

Chapter 2: Sources and Deposition of Trace Metals

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2.0 Sources and Deposition of Trace Metals

Trace elements enter the atmosphere via both natural and anthropogenic processes (Fig. 2.1). Natural sources include wind-blown dust, volcanoes, forest fires and sea spray. Major anthropogenic sources consist of fossil fuel combustion, the mining, smelting and processing of metals, waste incineration, and industrial processes such as the production of iron and steel, phosphate fertilisers and cement (Nriagu, 1979; Nriagu and Pacyna, 1988). Their residence time in the atmosphere is however relatively short. Those bound to particulates are returned to the earth's surface by wet and dry deposition, whilst those in the gaseous phase are returned by condensation and diffusion. Even so, trace metals on fine particulates or in the gaseous phase may be transported over large distances causing regional or global pollution.

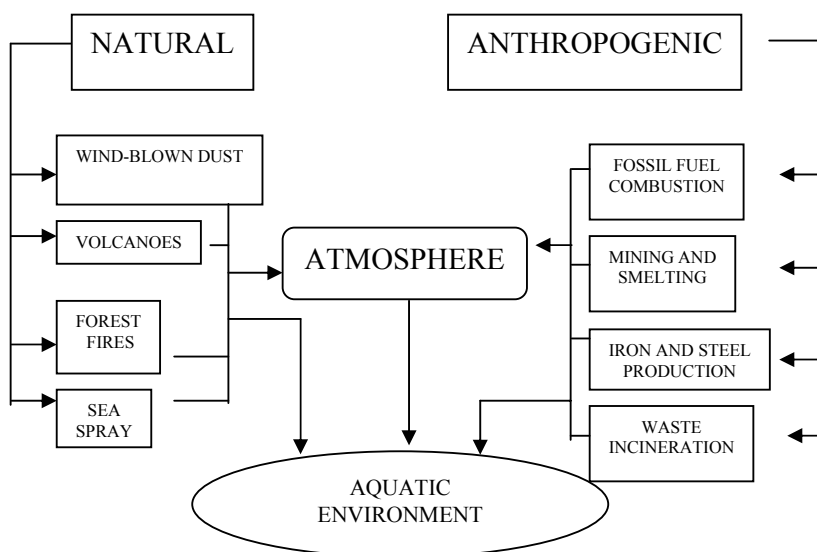


Fig. 2.1: Sources of trace metals in the environment.

Contamination of the atmosphere by pollutant trace metals affects the environment directly through its impact on air quality and indirectly by the impact on terrestrial and aquatic ecosystems following deposition on the land surface or in water bodies. To understand the effects, it is essential to quantify the extent and nature of the pollution and to identify its pathways through the system. To manage pollution incidents and predict their outcomes it is also essential to develop reliable models of the various transport processes, from the point of injection into the atmosphere to their ultimate removal from the biosphere.

The process of modelling trace metal pollution via atmospheric pathways and its impact on the environment will include several relatively distinct but overlapping stages:

- (i) injection into the atmosphere from both natural and artificial sources,

- (ii) circulation within the atmosphere and subsequent re-deposition back onto the land surface,
- (iii) transport by terrestrial and aquatic pathways and storage in long-term repositories, and
- (iv) long-term post-depositional migration within the repositories by mixing, advection and diffusion.

Models will invariably be composed of highly simplified descriptions of complex processes and to be of value they must be tested and validated against reliable data at as many stages as practicable. This data should include:

- (i) the relative abundance of different trace metals in the lithosphere and their isotopic composition,
- (ii) quantitative records of inputs to the atmosphere,
- (iii) measurements of atmospheric concentrations and fluxes,
- (iv) measurements of concentrations and fluxes in soils and water, and
- (v) records in natural archives.

The objective here is to provide quantitative information on the main sources of atmospheric trace metal deposition, to identify the main atmospheric transport pathways and to review methods of monitoring deposition. Also included is an overview of UK deposition levels for England, Ireland and Scotland.

