arsenic in the environment is the soil. The principal arsenic residues resulting from the use of agricultural pesticides and fertilizers are found in soils and to a lesser degree in plants and animals living on contaminated soils. Large accumulations of arsenic also occur in soils in the vicinity of smelters (60). The three major sources of arsenic in air are the burning of coal, smelting of metals and use of arsenical pesticides (60). Based on the estimate of 600 million tons of coal burned per year by power plants in the U.S., the mass emission of arsenic from these sources would correspond to the emission of 840 tons (70). In another study based on an annual consumption of 400 million tons of coal by power plants in the U.S., the mass emission of arsenic from these sources was estimated to be in the order of 3,000 tons/year (52). Crecelius et al. (73) estimated that input of arsenic from the copper smelter at Tacoma, Washington amounts to 222 tons of As₂O₃/year into the air via stack dust, 22-77 tons of arsenic into Puget Sound through dissolved arsenicals in its liquid effluent discharge, and 1.5 million kg of arsenic/year in crystalline slag dumped into the Sound.

Cotton ginning dusts and the combustion of cotton gin wastes containing residues of the cotton desiccant, arsenic acid, have been reported as creating significant concentrations of arsenic in the air (52).

Arsenic is found generally at low levels in all waters (69). In one study of selected minor elements in 72 samples of U.S. surface waters, the concentration of arsenic ranged from 10 to 1000 ppb (68). In another survey, except for local anomalies where arsenic concentrations could be traced to urban waters or to industrial sources, no major regional differences could be detected in average values or in percentage of contaminated samples (69). Hence, higher concentrations, other than those occurring naturally in spring waters, are usually in areas of high industrial activity (60). The question of whether arsenic in detergents adds significant quantities of arsenic to the river system has not been unambiguously resolved (76, 77).

It is important to note that the safe disposal of arsenic wastes still constitutes a major problem. The principal sources of arsenical wastes are residues in empty pesticide containers, surplus pesticides stored by government agencies, manufacturers, state and municipal facilities, and users, and soil contaminated by extensive use of arsenical pesticides and feed additives (60). The recommended procedure for the management of arsenical wastes (principally arsenic trioxide, cacodylic acid, the herbicides MSMA and DSMA, calcium and lead arsenates, copper acetarsenite, and sodium arsenite) are recycling and re-use, long-term storage and landfill in class 1 sites, recovery of other metals and long-term storage of As₂O₃ (60).

A summary of U.S. arsenic flow, dissipation and emission in 1974 is depicted in Table 6 (60), in which it is estimated that a total movement of about 119,000 tons of arsenic per year occurs. This table distinguishes between arsenic found in end products and arsenic that is dissipated onto land, emitted in air and water, or destined for landfills. Of the 119,000 tons, most arsenic is fixed in products in which it is immobile or is deposited in landfills as waste material, the remainder is in a form that can move readily within the environment (60).

It should be noted that approximately 50% of the mobile arsenic is derived from the use of pesticides. That which is applied to land becomes predominantly fixed in insoluble compounds and is only minimally available for transport. In contrast, arsenic which is emitted into air or water is most mobile and is of primary concern to the general population surrounding the points of emission (60).

Arsenic is continuously cycling in the environment owing to oxidation, reduction, and methyl-

| Location of arsenic          | Arsenic flow, tons   | Ready environmental transport |
|------------------------------|----------------------|-------------------------------|
| End products                 | 26,438               | No                            |
| Steel                        | 17,089               | No                            |
| Cast iron                    | 3,638                | No                            |
| Other                        | 5,711                | No                            |
| Dissipation                  | 63,080               | Unknown                       |
| Steel slag                   | 39,680               | Unknown                       |
| Pesticides                   | 11,565               | Yes                           |
| Copper leach liquor          | 9,702                | Yes                           |
| Other                        | 2,073                | Yes                           |
| Airborne emission            | 9,757                | Yes                           |
| Losses from copper-smelting  | 5,292                | Yes                           |
| Pesticides                   | 2,536                | Yes                           |
| Coal                         | 717                  | Yes                           |
| Other                        | 1,212                | Yes                           |
| Waterborne effluent          | 165                  | Yes                           |
| Phosphate detergents         | 121                  | Yes                           |
| Other                        | 44                   | Yes                           |
| Landfill wastes              | 19,691               | No                            |
| Copper flue dusts            | 10,584               | No                            |
| Copper-smelting slag         | 3,748                | No                            |
| Coal fly ash                | 1,984                | No                            |
| Other                        | 3,375                | No                            |

* NAS data (60).

b To convert tonnes, multiply values in table by 0.9072.
tion reactions. Several arsenic cycles have been proposed to interrelate the source, emission, movement, distribution, and sinks of various forms in the environment (4, 5, 6, 55-57, 60, 61, 76-79). The current knowledge of arsenic transformations and mobility in the environment as well as some gaps in this knowledge have been recently reviewed by Woolson (57), Brinkman et al. (55), Ridley et al. (56) and the National Academy of Sciences (60). In the model proposed by Sandberg and Allen (78) for the arsenic cycle in an agronomic ecosystem, 12 possible transfers to and from a field for the organoarsenical herbicides were considered. Transfers involving reduction to methylarsines, soil erosion, and crop uptake were the primary redistribution mechanisms in this model. It was concluded that arsenic is mobile and nonaccumulative in the air, plant, and water phases of the agronomic ecosystem. Arsenicals do accumulate in soil, but redistribution mechanisms preclude hazardous accumulations at a given site (78). Of all the arsenic sources reaching the soil, pesticides are the most widely distributed geographically. These include: arsenic acid (H$_3$AsO$_4$), lead and calcium arsenates, MSMA, DSMA, and cacodylic acid. Arsenates are the oxidized degradation products from the organoarsenicals, although it is recognized that under moderately reducing conditions arsenite may be formed both biotically and abiotically. All other transformations are biotic. As noted earlier, inorganic arsenic can exist in several oxidation states and forms in water, depending on the pH and Eh of the water (63), and hence many reactions can occur. For example, in a stratified lake, the adsorption of arsenate by Fe and Al oxides in sediments and formation of As$_2$O$_3$ removes arsenic from solution and prevents large arsenic concentrations from being present in water (57). Arsenate is reduced to arsenite apparently by bacteria in the marine environment.

The biomethylation of arsenic by methyl-B$_2$H$_4$ occurs in anaerobic ecosystems. The volatile species arsenic, dimethylarsine, and trimethylarsine will be released into the aerobic environment at the sediment/water, water/air, or soil/air interface (56). These alkylated arsenic compounds are slowly oxidized in air and water to give steady state concentrations of methylated arsenic compounds of higher oxidation state. Thus while the relative amounts of As$^{+3}$, As$^{+5}$, methane arsenic acid, and cacodylic acid (dimethyl arsinic acid) vary, generally As$^{+5}$ and cacodylic acid predominate in both fresh water and sea water (56, 57). Cacodylic acid should exist in a steady state concentration due to oxidative demethylation by aerobic bacteria (56).

While organisms accumulate organoarsenicals, regardless of the form (4, 5, 55-57, 80), biomagnification through the food chain does not occur with the arsenicals (57).

It is generally acknowledged that it is difficult to quantitate the degree of transport of arsenic due to complex multimedia (e.g., sediment/sediment/water/air) exchange of arsenic and the natural differences between air, soil, and water systems (55, 57). Cycling of arsenic in the environment is dominated by adsorption and desorption to soils and sediments, and is maintained at low concentrations in water and air (57). Alkyl arsines are formed in soils and possibly sediments and in sewage sludge (55, 57, 80), hence, transport can occur in air and water. While the transport of alkyl arsines in air may involve only the gaseous phase or a gaseous/particulate phase, the extent of transport in air is unknown (57). Recent studies by Parris and Brinkman (61) on oxidation of trimethylarsine and trimethylstibine by atmospheric oxygen showed that trimethylarsine reacts slowly with oxygen under normal conditions of concentration and temperature, suggesting that this compound can travel considerable distances without undergoing chemical change in aerobic systems.

Aspects of transport of alkyl arsenicals in waters are largely unknown (57). Fresh and salt waters have been shown to contain methanearsonic acid and cacodylic acids at low levels (80) and movement of the organoarsenicals is believed to occur both through physical transport and uptake by aquatic organisms (57, 80). According to Woolson (57), the data would appear to indicate that the fluvial transport of arsenic is appreciable from point sources. While the bottom sediment of natural aquatic systems functions as a temporary reservoir in the dispersive transport of arsenic, oceanic sediments are the ultimate sink for arsenic residues (57, 80).

**Beryllium**

A recent review by Drury et al. (81) of the environmental effects of beryllium is especially noteworthy. Beryllium is a moderately rare element, present in some 40 mineralized forms, principally beryl, (a beryllium aluminum silicate) and bertrandite (a hydrated beryllium disilicate). The main beryllium ore is beryl which contains about 5% Be metal (82).

Beryllium is used widely in industry in three principal forms: as the metal (33%), Be-Cu alloys (50%) and other alloys (10%), and as BeO (5%) (81). The estimated supply-demand relationships for beryllium in 1988 are illustrated in Figure 4 (81). The principal use for Be and its compounds is in electrical applications. Approximately 25% of all Be used is in switch gear; 30% in computers, radio,
television, and electrical applications; 10% in nuclear applications; 10% in missiles and space programs and the remainder in welding, aircraft engines, precision instruments and other applications. The U.S. production of Be metal from two plants is about 45-68 metric tons per year (81). The U.S. demand for Be is expected to be 1500 metric tons (1660 tons) in the year 2000, with that of the rest of the world projected to be 1200 metric tons during that period (81). About 95% of the beryllium ore used in the U.S. is imported chiefly from Brazil, the Republic of South Africa, India, Argentina, Uganda, and Mozambique (81). While U.S. reserves of beryllium are estimated at 72,000 metric tons (80,100 tons), data concerning Be reserves in the rest of the world are lacking (81, 82).

