Lead, Mercury, Cadmium and Arsenic in the Environment
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CHAPTER 17

Global Cycling of Arsenic

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ABSTRACT

In recent years, tentative estimates of arsenic fluxes among land, oceans, rivers, sediments and the atmosphere have highlighted the problems of obtaining a mass balance for arsenic on a global basis. Arsenic is mobilized by both natural and anthropogenic processes and these should be identified and located before quantification can be carried out. Much of the early data on arsenic concentrations and emission factors is outdated with regard to existing environmental control strategies and analytical techniques. Emission data for volcanoes can vary by more than two orders of magnitude, and the quantification of the natural low temperature volatilization of organo-arsenic compounds from soils is especially difficult.

In this study, current information on anthropogenic emission factors, including those for coal combustion, copper smelting and pesticide use, has been applied to present-day production data. Volcanic emissions have been updated and experimental data on the biological conversion of arsenate in soils have been used to estimate the extent to which methylated arsenic compounds contribute to the ambient atmospheric arsenic concentration.

The estimated ratio of natural to anthropogenic atmospheric inputs is 60:40. Copper smelting accounts for 40% of the anthropogenic input, while other non-ferrous metal production, coal combustion, agricultural chemicals and agricultural burning also emit significant amounts of arsenic. Low temperature volatilization and volcanism accounted for 97% of natural emissions. Atmospheric inputs were balanced with the calculated rain-out flux, while the net oceanic flux showed a small positive balance.

In this study, the uncertainties associated with published data have been noted and an attempt made at providing a more realistic basis for estimating present and future arsenic fluxes in the environment.

INTRODUCTION

In recent years, considerable attention has been directed towards the compilation of global inventories for natural and anthropogenic emissions of arsenic to the atmosphere (Lantzy and Mackenzie, 1979; Mackenzie *et al.*, 1979; NAS, 1977; Walsh *et al.*, 1979a). In some studies, important emission sources have not been adequately assessed and, in general, emission factors for industrial sources have not taken into account many of the variations in the world situation, including differences in source concentrations, industrial processes and environmental control strategies.

A previous study on global atmospheric fluxes of arsenic showed a gross imbalance which was attributed to biological volatilization of arsenic from the ocean surface to the atmosphere (Table 17.1) (Lantzy and Mackenzie, 1979). However, an examination of arsenic concentrations and speciation in sea water and atmospheric precipitation showed that this assumption was incorrect and that the tropospheric burden had been over-estimated (Andreae, 1980).

Table 17.1 A comparison of global estimates of natural arsenic emissions to the atmosphere (tonnes/year)

Source	Reference 1*	Reference 2†	Present study
Volcanoes	7 000	280	17 150
Low temperature volatilization	160	16 000	26 200
Wind erosion	240	2 500	1 980
Forest fires	160	—	125
Sea spray	28	194 790§	27
Total	7 800‡	213 570	45 480
Overall total (incl. anthropogenic emissions)	31 400	296 470	73 540

* Walsh *et al.*, 1979a.
† Mackenzie *et al.*, 1979.
‡ Also incorporates oceanic gas exchange, direct volatilization from earth's crust and particle emissions from plants.
§ Includes biological volatilization.
— Not determined.

The present study provides emission factors and a source inventory for anthropogenic inputs and indicates the magnitude of natural inputs of arsenic to the atmosphere. In addition, recent measurements of arsenic concentrations in the atmosphere have been applied to provide a rain-out flux. Information regarding anthropogenic inputs to rivers and coastal waters is limited but possible sources of arsenic are discussed as a guideline for future studies. A tentative estimate of the oceanic flux is provided.

The present chapter was prepared as part of an ongoing study to estimate anthropogenic and natural fluxes of arsenic to land, air and sea and to estimate future variations in the arsenic burden of the different environmental compartments. An outline of further research which is required to obtain a complete and accurate global cycle for arsenic is included.

CALCULATIONS OF ARSENIC EMISSIONS FROM ANTHROPOGENIC SOURCES

Copper Smelting

World smelter production for 1982 was 8.35 × 10^6 tonnes (World Bureau of Metal Statistics, 1984). However, this figure incorporated an estimated 300 × 10^3 tonnes of secondary blister produced from scrap. As such, smelter production from primary materials was 8.05 × 10^6 tonnes.

Air An emission factor of 3.9 kg As/tonne of Cu produced was calculated for the Ajo smelter in the USA from production data at 70 per cent of theoretical capacity (MINIMET, 1982) and an estimated emission of 163 tonnes of arsenic per year (Morse *et al.*, 1979). The copper concentrate at the Ajo smelter contains between 700 to 7000 ppm (average ~ 1300) of arsenic whereas the global average was assumed to be 500 ppm (Germani *et al.*, 1981); the emission factor was proportionately reduced to 1.5 kg As/tonne Cu produced. The estimated global emission from primary copper smelting is 12 080 tonnes/year (Table 17.2).

