



NATURAL SOURCES AND EMISSIONS OF ELEMENTS TO THE ATMOSPHERE¹

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Introduction

Industrial activities, such as ore processing, smelting and coal combustion, release metals to the atmosphere. However, these elements also occur naturally in the Earth's crust and are everpresent throughout air, water, soil, foods, plants and animals. Assessments of human exposure to these elements have routinely demonstrated that 90% or more of people's day-to-day intake occurs as a result of eating food that contains metals due to the ubiquitous nature of their natural occurrence in the environment, particularly in soil. Often, dissolved metals found naturally in drinking water, particularly that drawn from groundwater wells, comprises the majority of the remaining exposure.

Governments are concerned about the potential toxicity of these elements in the terrestrial and aquatic environments when released from industrial activities. In order to evaluate and control emissions of these elements, national and international databases and inventories of industrial emissions are maintained to track trends in anthropogenic emissions (those caused by human activity). Also, extensive national and international networks of air quality monitoring stations are maintained to track temporal changes in atmospheric loadings, concentrations and/or deposition. However, natural sources also contribute to the element load in the atmosphere, but the effort to inventory contributions from natural sources has

been less rigorous than for industrial sources. Unfortunately, the levels of metals detected by air quality monitoring networks can seldom be apportioned to specific sources (natural or industrial) based on the monitoring data alone. Sometimes, the ratios of different isotopes can be used to implicate certain sources; increases in the proportion of one isotope to another, relative to naturally occurring ratios, can assist with source identification. Also, detailed analysis of meteorological patterns prior to the day of measurement can identify the geographic location and/or source from which atmospheric metals were transported. However, these methods are applied only in rare circumstances and are not always highly predictive. As a result, except in those few instances when additional research is conducted, measured fluctuations in airborne levels of metals may as easily reflect fluctuations in natural source emissions as it may reflect changes in industrial output.

Natural Sources of Metals

There are four main natural sources of metals to the atmosphere:

- volcanic eruptions and emissions;
- entrainment, via wind erosion, of soil and dust particles into the air;
- entrainment of sea salt spray into the air and
- natural forest fires that emit ash, soot and smoke into the air.

¹ This fact sheet is based on recent efforts to quantify natural source emissions of metals in Canada, North America and globally, under the direction and with the assistance of the Geological Survey of Canada (GSC). A full report is available as a GSC Open File from the Geological Survey of Canada (Natural Resources Canada, Ottawa).

The meteorites and “space dust” that constantly bombard the Earth’s atmosphere also introduce metals to the atmosphere. However, available evidence suggests this is a relatively small contribution.

With the exception of mercury, which is liquid at typical ambient temperatures and has a high vapour pressure resulting in volatilization, metals generally exist within the atmosphere as a component of particulate matter. Therefore, any natural process or phenomenon that ejects or introduces particulate matter into the atmosphere will carry with it a certain amount of metal “contamination.” Except for meteorites and “space dust,” inputs to the atmosphere from natural sources are not net increases, but rather are simply movement of metals from one part of the global ecosystem to another.



| Range (kg/yr) | | | |
|---------------|-------------------|--------------------|-------------------|
| Metal | Mean | 5th percentile | 95th percentile |
| Cd | 1.6×10^6 | 0.38×10^6 | 3.8×10^6 |
| Cu | 9.0×10^6 | 2.1×10^6 | 20×10^6 |
| Pb | 4.7×10^6 | 1.1×10^6 | 10×10^6 |
| Ni | 3.2×10^6 | 0.74×10^6 | 7.0×10^6 |
| Zn | 54×10^6 | 10×10^6 | 130×10^6 |

Figure 1

Present estimates of global emissions due to volcanic eruptions

Volcanoes

Volcanic activity ejects massive amounts of particulate matter into the air, and metals are carried with those particles. Various estimates of the amount of particulate matter ejected annually by volcanoes have been published, with estimates ranging from less than 10 million metric tonnes/yr to as much as 150 million metric tonnes/yr. The resulting quantity of metals ejected from volcanoes amounts to thousands of kilograms per year (Figure 1). Individual metals may comprise several percent (by weight) of the ejected particles, and the concentrations of some metals and elements in volcanic plumes reach tens to thousands of micrograms per cubic metre. With volcanoes ejecting massive amounts of particles several kilometres into the sky, the particle-borne metals become globally distributed.