2.1 Main Sources of Atmospheric Pollution

Wind-blown dust accounts for 60-80% of natural emissions of Pb, Zn, Cu and Ni, with 15-25% coming from volcanoes. Forest fires and sea spray are minor sources accounting for less than 10% of all emissions. Estimates of total global natural emissions vary widely and are subject to large uncertainties. Values obtained by Nriagu (1979) are summarised in *Table 2.1*. The mean flux has been calculated by dividing total emissions by the earth's surface area ($510 \times 10^6 \text{ km}^2$). In practice it will vary widely from place to place depending on factors such as climate, wind velocity, surface topology, *etc.*

	<i>Total Natural Emissions ($\times 10^6 \text{ kg}$)</i>	<i>Mean Natural Flux ($\mu\text{g cm}^{-2} \text{ yr}^{-1}$)</i>
Pb	24.5	0.0048
Zn	43.5	0.0085
Cu	18.5	0.0036
Ni	26.0	0.0051

Table 2.1: World-wide emissions of trace metals from natural sources. Values are so-called 'most acceptable values'. For ranges see Nriagu (1979).

In recent decades anthropogenic emissions of Pb, Zn, Cu and Ni have exceeded natural emissions by 2-3 orders of magnitude (*Table 2.2*). By far, the greatest metal releases in the 20th century have been from mining, smelting and from vehicles (Nriagu, 1979; Nriagu and Pacyna, 1988). In the western

world the problem of emissions has been reduced over the last 20 years through the use of legislation and the appropriate emission control devices.

<i>Production ($\times 10^6$ kg yr⁻¹)</i>	<i>1975</i>				<i>1983</i>			
	<i>Pb</i>	<i>Zn</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>	<i>Cu</i>	<i>Ni</i>
Mining and Smelting	85	118	22	10	50	72	24	9
Iron and Steel Production	50	35	6	1	8	20	1	4
Fossil Fuel Combustion	292	90	17	31	261	13	8	42
Waste Incineration	9	37	5	3	2	6	2	0
Others	13	35	6	3	12	21	0	1
Total ($\times 10^6$ kg yr ⁻¹)	449	314	56	47	332	132	35	56
Mean Flux ($\mu\text{g cm}^{-2} \text{yr}^{-1}$)	0.088	0.062	0.011	0.009	0.065	0.026	0.007	0.011

Table 2.2: World-wide anthropogenic emission fluxes of trace metals during 1975 and 1983 (Nriagu, 1979; Nriagu and Pacyna, 1988).

2.2 Main Atmospheric Pathways

Trace metals in the atmosphere become attached to different size ranges of atmospheric particles. Atmospheric particulates can be usefully divided into two main groups according to particle size: fine particles (radius 0.5-1.0 μm) and coarse particles (radius $> 1 \mu\text{m}$). Coarse particles include material largely from the earth's surface, for example soil particles and sea spray, whereas fine particles are formed by chemical reaction and condensation of atmospheric gases and aerosols (Mészáros, 1981). Due to this difference in origin, fine and coarse particles in the atmosphere are chemically distinct (Sugimae, 1976). Since Pb, Zn, Cu and Ni are volatile metals which vaporise during high temperature production processes, the enrichment of these metals occurs predominantly in the smaller size fractions of atmospheric particles and are thus prone to long-range transport.

The long range atmospheric transport of trace metals is well documented. The influence of air masses which have passed over continental landmasses and delivered anthropogenically derived pollutants to relatively unpolluted regions has been observed as far as the polar regions. Measurements in southern Scandinavia indicate that the concentration of many trace elements is an order of magnitude higher in air masses that have passed the European continent than in air masses coming from the North Atlantic region (Lannefors *et al.*, 1983).

Removal from the atmosphere takes place through deposition and chemical reactions. Deposition may occur either in precipitation (termed wet deposition), or dry deposition. Wet deposition is an efficient but episodic cleansing mechanism of the atmosphere for both gases and particles whereas dry deposition is a continuous process depending on the properties of a surface and the depositing species.