Beryllium in the environment chiefly arises from coal combustion. World coals contain 0.1 to 1000 ppm Be (83-85). The U.S. Environmental Protection Agency estimates that 0.26 kg of Be is released for every 907 metric tons (1000 tons) of coal burned. About 133 metric tons (147 tons) of Be was emitted in the U.S. in 1968 due to coal combustion (81, 86). Phillips (87) suggested that 84% of the Be in Colorado coals is lost to the atmosphere upon combustion. The projected enhanced use of coal (particularly in the U.S.) for power generation and space heating could significantly increase the amount of Be emitted to the atmosphere. The potential magnitude of Be dissemination could be gleaned from the following considerations raised by Zubovic (88) and Tepper (89). If 500 million tons of Illinois and Appalachian coal with an average Be content of 2.5 ppm were burned annually, the potential production of Be from coal approximates 1,250 tons of beryllium metal. This is considered to be about five times the world production of the element (89). There is evidence that Be is predominantly associated with the organic material in coal, suggesting that much of the element would be contained in particles of small size and discharged to the atmosphere. Beryllium has been found in flue dusts at an average concentration of 20 ppm (89). Although the form in which Be occurs in the effluent from coal-burning utilities is not definitively known, it is generally believed they are oxides, mostly of the high fired and refractory type rather than beryl (a beryllium aluminum silicate, 3BeOAl₂O₃·6SiO₂) (88,89).

![Figure 4](image)

**FIGURE 4.** Supply-demand relationships for beryllium, 1968. Values are in metric tons of beryllium. e = estimate; a = Be-Cu master alloy; m = metal; SIC = Standard Industrial Classification. Adapted from Heindl (82).
The combustion of oil also contributes to the release of beryllium. It was estimated by EPA that oil used in 1968 contained 0.08 ppm Be, providing an emission of 7.3 metric tons (8 tons) of Be upon combustion (82).

Beryllium extraction plants emit many forms of beryllium including: beryl ore dust from ore crushing and milling; sodium fluoroberyllate from filtering; Be(OH)$_2$ slurry from high-purity beryllium hydroxide production; (NH$_4$)$_2$BeF$_4$ slurry, Be(OH)$_2$, BeF$_2$, Be, and BeO acid fume from beryllium metal production; BeO furnace fume and dust from beryllium oxide production and Be and BeO from beryllium-copper alloy production (90). These facilities are required to limit ambient Be concentrations to 0.01 \( \mu g/cm^3 \) (90). Beryllium fabrication results in the atmospheric release of 4.5 kg of Be for every ton of Be processed (86), with about 6 kg of Be emitted by this process in 1968 (81).

Ceramic plants release Be in the form of dusts, fumes and mists containing BeO (90), with about 0.45 kg of Be released for every ton of Be processed in the manufacture of beryllia ceramics (86). Approximately 14.5 metric tons (16 tons) of Be was released to the U.S. atmosphere in 1968 as a result of ceramic manufacture (81). Beryllium emission to the U.S. atmosphere in 1968 due to cast iron production (which releases particulates that contain about 0.003% Be) is estimated at 3.6 metric tons (4 tons) (86). Additional potential for Be emissions exist in the rocket propellant industry. These emissions can include Be powders during handling, mixing, casting, curing or polymerization of propellant and gases containing beryllium oxide, nitrate, carbide and chloride during test firing. A total of about 148 metric tons (164 tons) of Be was emitted to the U.S. atmosphere from all sources in 1968, with Pennsylvania and Ohio accounting for 25% of the total, due to Be production plants in these states (86).

Reports of the aerolization of beryllium from newly ignited camp lantern mantles additionally reinforces the concept that exposure to Be extends beyond the groups of employees working in industry that utilize the metal. For example, the mantle of a gas lantern contains about 600 \( \mu g \) of beryllium metal, most of which is volatilized and becomes airborne during the first 15 min of use of a new mantle (91).

In 1971, approximately 8000 large-scale processing plants and small plant operations were estimated to be in operation in the U.S. which were engaged in melting, casting, grinding, drilling, and machining of beryllium, its alloys and compounds (92). A 1970 survey conducted by the U.S. Public Health Service, Bureau of Occupational Safety and Health, estimated that about 30,000 individuals could be potentially exposed to dust or fumes of beryllium. (This would include approximately 2500 persons in the production industry) (92).

The beryllium content of common rocks and minerals ranges from less than 1 ppm to about 10 ppm, while Be ores contain several thousand ppm (81,82,83). Due to its prevalence in rocks, Be occurs in most soils with world soils averaging 6 ppm Be with a range of 0.1 to 40 ppm (81,85). Beryllium is almost nonexistent in natural waters. Fresh water averages less than 0.001 ppm while sea water contains about 6 \( \times 10^{-7} \) ppm (85). Finished U.S. waters average about 2 \( \times 10^{-4} \) ppm and range from 1 \( \times 10^{-5} \) to 1.2 \( \times 10^{-5} \) ppm (81,93). (The recommended provisional limit for Be in water is 1 ppm) (81). Unpolluted air contains less than 0.0001 \( \mu g/cm^3 \) Be with generally higher levels in urban air than rural air. The average daily atmospheric concentration of Be in the U.S. is less than 0.0005 \( \mu g/cm^3 \). In the past, Be concentrations have been found in air near Be processing plants. However, it should be noted that pollution control equipment is available to meet U.S. air standards (average of 0.01 \( \mu g/cm^3 \) Be over a 30-day period) (81).

In regard to waste management of beryllium, only a small amount of the total Be waste produced by industry is composed of actual beryllium scrap. The major portion of Be waste results principally from pollution control strategies. These wastes are in the form of either solid particulates or a dilute aqueous solution as in scrubber liquor. While the most desirable method of handling Be wastes is recycling them to producers (94), burial in plastic containers sealed in metal drums has been recommended for wastes which are not recycled (81,94). Data concerning the mobility and persistence of beryllium in soils, water and air are meagre. The chemistry of beryllium in soils is believed to be analogous to that of aluminum or zinc (81,95). Beryllium is strongly fixed in many soils and will displace divalent cations which share common sorption sites (81). Because the oxide and hydroxide of Be are relatively insoluble at the common pH of natural waters, Be does not readily enter into solution during weathering processes. Approximately 9600 metric tons (10,579 tons) of Be are added to the oceans yearly in water and sediments of which approximately 0.00002% is retained (96), with the residence time of Be in the oceans estimated to be in the order of a few hundred years (81,97).

The trend of global atmospheric beryllium concentrations during the last several decades is lacking, principally believed to result from earlier lack of adequate sensitive analytical methodology (98).
Beryllium in the atmosphere is believed to return to earth as dry fall or in precipitation (81).

There is no evidence of beryllium being transformed or biomagnified within food chains. Data concerning beryllium content of foods are meagre. In limited studies of Be in Australian and German foods, the levels in the former were generally low and ranged from 0.01 to 0.10 ppm (99), while those in German foods were slightly higher (100).

**Cadmium**

The recent International Conference on Environmental Cadmium held at Bethesda, Md., June 7-8, 1978 with subsequent publication of these proceedings is most relevant concerning the summarization of the current status of scientific knowledge about cadmium as an environmental agent and the identification of needed areas of research (101). The most germane papers at this conference with a focus on sources, transport and alterations of cadmium include: some aspects of Cd flow in the U.S. (102); industrial emission of Cd in Japan (103); exposure and accumulation of Cd in populations from Japan, the United States and Sweden (104); factors influencing Cd accumulations and its toxicity to marine organisms (105); bioaccumulation of Cd in marine organisms (106); deposit and mobility of Cd in a marsh-cove ecosystem and the relation to Cd concentration in biota (107); Cd in forest ecosystems around smelters (108); sewage sludge as a source of Cd in soil-plant-animal systems (109,110) and Cd uptake from feed and its distribution to food products from livestock (111).

Other recent relevant publications concern the occurrence of Cd in the environment and its biological and health effects (112,113), the influence of environmental factors on the effects of Cd on the biota (114), transformation (4,5), and bioaccumulation of cadmium (115,116) and Cd pollution from secondary metal refinery operations (117).

Although cadmium is one of the rarer elements in nature, frequently occurring with zinc in a Zn/Cd ratio of about 100, it is a recognized ubiquitous metal having widespread and generally increasing uses in a spectrum of products and applications including electroplating, pigments, plastics, Ni-Cd batteries, TV tubes, solar cells, alloys, fungicides, and as a catalyst.

Cadmium is recovered as a by-product from the smelting and refining of zinc ores. The world production of the metal in 1970 was 16,000 tons; it has increased yearly by approximately 14% during the preceding 5 years and is estimated currently to be about 18,000 tons (108). It is important to recognize the major differences in usage patterns.

Whereas in the U.S. the electroplating industry represents the single largest consumer of cadmium (utilizing almost half of the 12.5 million pounds in 1974), nearly half of the amount of Cd produced in Japan was used for pigments and plastic stabilizers (103), while in Sweden the main categories of Cd-containing products are polymers (pigments and stabilizers, electric accumulators and electroplated articles or goods containing Cd based alloys). Cadmium is released to the environment through smelting and refining of tin and other ores, by the above dissipative uses of Cd and by the large-scale use of materials in which cadmium is an impurity (e.g., coal, phosphate fertilizer, zinc products) (102-104). The estimated release of cadmium in the environment in 1968 was 5 to 8 million pounds (118).