Water An emission factor of 3.5 kg As/tonne of Cu produced was calculated from production and emission data for a copper smelter in Sweden (Lindau, 1977). The estimated global emission in the various waste waters which result from copper smelting is 28 175 tonnes/year (Table 17.3).

Land The amount of arsenic which is disposed of or included in landfill was calculated proportionately from the amount of arsenic dispersed to land in the USA in 1979 (Lowenbach and Schlesinger, 1979), USA production figures for 1979 and world production figures for 1982 (World Bureau of Metal Statistics, 1984). The estimated global arsenic content of slag and sludges dumped on land is 47 290 tonnes/year (Table 17.3).

Copper Refining (Non-thermal)

In 1982 world refined production was 9.55 × 10^6 tonnes (World Bureau of Metal Statistics, 1984). Approximately 90% was produced by non-thermal methods (MINIMET, 1982), while 1.122 × 10^6 tonnes were from secondary production (World Bureau of Metal Statistics, 1984).

Table 17.2 Production and emission factors utilized in the estimation of arsenic emissions to the atmosphere from anthropogenic sources

Source	Global production (tonnes/year)	Emission factor	Total arsenic emission (tonnes/year)
Copper smelting	8.05×10^6	1.5 kg As/tonne Cu produced	12 080
Lead smelting	3.58×10^6	0.4 kg As/tonne Pb produced	1 430
Zinc smelting	1.20×10^6[*]	0.65 kg/As tonne Zn produced	780
Steel production	645×10^6	0.091 gm As/tonne steel produced	60
Coal combustion	$3\,696 \times 10^6$	0.5, 1.0 and 2.0 gm As/tonne coal (dependent on use and control device)	6 240
Wood fuel	850×10^6	0.5 μg As/gm wood	425
Clearance of tropical forests	$3\,200 \times 10^6$	0.5 μg/gm vegetation	1 600
Clearance of woodland and savannah	640×10^6	0.5 μg/gm vegetation	320
Burning of pasture land	$2\,000 \times 10^6$	0.5 μg As/gm vegetation	1 000
Herbicides	8 000[†]	430 kg As/tonne As applied	3 440
Wood preservatives	150[†] (1976) 16 000[†] (1982)	100% released during burning of wood	150
Glass manufacture	4 000[†]	117 kg As/tonne As used	467
Waste incineration	150×10^6	0.52 gm As/tonne As waste	78

[*] Pyrometallurgical processes.

[†] Arsenic used.

Table 17.3 Estimated inputs of arsenic to land and water from anthropogenic sources

Source	Inputs to land (tonnes/year)	Inputs to water (tonnes/year)
Copper smelting	47 290	28 175
Copper refining	10 580	230
Lead smelting	3 580	NS
Zinc production	6 050	NS
Steel production	5 850	NS
Coal combustion	35 100	–
Herbicides	4 560	–
Desiccants	12 000	–
Waste incineration	–	–
Fertilizer application	–	–
Sludge application	–	–
Municipal waste water	–	–
Dumping of industrial wastes to sea	–	–

– Not determined.
NS = not significant.

Air Emissions were regarded as relatively insignificant, though local problems have been reported as a result of such As emissions.

Water An emission factor of 0.03 kg As/tonne of Cu produced (USEPA, 1976a) gives a global emission of 230 tonnes/year (Table 17.3).

Land The amount of arsenic which is landfilled was calculated proportionately from the amount of arsenic dispersed to land in the USA in 1979 (Lowenbach and Schlesinger, 1979), US non-thermal production of copper from primary materials in 1979 ($\sim 10^6$ tonnes) and world production figures for 1982 (MINIMET, 1982; World Bureau of Metal Statistics, 1984). The estimated global arsenic content of residues dumped on land is 10 580 tonnes/year (Table 17.3).

Lead Smelting

World production for 1982 was 3.578×10^6 tonnes (World Bureau of Metal Statistics 1984).

Air An emission factor of 0.4 kg/tonne of Pb produced (USEPA, 1976b) gives a global emission of 1430 tonnes/year (Table 17.2).

Land The amount of arsenic which is landfilled was calculated proportionately from the amount of arsenic dispersed to land in the USA in 1974, excluding residues entering the lead industry from electrolytic zinc production (Lowenbach and Schlesinger, 1979) and world production data for 1982 (World Bureau of Metal Statistics, 1984). The estimated global arsenic content of residues dumped on land is 3580 tonnes/year (Table 17.3).

Zinc Production

World production for 1982 was 6.51×10^6 tonnes (World Bureau of Metal Statistics, 1984) of which approximately 18% was produced by pyrometallurgical processes (International Lead and Zinc Study Group, 1983).

