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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 contaid 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.,

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*Department of Health, Education and Welfare, Food and Drug Administration, National Center for Toxicological Research, Jefferson, Arkansas 72079.

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 Lantzy 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 uneffective 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

Table 1. Annual air emissions of environmentally important metals from stationary sources.[a]

	Pollutants, tons/year		
Metal	1969-1971 Average	1978 Projection	1983 Projection
As	9,000	12,750	16,990
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	58,370
Zn	151,000	216,700	273,000

[a] 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 lithophilic metals such as Fe and Mn, interference factors are found to be small, while the atmophilic 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 10^8 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 × 10^{12} 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*).

Table 2. Percent of total air emissions of some environmentally important metals from stationary sources.[a]

Metal, %	Smelter/ metalurgical processing, %	Coal combustion, %	Oil combustion, %	Incineration, %
Be	3	88	6	—
Cd	43	—	—	52
Cr	68	9	—	—
Cu	84	7	—	—
Mn	57	11	—	—
Ni	11	—	83	—
Pb	2	—	—	1
Ti	—	9	—	—
V	1	—	90	—

[a] Data of Lee and Duffield (*12*).

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

Table 3. Natural and anthropogenic sources of atmosphere emissions.[a]

Element	Flux, %/yr						Atmosphere interference factor, %[b]
	Continental dust flux	Volcanic dust flux	Volcanic gas flux	Industrial particulate emissions	Fossil fuel flux	Total emissions (industrial + fossil fuel)	
Al	356,500	132,750	8.4	40,000	32,000	72,000	15
Ti	23,000	12,000	–	3,600	1,600	5,200	15
Sm	32	9	–	7	5	12	29
Fe	190,000	87,750	3.7	75,000	32,000	107,000	39
Mn	4,250	1,800	2.1	3,000	160	3,160	52
Co	40	30	0.04	24	20	44	63
Cr	500	84	0.005	650	290	940	161
V	500	150	0.05	1,000	1,100	2,100	323
Ni	200	83	0.0009	600	380	980	346
Sn	50	2.4	0.005	400	30	430	821
Cu	100	93	0.012	2,200	430	2,630	1,363
Cd	2.5	0.4	0.001	40	15	55	1,897
Zn	250	108	0.014	7,000	1,400	8,400	2,346
As	25	3	0.1	620	160	780	2,786
Se	3	1	0.13	50	90	140	3,390
Sb	9.5	0.3	0.013	200	180	380	3,878
Mo	10	1.4	0.02	100	410	510	4,474
Ag	0.5	0.1	0.0006	40	10	50	8,333
Hg	0.3	0.1	0.001	50	60	110	27,500
Pb	50	8.7	0.012	16,000	4,300	20,300	34,583

[a] Data of Lantzy and MacKenzie (*6*).

[a] Interference factor = (total emissions/continental + volcanic fluxes) × 100.

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 cropland 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 10^5) 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*). A particularly

Table 4. Concentrations of trace metals in various materials.[a]

Element	Metal concn, ppm				Urban particulates, ng/m^3
	Soils	Andesites	Oil	Coal	
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	25	50
Ni	40	55	10	15	30
Sn	10	1.6	0.01	1	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	5	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*).

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

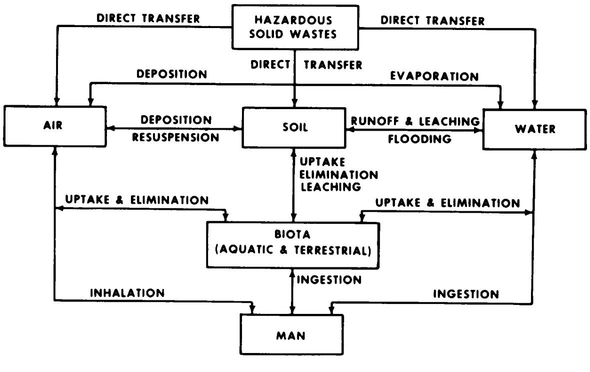

FIGURE 1. Major physical and biological transport pathways of hazardous chemicals derived from solid waste disposal. Data of Van Hook (*10*).