Cadmium metal has an appreciable vapor pressure at the temperatures used in smelting ores, in the manufacture of metallic alloys and in the reprocessing of Cd-containing alloys and of Cd-plated materials. These processes accounted for about 90% of the Cd emissions to the atmosphere in the U.S. in 1968 (119). Cadmium emissions (in metric tons) from other sources were as follows: production of secondary copper from automobile radiators, 114; incineration of solid waste, 86; pigment production, 9.5; automobile tire wear, 5.2; production of stabilizers for plastics, 2.7; production of brazing alloys and solders, 2.3; burning of automobile motor oils, 0.83; fertilizers, 0.41; mining, 0.24; fungicide spraying 0.23 and nickel-cadmium battery manufacture, 0.18. Since consumption of cadmium in the U.S. in 1968 was 6,068 metric tons, based on the above estimates, the atmospheric emissions of Cd amounted to approximately 34% of the Cd consumption for that year.

Yost (102) recently described the development of a cadmium flow model for the U.S. which involves simulating sources, use patterns, waste treatment and recovery technique, waste disposal options, and environmental flow mechanisms over a 10-year simulation period. The following sources of Cd discharge to the environment included electroplating facilities, pigment manufacturers, plasticizer producers, battery manufacturers, coal fired power plants, steel producers, sewage treatment plants and municipal/commercial incinerators. The annual Cd consumption for the 10-year period is assumed to be 5,000 metric tons initially (121) and to increase by 280 metric tons each year of the simulation period (102). The relatively modest, less than 5% annual increase in Cd consumption is a reflection of both the anticipated impact of present and proposed environmental restrictions which are expected to restrain growth in the cadmium market for the foreseeable future (102). [Analogous
restrictions are operative in Japan and Sweden (103,120,122). Table 7 summarizes on an aggregate/national basis the relative magnitudes of Cd discharges to major environmental and waste processing receptors for a 10-year simulation period (102). A major share of the use-related Cd movement in the U.S. environment is attributable to the electroplating industry which, it should be noted, is by far the largest consumer of Cd (about 55%) in the U.S. Steel scrap recycle; coal-fired power plants and refuse/slime incineration account for all of the Cd input to the atmosphere in this study. It should be noted at the time of this publication Cd discharges to the atmosphere from lead and zinc smelters were not included (102).

The combustion of coal for the generation of electricity in the projections of Yost (102) is a relatively small contributor to Cd discharge to the environment. The average Cd content of coal commonly used in the U.S. is 0.21 μg/g (84), which would indicate that $7.37 \times 10^4$ kg of cadmium passes through coal-fired power generating plants annually (102) based on the use of $3.51 \times 10^{11}$ kg of all types of coal in 1978 in the U.S. for generation of electricity (123). The discharge of Cd to the atmosphere as a component of power plant stack gas particulate results in a consequent deposit/fall out of Cd bearing particulate on both urban and rural areas. Although the exact form of Cd in particulates has rarely been reported, it is believed that cadmium oxides will constitute an important part (118). Rural soils are considered to be sinks for Cd generated from most U.S. coal-fired generating plants (102). Concentrations of cadmium in air normally range from 0.001 to 0.05 μg/m³, but may be as high as 5 μg/m³ near a point source of emission such as a smelter (124). Elevated levels have been found near Cd-emitting industries such as in Sweden and Japan where weekly means between 0.2 and 0.6 μg/m³, 500-1000 m from the source, have been noted (125).

Information on the chemical forms of cadmium in air is rather meagre, although there is considerable evidence that a number of metals including cadmium are concentrated in smaller, respirable particles (11-13).

Soil concentrations of cadmium are usually less than 1 ppm but may rise to approximately 100 ppm as a result of aerial deposition, irrigation with contaminated water, the application of sewage sludge-based fertilizers (29,124,126), super phosphate fertilizers, pesticides containing cadmium, or by the discharge of liquid or solid cadmium containing wastes from mining metallurgical, industrial or urban activities (120,125). It has been estimated that cadmium present as an impurity in phosphate fertilizers accounts for one-third to one-half of the total annual cadmium introduced into Swedish agricultural soils (122). However, the uptake of Cd in plants is not necessarily solely related to its concentration in the soil. Bioavailability of the metal depends upon a number of factors including the soil pH, plant species, presence of other trace materials and, in the case of soil treated with sewage sludge, the rate of sludge application (101,108,110).

Cadmium concentrations in non-polluted waters are usually lower than 1 μg/kg (69,93,120). Reported cadmium concentrations in natural waters can show more than two orders of magnitude variation (127). Of several heavy metal pollutants in the aquatic environment, Cd concentrations in some anthropogenic deposits have exhibited one of the largest relative increases, compared to natural conditions (115,128).

It has been suggested that increased utilization

---

Table 7. Comparative Cd flow analysis for ten-year simulation period.a

| Process                      | Atmosphere | Landfill | Natural waters | Sewage treatment |
|------------------------------|------------|----------|----------------|------------------|
| Electroplating               | –          | 27467    | 203            | 1580             |
| Pigments                    | –          | 5130     | –              | 176              |
| Plastics                     | –          | 8480     | 37             | 138              |
| Ni-Cd batteries             | –          | 2610     | 53             | 53               |
| Miscellaneous uses          | –          | 3720     | 8              | 165              |
| Steel scrap recycle         | 265        | 3500     | 102            | 57               |
| Coal-fired power plants     | 76         | 591      | 11             | 2.4              |
| Refuse-slime incineration   | 404        | 5595     | 167            | 95               |
| Sewage treatment            | –          | 1010     | 735            | –                |
| Total                       | 745        | 58103    | 1316           | 2266             |

a Includes all land disposed sludge. Data of Yost (102).
of compounds containing cadmium has accelerated the rates of mobilization and transport of Cd which far exceed the rates of the natural, abiotic cycling processes (114). These rates have led to increased deposition of cadmium in atmospheric, aquatic and terrestrial environments with subsequent increased uptake of Cd by accumulation in the biota (114). However, while cadmium is recognized as an important trace contaminant in both aquatic and terrestrial environments, comparatively little is known regarding definitive aspects of its environmental behavior. Utilizing tracer techniques with 109Cd in microcosm, field plant and stream studies, Van Hook et al. (129) suggested via food chain studies that the biological half-lives of cadmium ranged from 7 to 99 days for a variety of species. Stream-tagging experiments demonstrated cadmium to be accumulated, but not to the extent of methyl mercury. Cadmium appeared to be generally less mobile than mercury in the aquatic environment. In land-water (microcosm) studies, the majority of cadmium added via atmospheric input was tied-up in the soil while in aquatic systems, the majority accumulated in sediments. Increasing attempts are being made to predict the importance of natural versus anthropogenic sources of Cd in air, soil and waters, the distribution of various particle sizes in air, the proportion carried by waters in particulate form vs that in solution and the occurrence in deposits or sediments in water (101-116). In aqueous environments, including the soil solution, the Cd\(^{2+}\) ion may enter into a variety of reactions including formation of soluble, complex, ionic or molecular species [Cd(H\(_2\)O)\(_x\)]\(^{2+}\) etc., precipitation and coprecipitation, incorporation into mineral lattice structures, accumulation in or fixation by biologic materials, complexing with chelating agents, adsorption on clay minerals and humus materials (114).

Movement of cadmium through estuarine ecosystems and uptake by commercially important benthic shellfish was found to be influenced by a number of variables of which salinity is believed to be of primary importance (101,105,106).

Little is known of the microbial transformation of cadmium. Presumptive evidence for the volatilization of inorganic cadmium by conversion to the methylated species by a Pseudomonas has been reported (130). Identification of the volatile cadmium species was based on its ability to transfer a methyl group abiotically in water to Hg\(^{2+}\) hence resulting in the formation of methylmercury.

**Chromium**

General aspects concerning the distribution of chromium in the environment have been reviewed by NAS (131), NIOSH (132), IARC (133) and more recently by Langard and Norseth (134), Norseth (135), Langard (136), EPA/ORNL (137), and CEC/EOA (138).

Although chromium is an abundant element in the earth's crust and occurs in oxidation states ranging from Cr\(^{3+}\) to Cr\(^{6+}\), only the trivalent and hexavalent are of apparent significance, with the trivalent the more common form. Elemental Cr is not found in nature; the only major commercial chromium mineral is chromite, FeOCr\(_2\)O\(_4\) which is found in considerable quantities in Rhodesia, U.S.S.R., Republic of South Africa, New Caledonia, and the Philippines.

Approximately 57% of the imported chromite ore in the U.S. is used in the metallurgical industry, 30% in refractory materials and 13% in the chemical industry (139). The world production of chromites in 1971 has been estimated at 6.3 x 10\(^6\) tons, which is a 5% increase over 1970 (138). Metallurgical-grade chromite ore is usually converted into one of several types of ferrochromium or chromium metal that are alloyed with iron or other elements, usually nickel and cobalt (131). Ores used for ferrochrome production contain at least 50% chromic oxide. Ferrochrome is used primarily for the production of stainless steel and alloy steels. Over 60% of chromium used by the metallurgical industry is used for stainless steel production with other applications including high-speed and high-temperature steels, other alloy steels and nonferrous steels (131). Chromite is also used in the refractory industry as a furnace lining.

Chromium metal is made commercially in the U.S. by two principal processes: (a) an electrolytic and (b) an aluminothermic reduction procedure in which chromic oxide is reduced with finely divided aluminum (133). The U.S. production in 1970 of Cr metal and metal alloys other than ferrochromium alloys was reported to have been 31 million pounds, approximately 75% made by the electrolytic method. (This included production of Cr briquets, exothermic Cr additives, miscellaneous Cr alloys in addition to Cr metal) (133).