Air An emission factor of 0.65 kg/tonne of Zn produced gives a global emission of 780 tonnes/year (Table 17.2).

Land The total arsenic content of zinc ore smelted, less the amount of arsenic emitted to the atmosphere, was used to calculate the amount of arsenic dispersed to land as slag from smelters. Using an arsenic concentration of 1.05 gm/kg (USEPA, 1976a), approximately 586 tonnes/year are landfilled. Almost all of the arsenic present in residues from electrolytic refining is transferred to lead smelters where the ultimate fate is landfill. An emission factor of 1.05 kg/tonne (USEPA, 1976a) gives a total arsenic content for slag dispersed to land of 5466 tonnes/year. This gives a total to land of 6050 tonnes/year (Table 17.3).

Steel Production

In 1982 world steel production was 645×10^6 tonnes (International Iron and Steel Institute, 1984).

Air An emission factor of 0.091 gm/tonne of steel produced (USEPA, 1976a) gives a global arsenic emission of 60 tonnes/year (Table 17.2).

Land An emission factor of 9.1 gm/tonne of steel produced (USEPA, 1976a) gives the global amount of arsenic disposed to land as 5850 tonnes/year (Table 17.3).

Coal Combustion

Air Coal consumption was considered under five separate sections: electricity generation, metallurgical coal, other industrial consumption, retail use and coal conversion (Predicasts, 1982). The first three groups were categorized by country into those users which have good, moderate or poor emission control strategies. Assuming an average arsenic concentration of

15 gm/tonne of coal (Goetz *et al.*, 1981; Chadwick and Lindman, 1982) and removal efficiencies of 97% for electostatic precipitators, 95% for Venturi scrubbers and 80% for mechanical cyclone collectors (Table 17.4) (Klein *et al.*, 1975; Schwitzgebel *et al.*, 1975; Lowenbach and Schlesinger, 1979; Ondov *et al.*, 1979a,b; DOE, 1980; Sabbioni and Goetz, 1983; Elseewi *et al.* 1984), emission factors of 0.5, 1.0 and 2.0 gm/tonne were applied for the three groups of countries. Emission factors from electricity generation, metallurgical coal (coke production and use) and other industrial usage were considered to be the same. An emission factor of 2.0 gm/tonne was applied to residential/commercial consumption. Atmospheric emissions from coal conversion are not significant (Filby *et al.*, 1981). Total global estimates were 2410, 750, 1980 and 1100 tonnes/year for electricity generation, metallurgical coal, industrial use and retail use, respectively, giving a total atmospheric emission of 6240 tonnes (Table 17.2).

Table 17.4 A comparison of atmospheric emission factors for arsenic from coal combustion

Emission factor (gm As/gm As in coal)	Control device*	Reference
0.18	GA	DOE, 1980
0.01†	ESP	Elseewi *et al.*, 1984
0.01†	VS	Elseewi *et al.*, 1984
0.20†	CC	Elseewi *et al.*, 1984
0.03	ESP	Klein *et al.*, 1975
0.03	–	Lindau, 1977
0.25	–	Lowenbach and Schlesinger, 1979
0.01	ESP (99.8)‡	Ondov *et al.*, 1979a,b
0.12	ESP (97.0)‡	Ondov *et al.*, 1979a,b
0.02	–	Pacyna, 1984
0.03	ESP (99.5)‡	Sabbioni and Goetz, 1983
0.01	ESP	Schwitzgebel *et al.*, 1975
0.08	VS	Schwitzgebel *et al.*, 1975
0.21	CC	Schwitzgebel *et al.*, 1975

* GA—grit arrester; ESP—electrostatic precipitator; VS—Venturi scrubber; CC—cyclone collector.

† Based on fly ash removal efficiencies.

‡ Fly ash removal efficiencies (%).

Land Information is sparse regarding water-borne wastes from power plants and metallurgical industries, particularly those from control devices (e.g. wet scrubbers). It was assumed that contained arsenic was disposed to land, thereby giving an emission of (2.34×10^9 tonnes/year × 15 μg/gm) − 6240 tonnes = 35 100 tonnes/year to land (Table 17.3).

Wood Fuel

The consumption of wood fuel is estimated to be 850 × 10^6 tonnes/year (Logan et al., 1981). The emission factor is assumed to be the mean concentration of arsenic in vegetation, 0.5 μg/gm (NRCC, 1978). The same emission factor is used for tropical forests, grassland, woodland and savannah. The estimated global emission from fuel wood is 425 tonnes/year (Table 17.2).

Clearance of Land for Crops

Tropical forests An estimated 3200 × 10^6 tonnes of vegetation are burnt for agricultural purposes each year (Logan *et al.*, 1981). The estimated global emission is 1600 tonnes/year (Table 17.2).