2.3 Monitoring Deposition of Trace Metals: Direct Measurements

The most reliable method for measuring deposition is directly via wet and dry fallout. An atmospheric sampling programme requires several years of data, since the pollutant concentrations vary depending on the season, the wind direction, the amount of rainfall and the time since the last rainfall (Evans *et al.*, 1986). Direct measurement of the atmospheric flux of trace metals is achieved using one of two established methods. (i) Bulk or total deposition analysis of the contents of a rainfall collector at weekly or monthly intervals, and (ii) wet and dry deposition analysis involving the separate collection of atmospheric fallout.

Deposition data for Cumbria in the UK between 1975-1996 is shown in Fig. 2.2. Since dry deposition measurements are difficult and time consuming the Cumbria data concerns the soluble (*i.e.* wet) fraction only (Baker, *pers. comm.*). Samples were collected in bulk and then filtered. Historically, analysis was carried out on both insoluble and soluble fractions. However, since the mid-1980's only the soluble fraction was analysed. Past estimates of the dry depositional (*i.e.* insoluble) flux in the UK range between 20-40 percent of the total deposition (AEA, *pers. comm.*).

Measurements at four other sites in the UK cover the period 1986 to 1991 (Fig. 2.3). These measurements are based on bulk sampling methods and remain unfiltered (Foundation for Water Research, 1995). Comparing the UK to the rest of the world, deposition of trace metals is approximately 100 times the worldwide average level of emissions.

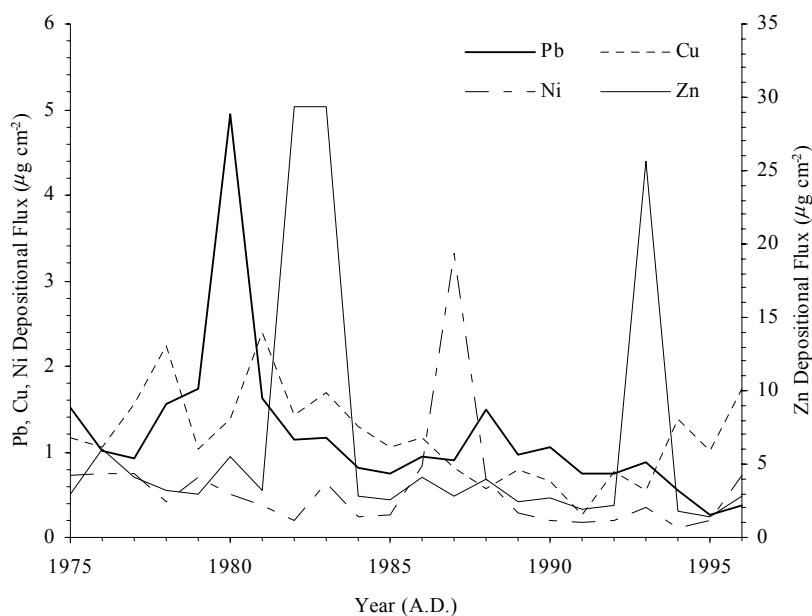


Fig. 2.2: Trace metal deposition (soluble fraction only) measured at Wraymires, Cumbria, UK (AEA, *pers. comm.*).