Chromates and dichromates are the major chromate compounds produced commercially. Chromates are produced by a smelting, roasting, and extraction process (e.g., by calcining a mixture of chromite ore, limestone, and soda ash). The residues from both soda ash or lime processes contain an unknown mixture of mostly insoluble chromium compounds (140). Sodium dichromate is produced industrially by the reaction of sulfuric acid on sodium chromate. Sodium chromate and dichromate are the principal substances for the production of all other chromium chemicals (137). The
The combined U.S. production of hydrated sodium chromate and hydrated sodium dichromate in 1971 was 276.4 million pounds (133). The principal use of sodium dichromate is in the production of chrome pigments (e.g., lead chromate) which are used in paints, printing inks, for coloring paper, rubber, linoleum, floor tile, etc. (133). Lesser amounts of sodium dichromate are used in the production of chromium trioxide via the reaction with sulfuric acid. Additional areas of application of sodium dichromate include the production of chrome salt used as a tanning agent for leather, mordant in dyeing, wood preservatives, fungicide and anti-corrosive in cooling systems, boilers and oil drilling muds (15). Chromium trioxide is used mainly in chromium plating in the production of automobiles and secondarily metal-finishing operations including aluminum anodizing, chemical conversion coatings, and the production of phosphate films on galvanized iron or steel. Significant nonplating applications of chromium trioxide include: corrosion inhibitor for ferrous alloys in recirculating water systems, in catalyst manufacture and as an oxidant in organic synthesis (133). In 1970 approximately 148.3 thousand short tons of sodium chromate were consumed in the U.S. of this 30% was used for pigment production, 25% for chromic acid, 15% for metal treating, 5% for textiles and dyes and 14% for miscellaneous applications (141). NIOSH estimated that about 175,000 workers in the U.S. are exposed directly to chromium (VI) compounds in tanning, primer paints, pigments, graphic arts, printing and reproducing, fungicides, wood preservatives and corrosion inhibitors (131).

Although production data for lead chromate are lacking it has been produced by the pigment industries of most industrialized countries. The combined production of chrome yellow and chrome orange in the U.S. in 1970 amounted to 64.9 million pounds (133). However, the ban in the U.S. imposed by the Environmental Protection Agency in 1973 on the domestic use of paints containing more than 0.06% lead significantly reduced the U.S. consumption of lead chromate pigments and hence the potential pollution contribution of these pigments (133).

Chromium in ambient air occurs from natural sources, industrial and product uses as well as burning of fossil fuels and wood. In rural areas the concentration of Cr seldom reaches 0.01 μg/m³ while that in the ambient air of large industrial cities of the U.S. usually ranges from 0.01 to 0.03 μg/m³ (131). About 68% of the Cr emitted to the atmosphere is estimated to be derived from ferrochrome production, while ore refining, chemical and refractory processing and indirect sources also contribute to the atmospheric burden. Of the indirect sources, the combustion of coal is by far the largest (137,139). Particulates emitted from coal-fired power plants have been reported to contain from 2.3 to 31 ppm Cr, depending on the type of boiler firing; the emitted gases contained 0.22-2.2 mg/m³. These concentrations were reduced by fly ash collection to 0.19-6.6 ppm and 0.018-0.5 mg/m³ respectively (139). Coal from many sources can contain as much Cr as soil and rocks, or approximately 60 ppm (141).

Cement-producing plants are a potential additional source of atmospheric chromium. Portland cement contains 41.2 ppm Cr (range 27.5-60 ppm) as might be expected from its presence in limestone. Soluble Cr in cement amounted to 4.1 ppm (range 1.6-8.8) of which 2.9 ppm (range 0.03-7.8) was hexavalent (143).

The wearing of brake linings containing asbestos represents another important source of Cr atmospheric emissions since asbestos can contain approximately 1,500 ppm of Cr (144).

An additional potential source of Cr to the atmosphere, particularly urban atmospheres, is the increased use of catalytic emissions control systems on passenger cars in the U.S. (beginning with the 1975 model year) (145). Reduction catalysts such as copper chromite (of variable composition) have been found to emit high concentration (>10⁶ metal-containing condensation nuclei/cm³) under a broad range of controlled conditions. Chromate chemicals are used as rust inhibitors in cooling towers, dissolving in recirculating water systems that continually discharge about 1% of their flow to waste. Both chromate and water are lost to the atmosphere, the water can contain 15-300 ppm chromate (139). In general, atmospheric concentration of chromium closely parallels geographic areas of high population and industrial activity (137).

Chromium is removed from the air by precipitation and fallout being deposited on both land and water; terrestrial fallout will eventually be carried to surface waters by runoff (50). The concentration of Cr in soil usually varies from traces to about 250 ppm (as chromic oxide). Very little Cr is released from soil by leaching due to its insoluble nature, but surface runoff carries some Cr to receiving waters, where it's mainly deposited in sediments (137).

The concentrations of Cr in sea water range from 0 to 0.36 ppb, mostly as hexavalent chromium. Although the trivalent form of Cr also exists in water, it may eventually precipitate or be absorbed (131,137,146). UNEP (145,146) estimates the total input of Cr to the Mediterranean from land-based sources at 2,760 tons/year.

August 1981
In rivers, concentration of Cr ranges between 1 and 10 ppb (131). It has been estimated that $6.7 \times 10^6$ kg of Cr are added to the oceans each year (142). Much of the Cr lost from land by erosion and mining is eventually deposited on the ocean floor (146). A potential Cr input of 0.02 million tons/year to the world’s oceans from atmospheric washout has been reported by UNEP (147).

Relatively large amounts of chromium are discharged in the form of wastewaters from the plating and finishing industries. It is important to note that only about 10-20% of the Cr used in chrome-plating processes ends up in the product. The textile industry which employs products containing chromium to control algae, prevent corrosion, and in the dyeing process also discharge effluents containing chromium (50,149). Chromium in industrial wastes occurs predominantly as the hexavalent form in chromate ($\text{Cr}_2\text{O}_7^{2-}$) and dichromate ($\text{Cr}_2\text{O}_4^{2-}$) ions. Hexavalent chromium treatment frequently involves reduction to the trivalent form prior to removing the chromium from the industrial waste. Hence, trivalent chromium in industrial wastes may result from one step of the wastewater treatment. Industries that employ trivalent chromium directly in manufacturing processes include glass, ceramics, photography, and textile dyeing (150). Plating wastes may also contain a few milligrams per liter of trivalent chromium in addition to the predominant hexavalent form (151).

The Cr content in most foods is considered to be extremely low (131,133) with vegetables (20-50 ppb), fruits (20 ppb) and grains and cereals (excluding fats, 40 ppb) as illustrative examples. Schroeder (144) estimated the mean daily intake of Cr from food, water, and air to be 280, 4, and 0.28 µg, respectively. It should also be noted that tobacco has been reported to contain up to about 30 mg/kg of Cr with most values being below 5 mg/kg (152). Neither the chemical form of chromium in tobacco smoke nor estimates of the inhaled amount of Cr from this source are known.

**Nickel**

General aspects of the sources and distribution of nickel in the environment have been reviewed by NAS (158), NIOSH (154), IARC (155), EPA (156), and most recently by Norseth and Piscator (157).

Similarly to many other trace elements, nickel is ubiquitous in the environment being present in natural waters and practically all soils and food. It is present to the largest extent in igneous rocks (approximately 0.01%) (153). Over 90% of the world’s nickel is obtained from pentlandite (FeNi)S, a mineral largely associated with large amounts of pyrrhotites and varying amounts of chalcopyrite (155). Nickel is also a natural impurity of some types of asbestos, particularly chrysotile (155). The estimated world’s total production of nickel in 1971 was 706,069 tons, the major producing countries being Canada, New Caledonia, Republic of South Africa, U.S.S.R., Australia, Rhodesia, and Indonesia.

All Canadian, Finnish, Rhodesian, and South African nickel and some Russian and Australian nickel are produced from sulfide ores and the remaining nickel is produced from oxide ores. In the U.S. in 1971, 2581 tons of Ni was produced as a by-product of metal refining and 13,073 tons recovered from domestic ore (153). The nature of the occurrence of nickel ore illustrates two distinct techniques for the mining and concentration. Whereas sulfide ore is mined chiefly underground, the Ni minerals concentrated by physical means and the concentrate is mostly smelted pyrometallurgically, oxide ore is mined in open pits, nickel extracted either in a chemical form by leaching or by smelting to yield ferronickel (153).

Nickel powder is produced commercially by the Mond process and its variations which generally involves the reaction of Ni or Ni ore with carbon monoxide to yield nickel carbonyl Ni(CO)$_4$ which is decomposed by heat to yield pure, finely-divided nickel powder (153,155). In 1970, U.S. imported 6.1 million pounds of Ni powder. The largest percentage of Ni powder is used in the production of other forms of Ni. The major area of application of nickel is in the production of alloys (e.g., stainless steel) to make a wide variety of consumer goods. It was estimated in 1970 that more than 600 companies in the U.S. are primary users of nickel. Among the approximately 1500 users that make alloys, about 55% produce castings and 45% produce forgings. Electric furnaces are employed by these consumers to melt nickel with other metals to produce the alloys (158).