Woodland and savannah An estimated 640 × 10^6 tonnes of vegetation are burnt for agricultural purposes each year (Logan *et al.*, 1981). The estimated global emission is 320 tonnes/year (Table 17.2).

Burning of pasture land In some parts of the world, the burning of savannah to maintain grassland for grazing involves large areas of land. An estimated 2000 × 10^6 tonnes/year are burnt (Logan *et al.*, 1981). The estimated global emission is 1000 tonnes/year (Table 17.2).

Arsenic Chemicals

World production and sales of refined arsenic trioxide are estimated to be approximately 50 000 tonnes/year (Metal Bulletin Ltd., 1977). Since 1976, wood treatment has increased from 7% to 33% of the market, while cotton desiccants (25%), herbicides (17%) and food additives (10%) utilize large amounts (Woolson, 1983). Alloys and glass utilize about 5% each and 5% is used in miscellaneous chemicals (Metal Bulletin, Ltd., 1977).

Herbicides An estimated 8000 tonnes of arsenic are used each year. An emission factor of 170 kg/tonne As applied has been reported (Lowenbach and Schlesinger, 1979), while an average of 260 kg/tonne As applied is volatilized per year. The total non-accumulative emission factor is 430 kg/tonne. An estimated 3440 tonnes of arsenic are emitted from herbicide application per year (Table 17.2).

Desiccants An estimated 12 000 tonnes of arsenic are used each year but reliable estimates of atmospheric emissions during ginning operations and the proportion of ginning wastes which are incinerated are not available. It is assumed that the majority of waste is dispersed to land (Table 17.3).

Table 17.5 A comparison of global estimates of anthropogenic arsenic emissions to the atmosphere (tonnes/year)

Source	Reference 1[*]	Reference 2[†]	Present study
Non-ferrous metal production	15 200	60 000	14 290
Copper smelting	13 000	–	12 080
Lead smelting	2 200	–	1 430
Zinc smelting		–	780
Iron and steel production	4 200	–	60[‡]
Coal	550	15 800	6 240
Electricity generation	–	–	2 410
Metallurgical use	–	–	750
Other industrial consumption	–	–	1 980
Retail use	–	–	1 100
Coal conversion	–	–	NS
Wood used as fuel	60	–	425
Clearance for crops	–	–	1 920
Tropical forests	–	–	1 600
Woodland and savannah	–	–	320
Burning of pasture land	–	–	1 000
Agricultural burning	60	–	–
Agricultural chemicals	1 920	5 000	3 440
Wood preservatives	–		140
Glass manufacture	–	–	468
Cement production	–	2 100	–
Waste incineration	430	–	78
Total	23 600[§]	82 900	28 060[¶]

[*] Walsh *et al.*, 1979a.
[†] Mackenzie *et al.*, 1979.
[‡] Steel production only.
[§] Includes emissions from the combustion of light and residual fuels, mining mineral ore and arsenic chemicals.
[¶] An additional 2,000–3,000 tonnes could come from cement manufacture and agricultural burning.
– Not determined.
NS = Not significant.

Wood preservatives Although 16 000 tonnes/year of arsenic are used, the emissions from this source are low at present but could increase in the future as old treated timber is disposed of, usually by burning. Treatment of timbers from power plant cooling towers represented only 0.3% of the arsenic fungicide used in 1976 but this would represent an emission, if burnt, of 150 tonnes (DOE, 1980) (Table 17.2).

Glass manufacture An estimated 4000 tonnes As/year are used. An emission factor of 117 kg As/tonne of As used gives a global emission of 468 tonnes/year (USEPA, 1976a) (Table 17.2).

Waste Incineration

The global mass of waste material which is incinerated is approximately 150 × 10^6 tonnes (Nriagu and Davidson, 1980). An emission factor of 0.52 gm/tonne (Pacyna, 1984) gives a total emission of 78 tonnes/year (Table 17.1).

Summary

Table 17.5 compares the results of the present study with previous source inventories for anthropogenic sources.

CALCULATIONS OF ARSENIC EMISSIONS FROM NATURAL SOURCES

Sea-salt Spray

The total production of sea-salt particles was estimated to be 500 × 10^6 tonnes/year (Peterson and Junge, 1971). The arsenic concentration in sea water at the surface is approximately 1.6 μg/litre (Burton and Statham, 1982), while the salt content is approximately 3%. An emission factor of 0.053 μg As/gm sea-salt was derived to give a global emission of 26.5 tonnes/year (Table 17.6).