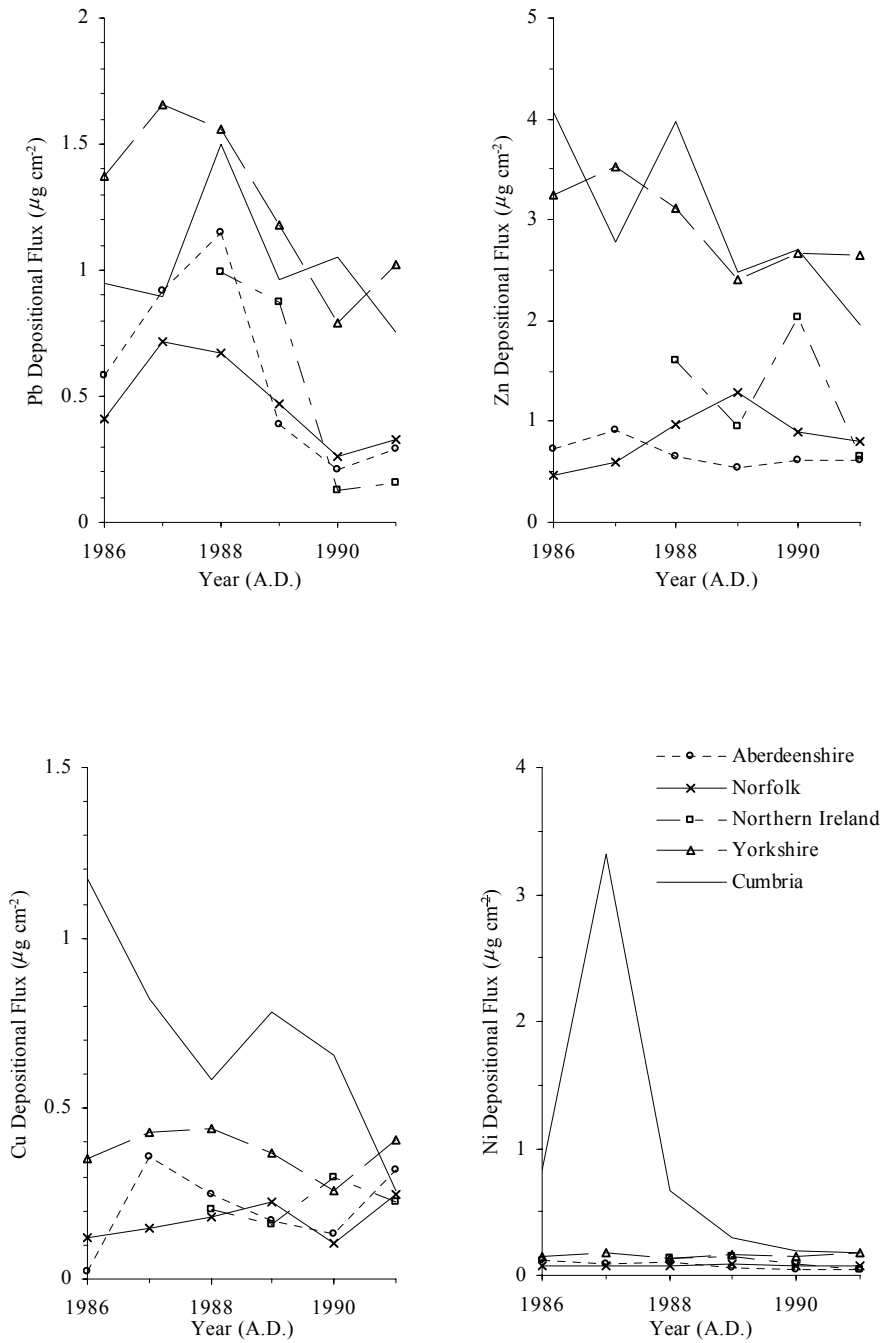


Fig. 2.3: Depositional flux of Pb, Zn, Cu and Ni at five UK locations, 1986-1992 (Foundation for Water Research, 1995; AEA, *pers. comm.*). Data for Cumbria represents the soluble fraction only.

2.4 Natural Archives: Indirect Measurements

Active monitoring over extended periods of time is expensive and difficult to manage and so records of trace metal depositional flux are often sparse. Natural archives such as lake sediments, peat bogs and ice sheets are often the only reliable source of information on past events. As each layer of sediment, peat or ice accumulates it carries a rich diversity of chemical and biological information about the contemporaneous environment. Varying accumulation characteristics between the three archives provide pollution records with very different degrees of definition. Because of the rapid rates of accumulation, ice deposits often provide the most detailed records including short-term fluctuations. Peat bogs and lake sediments are accumulated more slowly and hence provide more compact records.

Crucial to the interpretation of these records are reliable means for dating the information, and good quantitative models of the processes by which it is transported from the atmosphere and incorporated into the archive. One of the most widely used techniques for dating is from the decay of natural radionuclides included in the records. These include: (i) ^{14}C (half-life 5730 yrs), for dating on time-scales from 500 to 50,000 years, and (ii) ^{210}Pb (half-life 22.3 yrs), for dating on time-scales from 0-150 years. Artificial radionuclides such as ^{137}Cs and ^{241}Am from the atmospheric testing of nuclear weapons can provide invaluable supporting evidence. Atmospheric contamination by these radionuclides began in 1954, and reached a peak in 1963. Where the archive accurately records the subsequent fallout, depths corresponding to these dates can be identified. More recently, fallout from the Chernobyl reactor accident has been used to identify the 1986 horizon.