Another major application of nickel is for electroplating which is very widely used. (Approximately 24,500 and 21,000 tons of Ni were consumed in 1970 and 1971 for this purpose in the U.S.) (158). Electroplating accounts for approximately 16% of the total annual production in the U.S. (153). Other important uses of nickel are in Ni-Cd batteries, electronics and computers, production of nickel compounds, such as the acetate, carbonate, sulfate, and the oxide. Nickel carbonate is probably the largest produced nickel compound. An estimated 2 million pounds of the basic nickel carbonate is used for the production of nickel catalysts (e.g., Raney nickel) which are widely used in organic chemical manufacture, petroleum refining and edible oil
hardening (153,154). Nickel acetate is used principally as a mordant in the textile industry. Nickel carbonyl is employed widely in the refining of nickel and as noted above for the manufacture of high purity Ni powder for powder metallurgy fabrication of Ni and Ni alloy components and the manufacture of catalysts. The total U.S. production is estimated at less than 15 million pounds (155). Nickel sulfate (as millions of pounds) was used in the U.S. in 1970 as follows: plating baths 33.8-87.8; nickel carbonate catalysts, 3.6; organic nickel salts, 0.5; miscellaneous, 0.2-2.2 (total consumed was estimated to be 40.1-44.1 million pounds) (155). Nickel oxide is generally obtained by roasting Ni ores. The partially reduced nickel oxide products, known as “nickel oxide sinters” are produced commercially on a large scale and are used primarily in the production of stainless and alloy steels. U.S. consumption in 1970 and 1971 was estimated to have been 16.7 and 15.0 million pounds for nickel oxide and 69.6 and 69.0 million pounds for nickel oxide sinters (155). Nickel is found in the air of both urban and rural communities. From 1957 to 1968 the average Ni concentration in 30 cities in U.S. declined slightly from 0.047 to 0.026 μg/m³ (159). Both urban-rural and seasonal differences in airborne concentrations exist: urban areas have the highest Ni concentrations during fall and winter months (159). Airborne Ni particulate concentrations in New York showed a significant correlation between Ni content and such variables as air temperature, atmospheric stability and vanadium content (160). Although it appears that about half of the atmospheric nickel is associated with fine particulates, data on particle size are limited.

An increasing source of atmospheric nickel arises from the increasing combustion of fossil fuels, primarily coal for power generation and space heating which yields particulate matter in the respirable range (1 μm). Coal has an average of 35 ppm nickel and ash has 3 ppm to 1% nickel (189). Fly ash from residual oil contained 1.4-10% nickel as the oxide; crude oil, 55 ppm and the asphaltene fraction, 245 ppm nickel (161). It has been estimated that 14.8 million liters of fuel oil are used annually in Manhattan, New York, and allowing a Ni content of 10 ppm, an emission rate of 25%, the daily release rate of Ni into the atmosphere could be 156 kg daily during the cold winter months (153,156). Another potentially important source of nickel is consumption of diesel oil, which can contain 2 ppm nickel; particulates from diesel oil exhausts contain from 500 to 10,000 ppm nickel (160). Hence, there is an appreciable amount of atmospheric nickel independent of metallurgical processing particularly in urban areas. The major sources are exhausts of automobiles and trucks, burning of fuel oil for space heating and burning of coal and oil for power generation. Nickel may be inhaled by urban residents in amounts of 2-14 μg/day, depending on time and location (153).

The concentration of nickel in surface and ground water is generally quite low (0-12.5 μg/kg) (155). In most ground waters, Ni has not been detected (153). Nickel content in seawater ranges from 0.1 to 0.5 μg liter. In major river basins in the U.S. during 1962-1967, nickel was found with a frequency of 16% and an overall mean concentration of 19 μg liter (162). It should be noted that nickel sulfate, the most important compound of nickel in commerce, is released to aquatic environments in significant amounts from the nickel plating industry (156). A community water supply survey of eight metropolitan areas in the U.S. in 1967 included samples from 969 water supplies with nickel being found in 78% of the samples with a minimum level of 1 μg liter and an average concentration at the consumer's tap of 4.8 μg- liter. With an estimated consumption of 2 liters/day, the nickel intake via water for an adult would be approximately 10 μg/day (153).

Human exposure to nickel in food derives from its natural occurrence in food ingredients and from man-made sources such as food-processing equipment, alloys, and fungicides. Although the chemical form of nickel in foods is not known, the concentration of nickel in foods is low (153,163).

Other potential areas of concern involving nickel relate to its presence in tobacco, asbestos and possible synergistic effects with other atmospheric pollutants, e.g., benzo(a)pyrene. The reported mean values for the Ni content in cigarettes from various sources have ranged from 2 to 6.2 μg (164). Of the nickel present in cigarette smoke, 10-20% is released in the mainstream of smoke (165,166). An average of 84% of the nickel in the mainstream smoke is present in the gaseous phase; only 16% is present in the particulate phase (166). There is no conclusive evidence to date regarding the chemical form of the vaporized nickel compound or compounds in mainstream cigarette smoke although it has been earlier speculated that gaseous nickel in the mainstream smoke is in the form of nickel carbonyl (165).

It is also germane to consider aspects of waste disposal and scrap recycling of nickel. Approximately 15,000-25,000 tons of nickel are recycled each year in the U.S. through copper smelters and refineries and through nonferrous metal foundries and manufacturing plants. Nearly all the nickel-bearing scrap material processed in these plants in Ni-, Cu-, or Al-base alloy (153). Recycled scrap is

August 1981
generally melted and refined and subsequently used to produce alloys or steels similar in composition to those in which it entered the recycling process, and hence Ni-scrap recycling processes are analogous to those used for the primary metal.

Although nickel forms a significant part of industrial and municipal waste, the techniques for recovering it, beyond the laboratory research stage, are not apparently developed. The nickel composition of remelted, melted, and smelted metal wastes (e.g., cans, massive iron, iron wire, iron oxide products, nonferrous metals in residues) ranges from 0.02 to 6% (153).

In limited studies of contamination on street surfaces, composite samples have been collected in streets of five cities by sweeping, washing, and collecting runoff from the surfaces with no seasonal adjustments. The concentration of Ni as a surface contaminant was found to be 0.15 mg/ft² in commercial areas, 0.23 mg/ft² in residential areas, and 1.25 mg/ft² in industrial areas (153).

Summary

An overview is presented of the current state of knowledge of the salient aspects of the sources, transport and alterations of arsenic, beryllium, cadmium, chromium, and nickel. This information is considered vital for a better assessment of the scope of potential human hazard to these ubiquitous toxicants and their compounds. Stress is focused on both natural and industrial activities, particularly on the latter's projected trends. Both increasing use patterns per se of most of these metals, as well as aspects of waste disposal and the anticipated increased combustion of fossil fuels for power generation and space heating (particularly in the U.S.) are major causes of potential health concern. Additionally, attention is drawn to the need for increased research to fill the gaps in our knowledge in these vital areas, all in the hope of permitting a more facile identification and quantification of the potential hazard of exposure to these agents.

Recommendations

A number of studies and reviews previously cited in this overview (1-7, 55,56,60,101,131,153) delineated recommendations for research of a specific metal or metalloid which are still relevant. The recommendations listed below are an attempt to highlight and restress the continuing need for these recommendations as well as to treat the research requirements in a more general or cohesive sense for As, Be, Cd, Cr, and Ni, since in most cases the needs are common to all of these ubiquitous toxicants.

Initially, there is a need for practical, sensitive, and quantifiable analytical methodologies for metal and metalloid speciation (chemical form and complexation) in environmental samples and standard reference materials for environmental samples. This would be of immense utility in permitting a more facile evaluation of potential input arising from production emission (as well as emission arising from combustion of fossil fuels, etc.) in relation to natural flux, residence times in various reservoirs, physical and chemical properties relating to dispersion, transport, biotransformation and both active and passive bioaccumulation.

In order to better predict trends, additional data are required on a national and global level to determine metal and metalloid concentration patterns based on "natural" distribution cycles compared with those arising from anthropogenic sources. We must determine, to the fullest extent possible, the molecular form of the element in each significant environmental compartment, as well as in animal and plant tissues.

We must obtain data (to a considerably greater extent than is now available) regarding the dynamics of a metal's or metalloid's mobility through ecosystems with focus on the uptake, distribution and interactions of various metal species in ecosystems.

We need to know to what extent or at what rate organometallic transformations occur, as well as how and at what rate the resultant organometals or organometalloids are sequestered in food chains and ultimately in man. In the case of arsenic, for example, we need to acquire additional knowledge regarding rates of methylation and of demethylation, partition coefficients between aqueous and organic phases for various arsenicals, and the redox chemistry of organic species present in biological media.

Additional studies are required to evaluate the effects of multiple metal and metalloid pollutants on microbial activities and alterations and the dynamic interactions that occur among the pollutant, environment and the biota.

Research is required to further delineate the mechanisms involved in the continual steady-state transformations effected by the bacterial flora in the "normal" cycling of metals such as in the case of arsenite in sea water. We need to acquire additional data concerning the possible flux of metals from the sea surface to the atmosphere as aerosols. Additional research is needed on the fate of atmospheric emissions of these trace metals with respect to the residence times and fallout with rain or snow, as well as impact with acid rain, especially in areas of high emission. More data are required on the
emission of metals from processes of scrap reclamation, municipal incineration and from the disposal of sewage sludges. Additional data are required particularly on the rate of release of metals from soils treated with phosphate fertilizers and on the possible leaching of cadmium from galvanized plumbing. Further studies are required to identify other factors such as speciation of metals in soils which influence the rate and magnitude of their uptake by edible plants grown in different types of soil.

REFERENCES

1. Task Group on Metal Interaction, Factors Influencing Metabolism and Toxicity of Metals: A Consensus Report, Proceedings of an International Workshop Meeting Organized by the Scientific Committee on the Toxicology of Metals of the Permanent Committee and International Association Occupational Health, Stockholm, July 17-22 (1977); Environ. Health Perspect. 25: 3-41 (1978).

2. Friberg, L., Nordberg, G. F., and Vouk, V. B. Handbook on the Toxicology of Metals. Elsevier/North Holland Biomedical Press, Amsterdam, 1979.