Table 17.6 Production and emission factors utilized in the estimation of arsenic emissions to the atmosphere from natural sources

Source	Global production (tonnes/year)	Emission factor	Total arsenic emission (tonnes/year)
Sea-salt spray	500 × 10^6	0.053 μg As/gm sea-salt	26.5
Wind erosion	330 × 10^6	6 mg As/kg soil	1 980
Forest fires	250 × 10^6	5 μg As/gm vegetation	125
Volcanoes	25 × 10^6	686 gm As/tonne ash	17 150
Low temperature volatilization	Land area = 59 × 10^{12} m^2	0.044 μg/cm^2/year	26 200

Wind Erosion

Wind erosion contributes 330 × 10^6 tonnes of particulates to the atmosphere per year (Junge, 1979). Because soils cover most of the land surface, an emission factor equivalent to an average soil concentration of 6 mg/kg was used. This gives a global emission of 1980 tonnes/year (Table 17.6).

Forest Fires

An estimated 250 × 10^6 tonnes of vegetation are burnt in forest fires each year (Logan *et al.*, 1981). The estimated global arsenic emission is 125 tonnes (Table 17.6).

Volcanoes

The total production of $\leq 5\ \mu m$ diameter particles from volcanoes is estimated to be 25 × 10^6 tonnes/year (Peterson and Junge, 1971). The method of Walsh *et al.* (1979a) was applied to data from the Mount Augustine volcano, 1976 eruption (Lepel *et al.*, 1978). The product of the enrichment factor of 618 and an ash concentration of 1.11 $\mu g/gm$ gives an emission factor of 686 $\mu g/gm$. The global arsenic emission from volcanoes was estimated to be 17 150 tonnes/year (Table 17.6).

Low Temperature Volatilization

The methylation and subsequent volatilization of arsenic to the atmosphere from soils is dependent on the presence of organic matter and microbes and the availability of labile arsenic (Woolson, 1983). Certain environmental factors, including water content, temperature and aeration, will also affect arsenic emissions from soils. As such, in estimating the land area to be assessed, soils with low productivities ($<500\ gm/m^2/year$) and high water content were excluded. The area assumed to produce significant quantities of volatile arsenic compounds was 59 × $10^{12}\ m^2$ (Ajtay *et al.*, 1979). Woolson (1977) showed that soils treated with 10 mg/kg ^{74}As–sodium arsenate released 1.0% of the activity after 160 days. It was also demonstrated that approximately 18% of the arsenate applied was extractable after this time. Under natural conditions, only 1% of the arsenic in most soils is labile (NAS, 1977). Assuming an average soil concentration of 5 mg/kg and a diffusion layer of 5 cm depth, an emission factor 0.044 × $10^{-6}\ gm/cm^2/year$ was derived from the above information, giving a total global arsenic emission of 26.2 × 10^3 tonnes/year (Table 17.6).

Summary

Table 17.1 compares the results of the present study with previous source inventories for natural sources.

CALCULATIONS OF ARSENIC RESERVOIRS AND FLUXES

Global Atmospheric Burden

Arsenic concentrations in the atmosphere differ for marine and continental areas and differences have also been noted between the northern and southern hemispheres (Walsh *et al.*, 1979b). It is necessary, therefore, to calculate the arsenic burdens separately for each area of the Earth. To calculate the global atmospheric arsenic burden, the method of Walsh *et al.* (1979b) was slightly modified. The height of the lower troposphere (5 km) was used in the calculation rather than 3.9 km (small particle scale height) and an arsenic concentration of 2.8 ng/m^3 for northern continental air was applied to the calculation of the arsenic burden for continental air in the northern hemisphere (Austin and Millward, 1984) (Table 17.7).

Table 17.7 Estimated global tropospheric burden of arsenic*

	Northern hemisphere		
	Land	Atlantic	Pacific/Indian
Area (m^2)	1.0×10^{14}	4.5×10^{13}	1.1×10^{14}
Regional surface arsenic concentration (ng/m^3)	2.8†	0.16	0.072
Burden (tonnes As)	1400	36	40

	Southern hemisphere	
	Land	Ocean
Area (m^2)	4.8×10^{13}	2.0×10^{14}
Regional surface arsenic concentration (ng/m^3)	1.0	0.018
Burden (tonnes As)	240	18
Northern hemisphere total (tonnes As)	1480	
Southern hemisphere total (tonnes As)	260	
Global tropospheric total (tonnes As)	1740	

* Based on Walsh *et al.*, 1979a.

† Austin and Millward, 1984.

The global burden was estimated to be 1740 tonnes with a partition ratio of 0.85 : 0.15 between the northern and southern hemispheres, thereby demonstrating the high anthropogenic input in the former. In addition, 94 per cent of the atmospheric burden was over land areas, suggesting that major sources are predominantly land-based.

Global Atmospheric Fluxes to Land and Oceans

Table 17.8 shows the atmosphere to land/ocean flux of arsenic calculated by three methods:

Model 1 This assumes that there are 40 rainfalls/year which remove atmospheric particulates (Bruland *et al.*, 1974), which gives a total flux of 69 600 tonnes/year.