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

	Biological concentration factor[b]				
	As	Cd	Hg	Pb	Zn
Aquatic					
Water	1	1	1	1	1
Plants	170	1000	1000	200	1000
Invertebrates	330	2000	100,000	100	10,000
Fish	330	200	1000	300	1000
Terrestrial					
Soil	1	1	1	1	1
Plants	0.01	0.3	0.4	0.07	0.4
Invertebrates	0.01	17		0.02	8
Mammals	0.001	0.008	5	0.001	0.6
Birds	0.001		50	0.001	

[a] Data of Van Hook (*10*).

[b] Ratio of concentration in organism to concentration in substrate.

(*59*). Other recent relevant publications with focus as above include: the National Academy of Sciences report on arsenic (*60*); environmental mobility of arsenic (*61*); effects of microcosm size and substrate type on aquatic microcosm behavior and arsenic transport (*62*); cycle in natural waters (*63*); distribution and speciation of arsenic in natural waters and marine algae (*64*); biosynthesis and release of organoarsenic compounds by marine algae (*65*); accumulation of arsenic in sediments of lakes treated with sodium arsenite (*66*); and As in marine and aquatic environments (*67*).

Arsenic and its compounds are ubiquitous in nature and exhibit both metallic and nonmetallic properties. The trivalent and pentavalent cations are the most common oxidation states, although elemental arsenic also occurs. Although arsenic ranks 20th among the elements in abundance 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 arsenious 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 residues 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 30×10^6 kg/year (*63*). Arsenate in both fresh and salt water is metabolized to methylated compounds; mono-, di-, and trimethylarsenicals 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 metal ores, 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 arsonate (MSMA), disodium methane arsonate (DMSA), and cacodylic acid] and four feed additives that are substituted phenyl arsonic 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 As_2O_3 which was about 32,000 tons in 1974 and the world

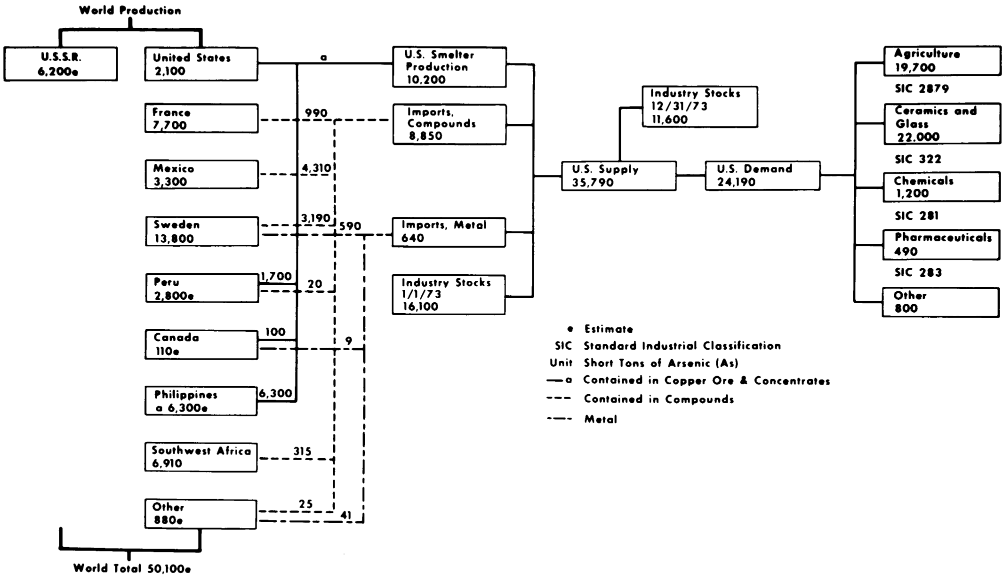

FIGURE 2. Arsenic supply-demand relationship (*60,70*).