3. Fishbein, L. Environmental metallic carcinogens: an overview of exposure levels. J. Toxicol. Environ. Health 2: 77 (1976).

4. Summers, A. O., and Silver, S. Microbial transformations of metals. Ann. Rev. Microbiol. 32: 637 (1978).

5. Saxena, J., and Howard, P. H. Environmental transformation of alkylated and inorganic forms of certain metals. Adv. Appl. Microbiol. 21: 185 (1977).

6. Lantzy, R. J., and Mackenzie, F. T. Atmospheric trace metals: Global cycles and assessment of man's impact. Geochim. Cosmochim. Acta. 43: 511 (1979).

7. Wagener, R. J., Greeney, W. J., and Jurink, J. J. Environmental transport model of heavy metals. J. Environ. Eng. Div. (Amer. Soc. Civ. Eng.) 104: 61 (1978).

8. Anderson, M. P. Using models to simulate the movement of contaminants through groundwater flow systems. CRC Revs. Environ. Control 9: 97 (1979).

9. Gibbs, R. J. Mechanism of trace metal transport in rivers. Science 180: 71 (1973).

10. Van Hook, R. I. Transport and transportation pathways of hazardous chemicals from solid waste disposal. Environ. Health Perspect. 27: 295 (1978).

11. Lee, R. E., Jr. and von Lehmden, D. J. Trace metal pollution in the environment. J. Air Pollut. Control Assoc. 73: 653 (1973).

12. Lee, R. E., Jr., and Duffield, F. V. Sources of environmentally important metals in the atmosphere. Adv. Chem. Ser. 172: 146 (1977).

13. Natusch, D. F. S., Wallace, J. R., and Evans, C. A., Jr. Toxic trace elements: preferential concentration in respirable particles. Science 183: 202 (1974).

14. Lee, R. E., Jr., Goranson, S. S., Enrione, R. E., and Morgan, G. B. National air surveillance cascade impactor network. II. Size, distribution, measurements of trace metal components. Environ. Sci. Technol. 6: 1025 (1972).

15. Flinn, J. E., and Reimers, R. S. Development of predictions of future problems. EPA Report No. 600/5-74-006, Washington, D.C., 1974, pp. 36-38.

16. U.S. Environmental Protection Agency. 1973 National Emissions Report, EPA-450/2-76-007, Research Triangle Park, N.C., May 1976.

17. Coughlin, W. J., Ed., Coal Daily, Casey Publishing Co., Washington, D.C., Nov. 17, 1976.

18. Kirsch, H. Composition of dust in the waste gases of incineration plants. Paper presented at the First International Conference and Technical Exhibition, Montreux-Switzerland, 1975; IEE Catalog No. 75 CH 1008-2 CRE.

19. Greenberg, R. R., Zoller, W. H., and Gordon, G. E. Composition and size distributions of particles released in refuse incineration. Environ. Sci. Technol. 12: 560 (1978).

20. Law, S. L., and Gordon, G. E. Sources of metals in municipal incinerator emissions. Environ. Sci. Technol. 13: 432 (1979).

21. UNESCO. Statistical Yearbook 1975, Statistical Division, United Nations, New York, 1975.

22. SCEP. Study of Critical Environmental Problems, Man's Impact on the Global Environment. Colonial Press, New York, 1970.

23. Hardy, K. A., Akselsson, R., Nelson, J. W., and Winchester, J. W. Elemental constituents of Miami aerosol as function of particle size. Environ. Sci. Technol. 10: 176 (1976).

24. Harrison, P. R., Rahn, K. A., Dams, R., Robbins, J. A., Winchester, J. W., Brar, S. S., and Nelson, D. M. Area wide trace metal concentrations measured by multielement activation analysis. APCA Journal 21: 563 (1971).

25. Dams, R., Heindryckx, R., and van Cauwenberghke, K. Scheikunde en analyse van luchtpolluatie. Deel III: Appendix. Ind. Chim. Belg. 38: 627 (1973).

26. Capar, S. G., Tanner, J. T., Friedman, M. H., and Boyer, K. W. Multielement analysis of animal feed, animal wastes and sewage sludge. Environ. Sci. Technol. 12: 785 (1978).

27. Lester, J. N., Harrison, R. M., and Perry, R. The balance of heavy metals through a sewage treatment works. I. Lead, cadmium and copper. Sci. Total Environ. 12: 13 (1979).

28. Stoveland, S., Astruc, M., Lester, J. N., and Perry, R. The balance of heavy metals through a sewage treatment works. II. Chromium, nickel and zinc. Sci. Total Environ. 12: 25 (1979).

29. Andersson, A., and Nilsson, K. O. Enrichment of trace elements from sewage sludge fertilizer in soils and plants. Ambio 1: 176 (1972).

30. Greig, R. A., Wenzloff, D. R., Adams, A., Nelson, B., and Shelpuk, C C Trace metals in organisms from ocean disposal sites of the middle eastern United States. Arch. Environ. Contam. Toxicol. 6: 395 (1977).

31. Mackenzie, E. J., and Purves, D. Agricultural consequences of trace elements contamination of sewage, Chem. Ind. 12 (1975).

32. Laxen, D. P. H., and Harrison, R. M. A specific conductance method for quality control in water analysis, Water Res. 11: 91 (1975).

33. Carrondo, M. J. T., Perry, R., and Lester, J. N. Comparison of a rapid flameless atomic absorption procedure for the analysis of the metallic content of sewages and sewage effluents with flame atomic absorption methods. Sci. Total Environ. 12: 1 (1979).

34. Neufeld, R. O., Gutierrez, J., and Novak, R. A. A kinetic model and equilibrium relationship for heavy metal accumulation. J. Water Pollut. Control Fed. 49: 489 (1977).

35. Neufeld, R. O., and Hermann, E. R. Heavy metal removal by aminated activated sludge. J. Water Pollut. Control Fed. 47: 310 (1975).

36. Jelinek, C. F., and Braude, G. L. Management of sludge use on land, FDA considerations. Paper presented at 3rd Natl. Conf. on Sludge Management, Disposal and Utilization, Miami, Fla., Dec. 14-16, 1976.