Model 2 This utilizes a deposition velocity of 0.5 cm/sec which is equivalent to 0.16×10^6 m/year (Bennett, 1981) and the atmospheric levels shown in Table 17.7. Deposition rates of 0.44 mg/m^2/year (land), 0.025 mg/m^2/year (Atlantic), 0.011 mg/m^2/year (Pacific/Indian) were obtained for the northern hemisphere and 0.16 mg/m^2/year (land) and 0.003 mg/m^2/year (ocean) for the southern hemisphere, which gave a total global flux of 54 600 tonnes/year.

Model 3 This utilizes a washout factor which is the ratio of the rain concentration in μg/litre to the air concentration in μg/m^3. This factor has been estimated to be 355 (Cawse, 1974). When applied to the observed atmospheric concentrations of arsenic (Table 17.7) and rainfall data (Bowen, 1979), the continental flux was estimated to be 73.6×10^3 tonnes/year while that for the oceans was only 6.2×10^3 tonnes/year, giving a total flux of 79 800 tonnes/year.

Net Atmospheric Flux

The estimates shown in Table 17.8 are in close agreement with the estimated influx of arsenic to the atmosphere from the anthropogenic and natural sources (73 540 tonnes/year) illustrated in Tables 17.1 and 17.5.

Global Oceanic Burden and Flux

To estimate the total arsenic burden of the oceans, separate estimates of arsenic in dissolved form, particulates, skeletal particulates, phytomass and animal biomass must be made.

Dissolved The total volume of the oceans is 1.37×10^{21} litres (Mackenzie *et al.*, 1979) and the average arsenic concentration is 1.7 μg/litre (Burton and Statham, 1982), which gives a dissolved arsenic burden of 2.33×10^9 tonnes.

Table 17.8 Information used in the estimation of arsenic fluxes from the atmosphere to land and oceans

	Model 1		Model 2		
	Atmospheric burden (tonnes)	Flux (tonnes/year)	Land area (m^2)	Deposition rate (mg/m^2/year)	Flux (tonnes/year)
Northern Hemisphere	1 480	59 200	2.55×10^{14}		46 400
Land	1 400	56 000	1.00×10^{14}	0.440	44 000
Atlantic Ocean	36	1 400	0.45×10^{14}	0.025	1 100
Pacific/Indian Oceans	40	1 600	1.10×10^{14}	0.011	1 300
Southern Hemisphere	260	10 400	2.48×10^{14}		8 200
Land	240	9 600	0.48×10^{14}	0.160	7 600
Ocean	18	720	2.00×10^{14}	0.003	600
Total flux		69 600			54 600

	Model 3		
	Rainfall (litres/year)	Atmospheric concentration (ng/m^3)	Flux (tonnes/year)
Land	9.9×10^{16}	2.220*	73 600
Ocean	3.47×10^{17}	0.053*	6 200
Total flux			79 800

* Weighted average of concentrations from Table 17.7.

Particulate The mean suspended particulate concentration of the world's oceans is approximately 1 mg/litre and the total volume of the oceans is 1.37 $\times 10^{21}$ litres (Mackenzie *et al.*, 1979). A mean concentration of arsenic in shales and clays of 14.5 μg/gm (Woolson, 1983) was applied to these data to give a particulate arsenic burden of 19.87×10^6 tonnes.

Skeletal particulate An estimate of 16.2×10^3 tonnes of arsenic (Mackenzie *et al.*, 1979) was used.

Phytomass The world's oceans contain about 40×10^9 tonnes of plant material (Duce *et al.*, 1983) with an average arsenic concentration of 4 μg/gm (Boyle and Jonasson, 1973), which gives a phytomass burden of 0.16×10^6 tonnes.

Animal biomass The world's oceans contain 1×10^9 tonnes of animal material (Whittaker and Likens, 1973) with an average arsenic concentration of 3 μg/gm (Fowler, 1977), which gives a total animal arsenic burden of 3000 tonnes.

The total oceanic burden of arsenic is thus 2.35×10^9 tonnes.

Oceanic Influx

The oceanic influx was calculated from the summation of river (dissolved and suspended) inputs and the atmospheric flux.

Dissolved 3.7×10^{16} litres of water enter the ocean from rivers each year (Bowen, 1979). The average arsenic concentration in the world's rivers is 1.7 μg/litre (Boyle and Jonasson, 1973), which gives a total arsenic load of 62.9×10^3 tonnes/year.

Suspended Approximately 8×10^9 tonnes of sediment enter the world's oceans each year (Milliman, 1981). Using the mean arsenic concentration of shales and clays of 14.5 μg/gm (Woolson, 1983), a total arsenic load of 0.116×10^6 tonnes/year was obtained, thereby giving a total river flux of 178.9×10^3 tonnes/year.