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

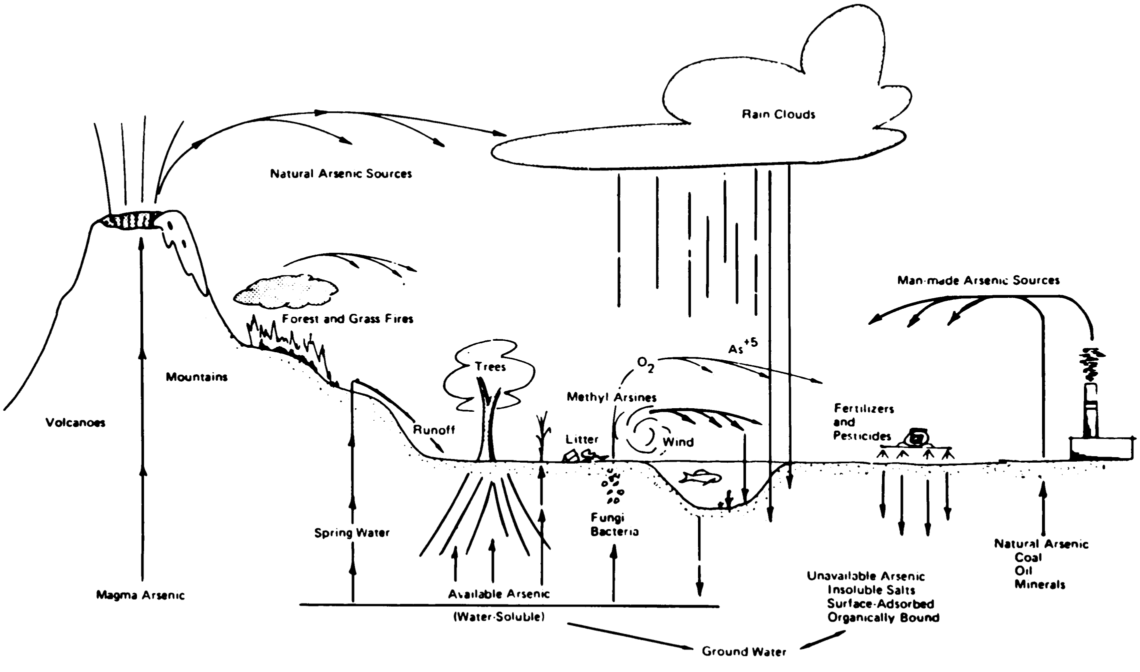

FIGURE 3. Environmental transfer of arsenic (*60*).

fuels, 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 As_2O_3/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 acetoarsenite, 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 As_2O_3 (*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 methyla-

Table 6. Summary of U.S. arsenic flow, dissipation, and emission, 1974.[a]

Location of arsenic	Arsenic flow, tons[b]	Ready environmental transport
End products	26,438	
Steel	17,089	No
Cast iron	3,638	No
Other	5,711	No
Dissipation	63,030	
Steel slag	39,690	Unknown
Pesticides	11,565	Yes
Copper leach liquor	9,702	Yes
Other	2,073	Yes
Airborne emission	9,757	
Losses from copper-smelting	5,292	Yes
Pesticides	2,536	Yes
Coal	717	Yes
Other	1,212	Yes
Waterborne effluent	165	
Phosphate detergents	121	Yes
Other	44	Yes
Landfill wastes	19,691	
Copper flue dusts	10,584	No
Copper-smelting slag	3,748	No
Coal fly ash	1,984	No
Other	3,375	No

[a] NAS data (*60*).

[b] To convert to 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*), Brinckman 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. Arsencials 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_3AsO_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_2O_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_{12} occurs in anaerobic ecosystems. The volatile species arsine, 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 arsonic 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/soil-water-biota-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 trimethylstilbene 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 beryllijm disilicate). The main beryllijm 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 1968 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 particulates 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, $3BeOAl_2O_3 \cdot 6SiO_2$) (*88*,*89*).

