

Atmospheric Heavy Metal Pollution

Development of Chronological Records and Geochemical Monitoring

Rohit Shrivastav

Rohit Shrivastav is at the Department of Chemistry in Dayalbagh Educational Institute, Agra.

Introduction

The term 'heavy metal' is often used to cover a diverse range of elements which constitute an important class of pollutants. Such pollutants have received the attention of researchers all over the world, mainly due to their harmful effects on living beings. Human biology is full of instances where heavy metal toxicity has led to mass deaths. Heavy metals enter into the environment mainly via three routes: (i) deposition of atmospheric particulates, (ii) disposal of metal enriched sewage sludges and sewage effluents and (iii) by-products from metal mining processes. The estimation of metal input into environment from the two latter sources is relatively easy to measure. However, atmospheric input is difficult to quantify accurately mainly due to atmospheric mixing of metal-bearing particulates and the diversity of metals and metal-emitting sources which contribute to the overall atmospheric metal pool.

Heavy Metal Deposition

Heavy metals occur, in atmosphere, basically in particulate form. Hence, the transfer of air borne particles to land or water surfaces by dry, wet and occult deposition¹ constitutes the first stage of accumulation of atmospheric heavy metals. Dry deposition involves four distinct processes: gravitational settling, impaction, turbulent transfer and transfer by Brownian motion. The relative importance of these processes depends primarily on the size of the particles. Anthropogenically added particulates and aerosols in atmosphere show a broad size distribution from 0.001 μm to 50 μm (*Figure 1*) and is strongly influenced by atmospheric transport processes. In rural regions anthropogenic

Deposition which is due to an obscure/unknown process.



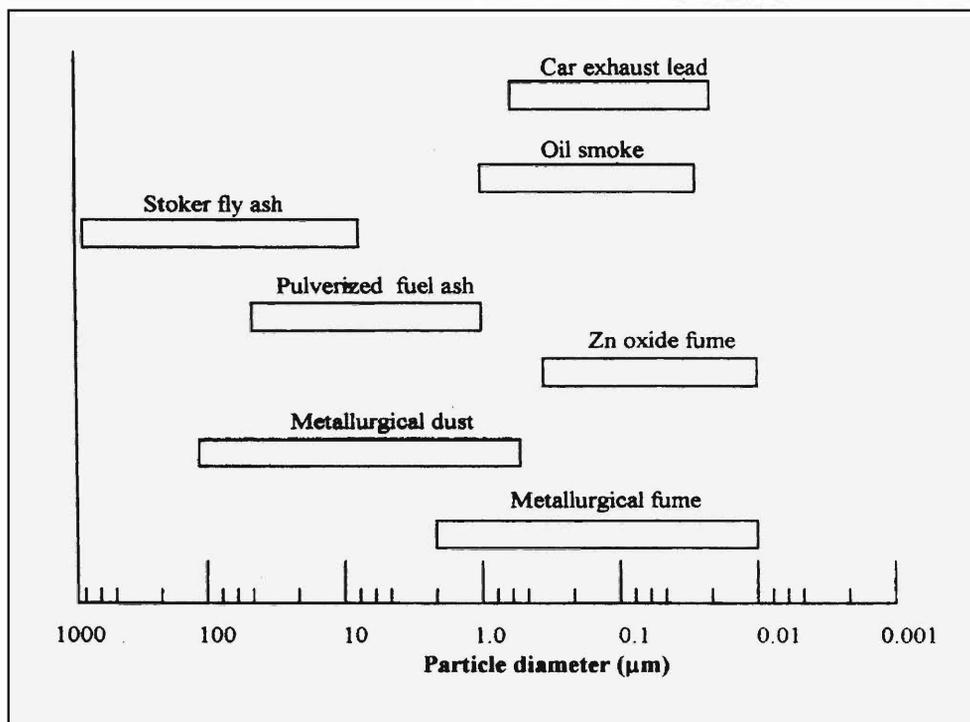


Figure 1. Particle sizes of some atmospheric pollutants.

particles $>5 \mu\text{m}$ are absent [1] and in polar regions heavy metals are mostly associated with small aggregated particles in the range of $0.1\text{-}10 \mu\text{m}$ [2]. Dry deposition of heavy metals in rural and remote regions is, therefore, through impaction and turbulent transfer. Wet deposition involves two processes: nucleation and within and below cloud scavenging, whereby the wet aerosol particles are collected by falling raindrops. In occult deposition, wetted particles (fog and mist) are deposited by impaction or turbulent transfer [3].