Since the radionuclides ^{210}Pb and ^{137}Cs have undergone exactly the same transport processes as the records they are being used to date, reliable models of these processes are important to accurate dating. ^{210}Pb and ^{137}Cs are also useful tracers for validating these models since:

- (i) they have well defined but contrasting input functions;
- (ii) they have contrasting geochemistry, ^{210}Pb being strongly particle bound and ^{137}Cs relatively more soluble;
- (iii) they are easily and unambiguously determined, with little or no problem of confusion with non-atmospherically derived sources; and
- (iv) there is a large data-base on these radionuclides in sediment records from numerous palaeolimnological studies.

Natural archives have been used to provide a historical record of the spatial distribution of trace metal deposition. The following figure (*Fig. 2.4*) shows estimates, from historical texts, of lead production during the last 5000 years (Hong *et al.*, 1994). Also shown is atmospheric lead deposition calculated from records in a Swiss peat bog (Shotyk *et al.*, 1998) and a Greenland ice core (Hong *et al.*, 1994). Contemporary lead fluxes recorded in the Swiss peat bog (*c.* $0.83 \mu\text{g m}^{-2} \text{yr}^{-1}$) are about 10 times higher than the global average. Those recorded in the Greenland ice core are 30 times lower.

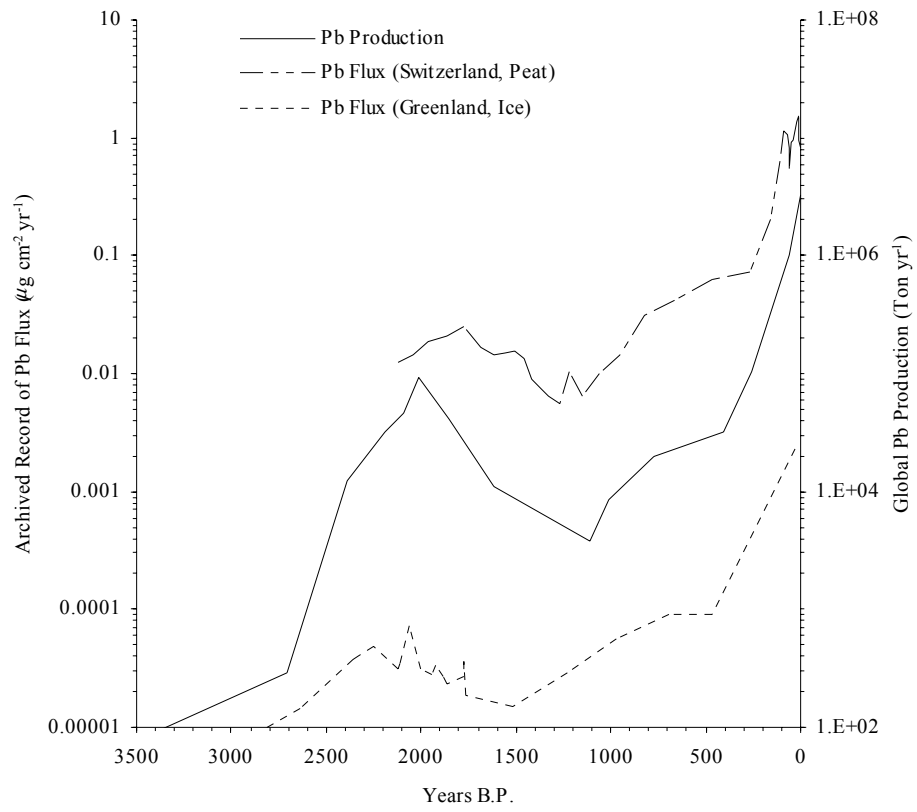


Fig. 2.4: Global lead production and archived records of atmospheric deposition calculated from records in a Swiss peat bog (Shotyk *et al.*, 1998) and a Greenland ice core (Hong *et al.*, 1994).