Atmosphere The average flux of arsenic from the atmosphere to the oceans is 4310 tonnes/year (average of the fluxes calculated by the three models used previously).

The total influx of arsenic to the oceans is thus 183.2×10^3 tonnes/year.

Oceanic Outflux

The oceanic outflux was calculated from the summation of the amounts of arsenic which are lost as sea-salt spray and the amounts of arsenic precipitated in sediments each year.

Sedimentation Approximately 3.2 × 10^9 tonnes of sediments are deposited each year (Garrels and Mackenzie, 1971). By applying an average arsenic concentration for shales and clays of 14.5 μg/gm (Woolson, 1983), a total deposition rate of 46.4 × 10^3 tonnes/year is obtained.

Sea-salt spray An estimated 26.5 tonnes of arsenic per year is lost from the ocean surface by this process (cf. p. 288).

This gives a total oceanic outflux of 46.4 × 10^3 tonnes/year.

Net Oceanic Flux

The net ocean flux was calculated to be +136.8 × 10^3 tonnes/year. If it is assumed that most of this arsenic has a long retention time in the oceanic surface layer (depth = 300 m) and the area of the oceanic surface layer is 360 × 10^{12} m^2 (volume of surface layer = 1.08 × 10^{17} m^3), then the rate of increase in arsenic concentration in the surface layer would be 1.27 ng/litre/year, which would represent a concentration increase of 0.1% per year (Andreae, 1979).

DISCUSSION

Anthropogenic Emissions

Over 40% of anthropogenic emissions to the atmosphere were accounted for by copper smelting. Other non-ferrous metal industries contributed less than 10%, while coal combustion contributed over 20% with approximately equal amounts coming from electricity generation, industrial consumption and retail use and less than 2% from metallurgical coal. The burning of vegetation for agricultural purposes contributed approximately 10% of the atmospheric burden, while the use of chemicals in agriculture added a similar amount.

Large inputs were expected from non-ferrous metal smelting due to the high arsenic content of concentrates and the high temperatures of stack gases. The removal efficiencies are therefore low, due to the fact that a large proportion of the arsenic is in the vapour phase or is associated with < 1 μm diameter particles (Piver, 1983). It is extremely difficult to calculate arsenic emissions from smelting operations; the extensive range of concentrations found in concentrates results in a range of emission factors (Table 17.9). In the USA, arsenic concentrations in copper concentrates range from 0.003 to 11% (Parker, 1978) but most contain between 0.02 and 0.15%. The average arsenic concentration used in the calculations shown above was based on an estimate of the relative importance of each ore, especially those ores from Canada, Peru and the Philippines which contain large amounts of arsenic

(Parker, 1978; World Bureau of Metal Statistics, 1984). Different emission factors were not applied to smelters on a regional basis because present control technology is not efficient in removing arsenic from copper smelter stack gases (Piver 1983).

Table 17.9 A comparison of atmospheric emission factors for arsenic from copper smelters*

Source (study dates)	Emission factor (kg As/tonne Cu produced)	Reference
Tacoma, Washington (1970–72)	3.2	Crecelius *et al.*, 1975
Tacoma, Washington (1971)	16.8	PSAPCA, 1980
Tacoma, Washington (1971–73)	1.8	PSAPCA, 1974
Tacoma, Washington (1974–76)	8.0	Lowenbach and Schlesinger, 1979
Tacoma, Washington (1980)	5.7	PSAPCA, 1980
Ajo, Arizona (1977)	3.9	Schwitzgebel *et al.*, 1978
USA smelters	1.5 (range 0.01–8.0)	Lowenbach and Schlesinger, 1979
Sweden (1976)	0.6	Lindau, 1977
European smelters	3.0	Pacyna, 1984
World average (1982)	1.5	Present study

* Production data assumed to be 70% of production capacity from MINIMET publications.

The processing of iron ore was not considered because almost all of the arsenic is transferred to the product during primary production (DOE, 1980). In steel production, 90% of the arsenic appears in the steel product, 7% occurs in iron and steel-making slags, 2% in slurries and solid wastes and less than 0.5% is discharged to the atmosphere (DOE, 1980).

In the calculations of arsenic emissions from coal combustion it is necessary to consider emissions on a regional basis. The implementation and use of control devices will vary by region and emission factors will also be dependent on the type of combustion process. For example, in China, 20%, 8%, 47% and 25% of coal consumed is used for electricity production, metallurgical coal, industrial and retail use, respectively, which compares with

81%, 9%, 9% and 1% in the USA (Predicasts 1982). As such, it is relatively more difficult to control arsenic emissions from coal combustion in China.