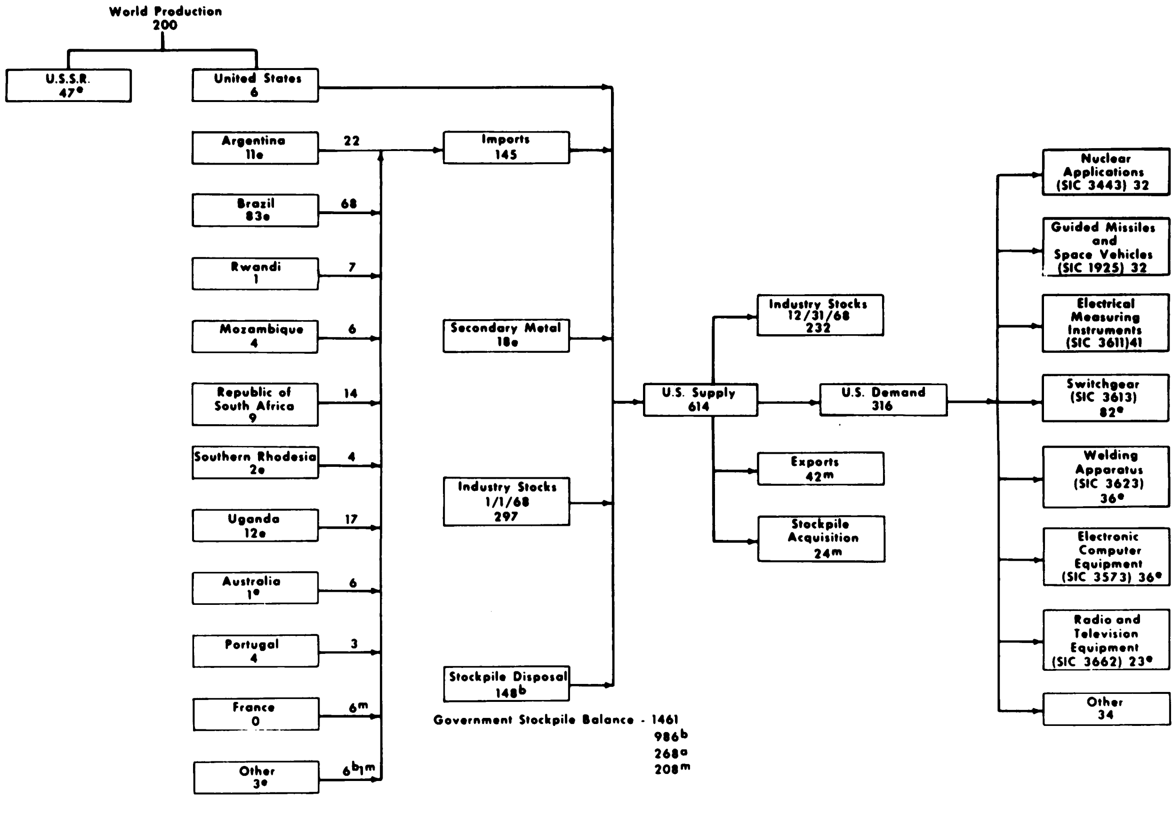

FIGURE 4. Supply-demand relationships for beryllium, 1968. Values are in metric tons of beryllium. e = estimate; a = Be-Cu master alloy; m = metal; SIC = Standard Industrial Classification. Adapted from Heindl (*82*).

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; $(NH_4)_2BeF_4$ 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 $\mu g/m^3$ (*90*). Beryllium fabrication results in the atmospheric release of 4.5 kg of Be for every 907 metric tons (1000 tons) 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 μg 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 (*81,82,85*). 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 6×10^{-7} ppm (*85*). Finished U.S. waters average about 2×10^{-4} ppm and range from 1×10^{-5} to 1.2×10^{-3} ppm (*81,93*). (The recommended provisional limit for Be in water is 1 ppm) (*81*). Unpolluted air contains less than 0.0001 $\mu g/m^3$ 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 $\mu g/m^3$. 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 $\mu g/m^3$ 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 accmumlations 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 (*103*). 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

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

Process	Cd flow, Mt/10 yr			
	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-sludge incineration	404	5595	167	95
Sewage treatment	–	1010	735	–
Total	745	58103	1316	2266

[a] Includes all land disposed sludge. Data of Yost (*102*).

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/sludge 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 7.37×10^4 kg of cadmium passes through coal-fired power generating plants annually (*102*) based on the use of 3.51×10^{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/m^3, but may be as high as 5 μg/m^3 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/m^3, 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 coniderable 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 (*101,109,110*).

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 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 ^{109}Cd 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 [$Cd(H_2O)_x{}^{2+}$ 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^{+2} 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, $FeOCr_2O_3$ 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 6.3×10^6 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 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, lineoleum, 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 anticorrosive 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/m^3 while that in the ambient air of large industrial cities of the U.S. usually ranges from 0.01 to 0.03 μ/m^3 (*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/m^3. These concentrations were reduced by fly ash collection to 0.19-6.6 ppm and 0.018-0.5 mg/m^3 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 ($>10^6$ metal-containing condensation nuclei/cm^3) 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.

In rivers, concentration of Cr ranges between 1 and 10 ppb (*131*). It has been estimated that 6.7 × 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 (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) 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 (*153*), 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 (*153*).

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 33.8-37.8; 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 $\mu g/m^3$ (*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 (*139*). 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 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/ft^2 in commercial areas, 0.23 mg/ft^2 in residential areas, and 1.25 mg/ft^2 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.

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