37. Leonard, R. D. Hazardous solid waste from metallurgical
industries. Environ. Health Perspect., 27: 251 (1978).
38. Shuman, M. S., Haynie, C. L., and Smock, L. A. Modes of metal transport above and below waste discharge on the Haw River, North Carolina. Environ. Sci. Technol. 12: 1066 (1978).
39. Rasmussen, L., and Sand-Jensen, K. Heavy metals in acid streams from lignite mining areas. Sci. Total Environ. 12: 11 (1979).
40. Wilson, A. L. Concentrations of trace metals in river waters: a review. WRC Tech. Rept. TR16, 1976.
41. Turekian, K. K. The fate of metals in the oceans. Geochim. Cosmochim. Acta 41: 1139 (1977).
42. Hinesly, T. D., Jones, R. L., Ziegler, E. L., and Tyler, J. J. Effects of annual and accumulative applications of sewage sludge on assimilation of zinc and cadmium by corn (Zea mays L.). Environ. Sci. Technol. 11, 182 (1977).
43. Furr, A. K., Kelly, W. C., Bache, C. A., Gutenmann, W. H., and Lisk, D. J. Multielement absorption by crops grown in pots on municipal sludge-amended soil. J. Agr. Food Chem. 24: 889 (1976).
44. Thompson, S. E. Concentration factors of chemical elements in edible aquatic organisms. Lawrence Livermore Laboratory, Livermore, Cal. UCRL-50654, 1972.
45. Van Hook, P. I. Cadmium, lead and zinc distributions between earthworms and soils: potentials for biological accumulation. Bull. Environ. Contam. Toxicol. 12: 509 (1974).
46. Fimreite, N. Mercury in fish and fish-eating birds near sites of industrial contamination in Canada. Can. Field Natuinalist 65: 211 (1971).
47. Bernhard, M. Heavy metals and chlorinated hydrocarbons in the Mediterranean Sea. Ocean Management 3: 253 (1978).
48. Bernard, M., and Zattera, A. Major pollutants in the marine environment. In: Marine Pollution and Marine Waste Disposal, E. Pearson and E. Frangipane, Eds., Pergamon Press, Oxford, 1975, pp. 195-300.
49. GESAMP. Joint Group of Experts on the Scientific Aspects of Marine Pollution. Review of harmful substances. Reports and Studies No. 2, Doc. No. 76-98245, United Nations, New York, 1976.
50. IRTPC. Data profiles for chemicals for the evaluation of their hazards to the environment of the Mediterranean Sea. International Register of Potentially Toxic Chemicals, United Nations Environment Programme, Geneva, Switzerland, 1978.
51. Stoeppler, M., and Nurenberg, H. W. Comparative studies on trace metal levels in marine biota. III. Typical levels and accumulation of toxic trace metals in muscle tissue and organs of marine organisms from different European seas. Ecotox. Environ. Safety 3: 385 (1979).
52. Nelson, K. W. Industrial contributions of arsenic to the environment. Environ. Health Perspect. 19: 31 (1977).
53. Lindsey, L. Emissions of arsenic in Sweden and their reduction. Environ. Health Perspect. 19: 25 (1977).
54. Lunde, G. Occurrence and transformation of arsenic in the marine environment. Environ. Health Perspect. 19: 47 (1977).
55. Brinckman, F. E., Parrn, G. E., Blair, W. R., Jewett, K. L., Iverson, W. P., and Bellama, J. M. Questions concerning environmental mobility of arsenic: Needs for a chemical data base and means for speciation of trace organo arsenicals. Environ. Health Perspect. 19: 11 (1977).
56. Kidley, W. P., Dizikes, L., Cheh, A., and Wood, J. M. Recent studies on biomethylation and demethylation of toxic elements. Environ. Health Perspect. 19: 43 (1977).
57. Woolson, E. A. Fate of arsenicals in different environmental substrates. Environ. Health Perspect. 19: 73 (1977).
58. Walsh, L. M., Sumner, M. E., and Keenev, D. R. Occurrence and distribution of arsenic in soils and plants. Environ. Health Perspect. 19: 67 (1977).
59. Penrose, W. R., Conacher, H. B. S., Black, R., Meranger, J. C., Miles, W., Cunningham, H. M., and Squires, W. R. Implications of inorganic/organic interconversion of fluxes of arsenic in marine food webs. Environ. Health Perspect. 19: 53 (1977).
60. NAS. Arsenic, National Academy of Sciences, Washington, D.C., 1977.
61. Parris, G. E., and Brinkman, F. E. Reactions which relate to environmental mobility of arsenic and antimony. II. Oxidation of trimethylarsine and trimethylstibine. Environ. Sci. Technol. 10: 1128 (1976).
62. Giddings, J. M., and Eddlemon, G. K. The effects of microcosm size and substrate type on aquatic microcosm behavior and arsenic transport. Arch. Environ. Contam. Toxicol. 6: 491 (1977).
63. Ferguson, J. F., and Gavis, J. A review of the arsenic cycle in natural waters. Water Res. 6: 1259 (1972).
64. Andrae, M. O. Distribution and speciation of arsenic in natural waters and some marine algae. Deep Sea Res. 25, 391 (1978).
65. Andrae, M. O., and Klump, D. Biosynthesis and release of organoarsenical compounds by marine algae. Environ. Sci. Technol. 13: 738 (1979).
66. Kobayashi, S., and Lee, G. F. Accumulation of arsenic in sediments of lakes treated with sodium arsenite. Environ. Sci. Technol. 12: 1195 (1978).
67. Penrose, W. R. Arsenic in the marine and aquatic environments: Analysis, occurrence and significance. CRC Crit. Rev. Environ. Control 4: 465 (1974).
68. Durum, W. H., Hem, J. D., and Heidel, S. G. Reconnaissance of selected minor elements in surface waters of the United States. Geological Survey Circular 643, OSD1, Washington, D.C., 1971.
69. NAS. Drinking Water and Health, National Academy of Sciences, Washington, D.C., 1977.
70. U.S. Bureau of Mines. Minerals in the U.S. Economy. Washington, D.C., 1975.
71. EPA. Quality Criteria for Water. US Environmental Protection Agency, Washington, D.C., 1976.
72. Bolton, N. E., Van Hook, R. I., Fullkerson, W., Lyon, W. S., Andren, A. W., Carter, J. A., and Emery, J. F. Trace element measurements at the coal-fired Aller steam plant. Progress Report June 1971-January 1973. Oak Ridge National Laboratory Report ORNL-NSF-EP-43, US Atomic Energy Commission, Oak Ridge, Tenn., 1973.
73. Crecelius, E. A., Bothner, M. H., and Carpenter, R. Geochemistries of arsenic, antimony, mercury and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9: 326 (1975).
74. Sollins, L. V. Arsenic and water pollution hazard. Science 170: 871 (1970).
75. Patterson, E. S. Arsenic and water pollution hazard. Science 170: 870 (1970).
76. Wood, J. M. Biological cycles for toxic elements in the environment. Science 183: 1049 (1978).
77. Cox, D. P. Microbiological methylation of arsenic. In: Arsenical Pesticides, (American Chemical Society Symp. Ser. No. 7) E. A. Woolson, Ed., American Chemical Society, Washington, D.C., 1975, pp. 81-90.
78. Sandberg, G. R., and Allen, I. K. A proposed arsenic cycle in an agronomic ecosystem. In: Arsenical Pesticides (American Chemical Society Symp. Ser. No. 7, 7) E. A. Woolson, Ed., American Chemical Society, Washington, D.C., 1975, pp. 124-147.
79. Frost, D. V. Arsenicals in biology-retrospect and prospect. Fed. Proc. 26: 194 (1967).
80. Braman, R. S. Arsenic in the Environment. In: Arsenical
Pesticides (American Chemical Society Symp. Ser. No. 7), E. A. Woolson, Ed., American Chemical Society, Washington, D.C., 1975.

81. Drury, J. S., Shriner, C. R., Lewis, E. B., Towill, L. E. and Hammons, A. S. Reviews on the Environmental Effects of Pollutants: VI. Beryllium. ORNL/EIS-87, EPA-600/1-78-026, Oak Ridge National Laboratory, Oak Ridge, Tenn. Nov. 1978.

82. Heindl, R. A. Beryllium. In: Mineral Facts and Problems. U.S. Bureau of Mines, Bulletin 650. U.S. Govt. Printing Office, Washington, D.C., 1970, pp. 489-501.

83. Ruch, R. R., Gluskoter, H. J., and Shimp, M. F. Occurrence and distribution of potentially volatile trace elements in coal: a final report. Environ. Geol. Notes, Illinois State Geol. Survey 72, 1974.

84. Gluskoter, H. J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B. and Kuhn. J. K. Trace elements in coal: occurrence and distribution. Illinois State Geological Survey, Circular 499, 1977.

85. Bowen, H. J. M. Trace Elements in Biochemistry. Academic Press, New York, 1966, pp. 176-177.

86. US Environmental Protection Agency. National Inventory of Sources and Emissions: Beryllium-1968. EPA Report No. APTD-1508, Office of Air and Water Programs, Research Triangle Park, N.C., 1971.

87. Phillips, M. A. Investigations into levels of both airborne beryllium and beryllium in coal at the Hayden Power Plant near Hayden, Colorado. Environ. Lett. 5: 183 (1973).

88. Zubovic, P. Proceedings of Beryllium Conference, Cambridge, Mass. Massachusetts Institute of Technology, Cambridge, Mass., 1969.

89. Tepper, L. B. Beryllium. CRC Crit. Rev. Toxicology 1: 235 (1972).

90. US Environmental Protection Agency. Control techniques for beryllium air pollutants. EPA Report AP-116, U.S. Govt. Printing Office, Washington, D.C., 1973.

91. Griggs, K. Toxic metal fumes from mantle-type camp lanterns. Science 181: 842 (1973).

92. NIOSH. Occupational exposure to beryllium. Rept. TR-005-72, National Institute for Occupational Safety and Health, Rockville, Md., 1972.

93. Kopp, J. F., and Kroner, R. C. Trace metals in waters of the United States. U.S. Federal Water Pollution Control Administration, Cincinnati, Ohio, 1968, pp. 8, 14, 22.

94. Ottinger, R. S., Blumenthal, J. L., Dalporto, D. F., Gruber, G. I., Santy, M. J., and Shih, C. C. Recommended methods for reduction, neutralization, recovery or disposal of hazardous wastes. Vol. XII. EPA Rept. No. EPA-670/2-3-063-1, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1973, pp. 244-268.

95. Bohn, H. L. Soil absorption of air pollutants, J. Environ. Qual. 1: 372 (1972).

96. Schroeder, H. A. The Poisons Around Us. Toxic Metals in Food, Air and Water. Indiana University Press, Bloomington, Ind., 1974, p. 30.

97. Merrill, J. R., Lyden, E. F. X., Honda, M., and Arnold, J. R. The sedimentary geochemistry of the beryllium isotopes. Geochim. Cosmochim. Acts 18: 108 (1960).

98. Reeves, A. L. Beryllium in the environment. Clin. Toxicol. 10: 37 (1977).

99. Meehan, W. R., and Smythe, L. E. Beryllium as a trace element in environmental materials. Environ. Sci. Technol. 1:PA-199-79-028, Oak Ridge National Laboratory, Oak Ridge, Tenn., Nov. 1978.

100. Zorn, H., and Diem, H. Significance of beryllium and its compounds to the industrial physician. Zentralbl. Arbeitsmed. Arbeitsbesch. 24: 3 (1974).

101. Fowler, B. A. International Conference on Environmental Cadmium: an overview. Environ. Health Perspect. 28: 279 (1979).

102. Yost, K. J. Some aspects of cadmium flow in the U.S. Environ. Health Perspect. 28: 5 (1979).

103. Yamagata, N. Industrial emission of cadmium in Japan. Environ. Health Perspect. 28: 17 (1979).

104. Kjellstrom, T. Exposure and accumulation of cadmium in populations from Japan, the United States, and Sweden. Environ. Health Perspect. 28: 169 (1979).

105. Engel, D. W. and Fowler, B. A. Factors influencing cadmium accumulation and its toxicity to marine organisms. Environ. Health Perspect. 28: 81 (1979).

106. Frazier, J. M. Bioaccumulation of cadmium in marine organisms. Environ. Health Perspect. 28: 75 (1979).

107. Kneip, T. J. and Hazen, R. E. Deposit and mobility of cadmium in a marsh-cove ecosystem and the relation to cadmium concentration in biota. Environ. Health Perspect. 28: 67 (1979).

108. Gale, N. L. and Wixson, B. G. Cadmium in forest ecosystem around lead smelters in Missouri. Environ. Health Perspect. 28: 23 (1979).

109. Baker, D. E., Amacher, M. C., and Leach, R. M. Sewage sludge as a source of cadmium in soil-plant-animal systems. Environ. Health Perspect. 28: 45 (1979).

110. Bingham, F. T. Bioavailability of Cd to food crops in relation to heavy metal content of sludge amended soil. Environ. Health Perspect. 28: 39 (1979).

111. Sharma, R. P., Street, J. C., Verma, M. P., and Shupe, J. L. Cadmium uptake from seed and its distribution to food products of livestock. Environ. Health Perspect. 28: 59 (1979).