In this study, an emission factor of 3% was applied to those power plants which had electrostatic precipitators or other high efficiency particulate removal devices. However, it has been shown that as control equipment increases in age, a small reduction in the efficiency of particulate removal may result in a large increase in the amount of arsenic released in stack gases (Ondov *et al.*, 1979a,b). As such, we may have underestimated the amount of arsenic emitted from coal combustion. Information on the implementation of control devices and their operating efficiencies is therefore required.

In the future, arsenic emissions from energy production may increase because of the additional use of synfuel technology (Filby *et al.*, 1981; Ghassemi *et al.*, 1981) and geothermal power (Sabadell and Axtmann, 1975).

The large arsenic emission from the use of arsenic containing chemicals in agriculture is mainly due to poor application procedures but is also due to the initially high rate of volatilization. In addition, there may be considerable emissions from the disposal of cotton ginning wastes.

Future Trends in Anthropogenic Emissions

Copper smelting Long-term forecasts for the production and consumption of copper indicate that for the period 1986–91 an annual rate of growth of 1.1% per annum is expected (International Wrought Copper Council, 1984). With regard to atmospheric arsenic emissions, this is likely to be easily offset by improvements in control technology and the use of copper ores which contain less arsenic. However, with the implementation of control devices, particularly wet scrubbers, large volumes of contaminated water and sludges are produced, thereby shifting the arsenic burden to the aquatic compartment. Severe local aquatic pollution problems could be averted by the installation of adequate removal devices (Bhattacharyya *et al.*, 1979) but, as demonstrated in Sweden during the 1970s, it is probable that the initial result will be to discharge more arsenic to waters (Lindau, 1977). If world demand for arsenic compounds increases at its present rate, then more companies will install equipment to collect and refine the arsenic. However, the present aquatic input of 28 175 tonnes/year from copper smelting (Table 17.3) is likely to increase.

Other non-ferrous metal production The major factor which will affect arsenic emissions from the lead and zinc industries will be the reduction in the use of pyrometallurgical processes and a concomitant increase in the use of electrolytic techniques. As with copper production, this will result in an increase in arsenic emissions to the aquatic environment. The largest source of arsenic-bearing waste in the United Kingdom is the Capper Pass tin smelter (DOE, 1980) which discharges approximately 500 tonnes/year of arsenic to the North Sea (Mance and O'Donnell, 1984) while producing only 15 000 tonnes of tin per annum (Williamson and Fromson, 1982). As more primary tin smelters utilize low grade ore, it is likely that large quantities of arsenic will be emitted to the atmosphere, rivers and coastal waters.

Coal combustion Coal consumption is expected to increase by 3-4% per year until the year 2000 (Chase Manhattan Bank, 1981; IEA, 1982; Predicasts, 1982; Frisch, 1983). However, a considerable proportion of the increased coal utilization will be in new power plants and coal-fired heating systems which will presumably employ control devices. Older power plants may also have control devices installed. The increased utilization of coal is not expected to cause a dramatic increase in the atmospheric burden of arsenic in IEA countries. However, the higher growth rates for coal use in some Eastern European countries that lack adequate control strategies may result in large inputs, particularly from residential use. The development and diffusion of large-scale systems using fluidized bed technology, beginning in the early 1990s, will have some effect, due to a larger particulate load. The environmental impact of the future magnetohydrodynamic (MHD) process should also be investigated.

Arsenic chemicals World demand for arsenic is likely to increase due to the rapid growth of its use in wood preservatives (Woolson, 1983). This will not have an immediate effect on the environment but disposal of treated timber may pose a problem for the future. A major source of arsenic contamination may be the use of desiccants but reliable data do not exist on the fate of these chemicals.

Natural Emissions

This study illustrated the extent to which natural emissions can contribute to the global arsenic cycle. From our preliminary calculations, it appears that at least 60% of atmospheric inputs are derived from natural sources, with nearly 60% of the total natural flux coming from low temperature volatilization from soils and most of the remainder from volcanoes. These emissions can be regarded as minimum amounts due to the fact that it was assumed that (i) only 0.126% of soil arsenic is volatilized per year, and (ii) the volcanic emission was calculated for a year with no large eruptions.

CONCLUSIONS

The present chapter updates and improves our knowledge of global arsenic cycling and indicates areas where additional information is required, particularly for the aquatic compartment. A rapid growth in energy production may well increase arsenic emissions, particularly from geothermal power, synfuel processes and changes in coal combustion technology. At present, the activities of man result in large inputs of arsenic to the environment but anthropogenic inputs are unlikely to influence average concentrations significantly in the major global reservoirs. However, local accumulation of arsenic in the atmosphere, soils, rivers and coastal waters is of some concern, especially from the smelting of ores and the use of arsenical compounds.

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