A high proportion of atmospheric heavy metals entering aquatic systems is in small particulate ($< 1 \mu\text{m}$) or soluble form. The first site of chemical interaction is the micro layer (a surface film of thickness $0.1\text{-}1.0 \mu\text{m}$) [4], where often high concentrations of surface active molecules act as heavy metal traps. In the main water body of lacustrine and marine systems, the following are the most important reactions in the transfer of metals from aqueous to solid phase: precipitation and co-precipitation with hydroxides, sulphides or carbonates; cation exchange/sorption



Heavy metals are incorporated very efficiently by bryophytes, where the absence of a vascular system necessitates a relatively unrestricted exchange of solutes between the atmosphere and the living plant tissue.

on clay minerals, iron/manganese oxides and sulphides, carbonates, and phosphates. Organic matter in various forms is also an important scavenger of heavy metals in natural waters. When newly deposited metals enter the primary sediment layers, their associations are subjected to diagenetic modifications. The first of these is the degradation of organic matter, which takes place rapidly in aerobic conditions and slowly in anaerobic conditions. The subsequent fate of released metals is determined primarily by the redox potential of the sediments and overlying water. Metals can be classified into three groups on the basis of their response of redox potential: those which are fixed in reducing conditions (Cd, Cu, Ni, Pb, Zn), those which are fixed in oxidizing conditions (Fe, Mn) and those which are unaffected by redox potential (Cr, Hg). Acidification of water not only reduces heavy metal scavenging but also remobilizes metals from the surface sediment layers.

The initial associations of heavy metals in the peat system are determined by the nature of the surface on which the metals are deposited. Heavy metals are incorporated very efficiently by bryophytes, where the absence of a vascular system necessitates a relatively unrestricted exchange of solutes between the atmosphere and the living plant tissue. Once penetration has occurred the principal site of accumulation of atmospheric heavy metals in both higher plants and cryptogams is the cell wall and intracellular membrane. As plant litter is converted into peat, its heavy metal content is increasingly influenced by the newly-synthesized organic matter.

In ice and snow, in contrast to aquatic sediments and peat, heavy metals are held by physical bonds in the ice crystalline matrix and virtually no chemical transformation occurs after deposition. The stability of metals in ice deposits depends solely on meteorological factors. Newly-deposited snow layers containing contemporary inputs of heavy metals can be subjected to mass redistribution by strong winds, notably in parts of Antarctica. But the fate of the stratified deposit, consisting of successive



winter and summer layers, depends on the constant maintenance of subzero temperature. Occasionally, episodes of melting may result in slight merging of these annual layers, but evidence suggests that surface meltwater is usually re-frozen before it penetrates to any great depth.

Geochemical Monitoring of Heavy Metal Pollution

Employing all the three above mentioned natural deposits viz., aquatic sediments, peat and ice deposits as geochemical monitors of atmospheric heavy metal pollution, many studies have been carried out in recent years in relation to the historical aspects of pollution, mainly in North-west Europe, North America and remote polar regions. Records from peat deposits and lake sediments in Europe document the growth and development of the industry there over the last 2000 years [5, 6]. Reconstructed historical deposition rates have demonstrated the severity of pollution in urban areas of northern Britain in the eighteenth and nineteenth centuries, whereas analysis of recent sediments reveal a variable pattern of present-day pollution, with some areas experiencing increasing levels of deposition and others decreasing ones [7, 8]. In North America, deposition records show a comparatively shorter history of atmospheric pollution and document the rapid spread of heavy metals during the mid and late nineteenth century [9]. For most other parts of the world no such detailed information exists.

With vastly differing accumulation characteristics and widely varying time spans, the three above mentioned geochemical monitors provide pollution records with different degrees of definition. For dating the records, a wide range of techniques such as stratigraphic, biostratigraphic, radiometric and geomagnetic techniques are employed. For dating ice deposits the choice of methods though limited are quite accurate. The choice is wider for peat deposits and aquatic sediments, but physical and chemical processes within them can reduce the reliability of the dating determinations. A recent development in the search for

Reconstructed historical deposition rates have demonstrated the severity of pollution in urban areas of northern Britain in the eighteenth and nineteenth centuries.

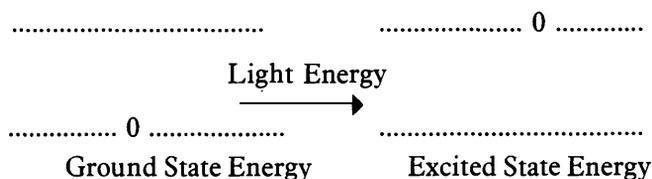


The use of flame atomic absorption spectrometer is still regarded as the most convenient and appropriate technique for the purpose of heavy metal analysis in most cases.

the most suitable geochemical monitor for heavy metal pollution has been the use of bricks. By analyzing the bricks of different ages, extracted from the walls of old buildings, monuments, etc., [10, 11] the history of heavy metal pollution, since 1900, in the soil around a north Indian city has been successfully traced.