112. Fassett, D. W. Cadmium: Biological effects and occurrence in the environment. Ann. Rev. Pharmacol. 15: 425 (1975).

113. U.S. Environmental Protection Agency. Cadmium Health Effects: Implications for Environmental Regulations. Office of Research and Development, Washington, D.C., 1979.

114. Babich, H., and Stotzky, G. Effects of cadmium on the biota: Influence of environmental factors. Adv. Appl. Microbiol. 23: 55 (1978).

115. Foldesi, J. E. Cadmium bioaccumulation assays. Their relationship to various ionic equilibria in Lake Superior water. Environ. Sci. Technol. 13: 701 (1979).

116. Cooley, T. N., and Martin, D. F. Cadmium in naturally-occurring water hyacinths. Chemosphere 2: 75 (1979).

117. Muskett, C. J., Roberts, L. H., and Page, B. J. Cadmium and lead pollution from secondary metal refinery operations. Sci. Total Environ. 11: 73 (1979).

118. Goeller, H. E., Hise, E. C., and Flora, H. B. Societal flow of zinc and cadmium. In: Cadmium in the Dissipated Element, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1973, pp. 61-134.

119. Davis, W. E. National inventory of sources and emissions, 1964. Cadmium: Report to National Air Pollution Control Admin., Feb., pp. 1-44. Rept BP 192250; NTIS, Springfield, Va. 1970; quoted in Nordberg, G. F. Health hazards of environmental cadmium pollution. Ambio 3: 55 (1974).

120. Nordberg, G. F. Health hazards of environmental cadmium pollution. Ambio 3: 55 (1974).

121. American Metal Market. Metal Statistics, 1977. Fairchild Publishers, New York, 1977.

122. Anon. Sweden bans major uses of cadmium. Environ. Health Lett. 4 (Nov. 1, 1979).

123. U.S. Bureau of Mines, Minerals Yearbook, Vol. 1, Washington, D.C., 1974, p. 439.

124. Morgan, W. D. New ways of measuring cadmium in man. Nature 282: 673 (1979).

125. Friberg, L., Piscator, M., Nordberg, G. F., and Kjellstrom, T. Cadmium in the Environment, 2nd ed., Chemical Rubber Co., Cleveland, Ohio, 1974.
126. Berrow, M. L., and Webber, J. Trace elements in sewage sludges. J. Sci. Food Agr. 23: 93 (1972).
127. Poldoski, J. E., and Glass, G. E. In: Proceedings, International Conference on Heavy Metals in the Environment, Vol. II. T. C. Hutchinson, et al., Eds., Toronto, Canada, 1977, pp. 901-922.
128. Hueck, H. J. Physiological and biochemical aspects of heavy elements in our environment. Proceedings of the Symposium, Utrecht, The Netherlands, May 9, 1974, Delft University Press, Delft, 1975.
129. Van Hook, R. I., Jr., Blaylock, B. G., Bondietti, E. A., Francis, C. W., Huckabee, J. W., Reichel, D. E., Sweeton, F. H., and Witherspoon, J. p. Radiosotope techniques to evaluate the environmental behavior of cadmium. In: Comparative Studies of Food and Environmental Contamination, Proceedings of a Symposium, Oatneimi, Finland, 27-31 August, 1973. Int. Atomic Energy Agency, Vienna, 1974.
130. Huey, C. W., Brinkman, F. E., Iverson, W. P., and Grim, S. O., Abstr. Int. Conf. Heavy Metals Environ. 1975, Paper C-214 (1975).
131. NAS. Chromium. National Academy of Sciences, Washington, D.C., 1974.
132. NIOSH. Occupational exposure to chromium (VI). National Institute of Occupational Safety and Health, Washington, D.C., 1975.
133. IARC. Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. Vol. 2. Some Inorganic and Organometallic Compounds. International Agency for Research on Cancer, Lyon, 1973, pp. 100-125.
134. Langard, S., and Norseth, T. Chromium. In: Handbook on the Toxicology of Metals, L. Friberg, G. F. Nordberg, and V. B. Vouk, Eds., Elsevier/North-Holland, Biomedical Press, Amsterdam, 1979.
135. Norseth, T. Health effects of nickel and chromium. In: Trace Metals. Exposure and Health Effects, E. DiFerrante, Ed., Pergamon Press, New York, 1979.
136. Langard, S. Chromium. In: Metals in the Environment, H. A. Waldrom, Ed., Academic Press, New York-London, 1979.
137. EPA/ORNL. Reviews of the Environmental Effects of Pollutants: III. Chromium. Environmental Protection Agency, Oak Ridge National Laboratory, National Technical Information Service, Springfield, Va., 1978.
138. CEC/EOA. Metallic Effluents of Industrial Origin in the Marine Environment. The Commission of the European Communities/European Oceanic Association, London, 1977.
139. Sullivan, R. J. Preliminary air pollution survey and its compounds. A literature review. NAPCA Publication APTD 69-34, National Air Pollution Administration, Raleigh, N.C., 1969.
140. Gemmel, R. P. Revegetation of direct land polluted by a chromate smelter. I. Chemical factors causing substrate toxicity in chromate smelter waste. Environ. Pollut. 5: 181 (1973).
141. SRI. Chemical Economics Handbook. Stanford Research Institute, Menlo Park, Cal., 1971, p. 733.
142. Bowen, H. J. M. Trace Elements in Biochemistry, Academic Press, New York, 1966.
143. Denton, C. R., Keenan, R. G., and Birmingham, D. J. The chromium content of cement and its significance in cement dermatitis. J. Invest. Derm. 25: 189 (1954).
144. Schroder, H. J. Chromium Air Quality (Monograph No. 7-15). American Petroleum Institute, Washington, D.C., 1970.
145. Balgor, D. W. D., Fine particles produced from automotive emissions-control catalysts. Science 180: 1168 (1973).

146. Mertz, W. Chromium occurrence and function in biological systems. Physiol. Revs. 49: 163 (1969).
147. UNEP. Preliminary Report on the State of Pollution of the Mediterranean Sea. IGI/INF4. United Nations Environmental Programme, Geneva, Switzerland.
148. UNEP. Pollutants from Land-Based Sources in the Mediterranean. IGI/INF5. United National Environmental Programme, Geneva, Switzerland, 1977.
149. NATO. Disposal of Hazardous Wastes, Manual on Hazardous Substances in Special Waters. No. 55. Federal Environment Agency on behalf of Federal Ministry of Interior, North Atlantic Treaty Organization, West Berlin, Germany, 1976.
150. Sitting, M. Chromium. In: Pollution Detection and Monitoring Handbook. Noel Data Corp., Park Ridge, N.J., 1974, pp. 102-109.
151. Anderson, J. S., and Lobst, E. H., Jr. Case History of wastewater treatment in a General Electric Appliance Plant. J. Water Pollut. Control Fed. 10: 1758 (1968).
152. Frank, R., Brown, H. E., Holdrieneb, M., and Stonefield, K. I. Metal content and insecticide residues in tobacco soils and cured tobacco leaves in Southern Ontario. Tob. Sci. 21: 79 (1977).
153. NAS. Nickel. National Academy of Sciences, Washington, D.C., 1975.
154. NIOSH. Criteria for a Recommended Standard. Occupational Exposure to Inorganic Nickel, National Institute for Occupational Safety and Health, US Govt. Printing Office, Washington, DC (1977).
155. IARC. Some Inorganic and Organometallic Compounds, (Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol. 2), International Agency for Research on Cancer, Lyon, 1973, pp. 126-149.
156. EPA. Scientific and Technical Assessment Report on Nickel. U.S. Environmental Protection Agency, Washington, D.C., 1975.
157. Norseth, T., and Piscator, M. Nickel. In: Handbook on the Toxicology of Metals, L. Friberg, G. F. Nordberg, and V. B. Vouk, Eds., Elsevier/North-Holland Biomedical Press, Amsterdam, 1979.
158. Reno, H. T. Nickel. In: Minerals Yearbook 1972. Vol. 1, Metals, Minerals and Fuels, U.S. Govt. Printing Office, Washington, D.C., 1974, pp. 871-879.
159. NASN. Air Quality Data from the National Air Surveillance Networks and Contributing State and Local Networks. 1966 Publ. No. APTD 68-9. National Air Pollution Control Admin., Durham, N.C., 1968, p. 157.
160. Kneip, T. Jr., Eisenbud, M., Strehlow, C. D., and Freudental, P. C., Airborne particulates in New York City. J. Air Pollut. Control Assoc. 20: 144 (1970).
161. Schroeder, H. A. A sensible look at air pollution. Arch. Environ. Health 21: 798 (1970).
162. Kopp, J. F., and Kroner, R. C. Trace Metals in Waters in the United States, A Five Year Summary of Trace Metals in Rivers and Lakes of the United States, Oct. 1, 1962-Sept. 30, 1967. Federal Water Pollution Control Admin., Cincinnati, Ohio, 1970.
163. Tiffin, L. O. Translocation of nickel in zylem exudate of plants. Plant Physiol. 48: 273-277 (1971).
164. Sunderman, F. W., Jr. The current status of nickel carcinogenesis. Am. Clin. Lab. Sci. 3: 156 (1973).
165. Sunderman, F. W., and Sunderman, F. W., Jr., Implication of nickel as a pulmonary carcinogen in tobacco smoke. Am. Clin. Lab. Sci. 35, 203 (1961).
166. Sladkowski, D., Schultz, H., Schaller, K. H., and Lehnert, G., Zur onkologischen Bedeutung des schwermetall Gehaltes von Zigarren. Arch. Hyg. 158: 1 (1969).