Heavy Metal Analysis in Environmental Samples: Atomic Absorption Spectrometry

The use of flame atomic absorption spectrometer is still regarded as the most convenient and appropriate technique for the purpose of heavy metal analysis in most cases. Flame atomic absorption spectrometry is based upon the estimation of the capacity of an atom to absorb very specific wavelength of light as it enters an excited state in a process known as atomic absorption.



The atomic absorption spectrometer measures the amount of light absorbed at the resonant wavelength, as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of other elements. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy through a flame to the sample to dissociate the chemical compound into free atoms. The whole process is summarized in *Table 1*.

The flame temperature is an important parameter because the thermal energy is responsible for producing the absorbing species. The temperatures of some flames are shown in *Table 2*.

Stage		Description
Nebulization	→	$M^+ + A^-$ (solution)
↓		
Desolvation	→	$M^+ + A^-$ (aerosol)
↓		
Liquefication	→	MA (solid)
↓		
Vaporization	→	MA (liquid)
↓		
Atomization	→	MA (gas)
↓		
Excitation	→	$M^o + A^o$ (gas)
↓		
Ionisation	→	M^+ (gas)
↓		$M^+ + e^-$ (gas)

Table 1. Various stages of atomic absorption process occurring in a flame atomic absorption spectrometer.

Cooler flames are subject to more interference problems resulting from insufficient energy for complete atomization. The atomization step of flame process will determine the amount of light absorbed.

After feeding the most appropriate wavelength and slit valve and adjusting the desired flame condition, the instrument is calibrated with the help of standard solutions, which are usually prepared by diluting stock solutions with doubled distilled deionized water. Metal concentration in the sample solution is then determined by aspirating it through a nebulizer for ≈ 60 seconds and recording an average of ten measurements within this span of time. During the course of analysis, instrument is checked frequently for calibration and in between the two samples, sufficient volume of water is aspirated. The ease and speed at which

Oxidant - Fuel	Temperature ($^{\circ}\text{C}$)
Air - methane	1850 - 1900
Air - natural gas	1700 - 1900
Air - hydrogen	2000 - 2050
Air - acetylene	2125 - 2400
N_2O - acetylene	2600 - 2800

Table 2. Temperature of certain flames.

precise and accurate determination can be made with this technique has made flame atomic absorption spectrometry one of the most popular methods for the analysis of metals in environmental samples.

The problem of atmospheric heavy metal pollution is not going to disappear overnight. On the contrary it will remain as a legacy of mass industrial activity for many generations and is likely to escalate further in future. In this regard the compilation of past and present catalogues of atmospheric heavy metal concentrations is an activity of great importance.

Suggested Reading

- [1] N I Ward, R D Reeves and R R Brooks, Lead in soils and vegetation along a New Zealand State highway with low traffic volume, *Environ. Pollut.*, 9, 243-251, 1975.
- [2] L A Barrie, Arctic air pollution: An overview of current knowledge, *Atmos Environ.*, 20, 643-663, 1986.
- [3] L A Barrie and R S Schemenauer, Pollutant wet deposition mechanisms in precipitation and fog water, *Water Air Soil Pollut.*, 30, 91-104, 1986.
- [4] P S Liss, Chemistry of the sea surface microlayer, In: *Chemical Oceanography* (Ed. by J P Riley and G Skirrow), New York, Academic Press, 193-243, 1974.
- [5] J G Farmer D S Swan and M S Baxter, Records and sources of metal pollutants in a dated Loch Lomond sediment core, *Sci. Total Environ.*, 16, 131-147, 1980.
- [6] E A Livett, J A Lee and J H Tallis, Lead, Zinc and copper analyses of British blanket peats, *J. Ecol.*, 67, 865-891, 1979.
- [7] F M Batifol and C Boutron, Atmospheric heavy metals in high altitude surface snows from Mount Blanc, French Alps, *Atmos. Environ.*, 18, 2507-2515, 1984.
- [8] M Thomas, D Petit and L Lamberts, Pond sediments as historical records of heavy metals fallout, *Water Air Soil Pollut.*, 23, 51-59, 1984.
- [9] H K T Wong, I O Nriagu and R D Coker, Atmospheric input of heavy metals chronicled in lake sediments of the Algonquin Provincial Park, Ontario, Canada, *Chem. Geol.*, 44, 198-201, 1984.
- [10] R Shrivastav and others, Bricks as historical record of heavy metals fallout: Study on copper accumulation in Agra soils since 1910, *Environ. Mon. Ass.*, 40, 271-278, 1996.
- [11] R Shrivastav and others, Bricks reveal recent history of heavy metal pollution in soil around a north Indian city, *Sci. Total Environ.*, 209, 41-46, 1998.

Address for Correspondence

Rohit Shrivastav
 Department of Chemistry
 Faculty of Science
 Dayalbagh Educational Institute
 Dayalbagh
 Agra 282 005, India.