The distribution of volcanoes around the globe is very patchy, so the contribution from volcanoes, on a regional or more local basis, is extremely variable. Canada, as well as Australia and many parts of Europe, Africa and Asia, has no active volcanoes. So, although suspended volcanic particles may be deposited from the atmosphere to those countries and regions, they will not be a source of these natural emissions.

The continental United States (including Alaska and the Aleutian Islands) has approximately 10% of the total active volcanoes in the world. The vast majority (>94%) of known volcanic eruptions occur within the “volcanic belts,” which encompass only 32 000 km in length and represent <0.1% of the Earth’s surface.

Volcanic activity also fluctuates over time. From 1969 to 1973, for example, there were 109 reported volcanic events in any given year. Between 1975 and 1985, there were 158 reported volcanic eruptions in any given year. The types of volcanic activity include ash and cinder emission, central crater formation, dome formation, normal explosion (due to steam build-up) and sub-marine eruptions.



| Range (kg/yr) | | | |
|---------------|------------------------|-----------------------|------------------------|
| Metal | Mean | 5th percentile | 95th percentile |
| Cd | 24 x 10 ⁶ | 3.0 x 10 ⁶ | 69 x 10 ⁶ |
| Cu | 2000 x 10 ⁶ | 240 x 10 ⁶ | 5500 x 10 ⁶ |
| Pb | 1700 x 10 ⁶ | 200 x 10 ⁶ | 4900 x 10 ⁶ |
| Ni | 1800 x 10 ⁶ | 210 x 10 ⁶ | 4900 x 10 ⁶ |
| Zn | 2700 x 10 ⁶ | 350 x 10 ⁶ | 7400 x 10 ⁶ |

Figure 2

Present estimates of global emissions due to wind erosion

Wind-borne Atmospheric Entrainment of Soil Particles

Windblown soil is one of the largest sources of natural metal emissions to the atmosphere (Figure 2). Through the process of weathering and erosion, metals that naturally occur in the Earth's crust also are found in soil. So the metals go where soil particles go.

Wind erosion is an important source of total particulate mass and high particulate concentrations in the atmosphere. Several authors have estimated the amount of soil that is entrained into the global atmosphere via the wind, with some recent estimates approaching 3000 million metric tonnes/yr. Dust picked up by the winds from the deserts of Africa finds its way as far as North America. Dust flux from the Sahara desert alone may be 600 million metric tonnes/yr. Although the Sahara is a large contributor of windblown dust, there are several other arid areas in the world that contribute dust to the atmosphere.



| Range (kg/yr) | | | |
|---------------|------------------------|------------------------|--------------------------|
| Metal | Mean | 5th percentile | 95th percentile |
| Cd | 2.0 x 10 ⁶ | 0.13 x 10 ⁶ | 6.7 x 10 ⁶ |
| Cu | 13 x 10 ⁶ | 2.0 x 10 ⁶ | 36 x 10 ⁶ |
| Pb | 13 x 10 ⁶ | 2.7 x 10 ⁶ | 31 x 10 ⁶ |
| Ni | 0.17 x 10 ⁶ | 0.03 x 10 ⁶ | 0.46 x 10 ⁶ |
| Zn | 3100 x 10 ⁶ | 76 x 10 ⁶ | 11 000 x 10 ⁶ |

Figure 3

Present estimates of global emissions due to sea salt spray

Sea Salt Spray

Ocean storms and prevailing winds loft sea salt into the air and can carry it for great distances. Sea salt flux is highly dependent on wind speed, among other factors such as the frequency, duration and intensity of ocean storms. Estimates of global sea salt flux range from 1000 to 10 000 million metric tonnes/yr (Figure 3). Metals occur naturally in seawater, but they become concentrated in sea salt (relative to seawater) by up to several thousand fold for some elements such as zinc. As a result of this enrichment, the composition of sea salt particles is different than the composition of bulk seawater.

In addition to the variability in sea salt flux, there is also spatial variability in the concentrations of metals in seawater, and in the enrichment of different metals in sea salt. This is likely due to variable biological activity in different areas of the world's oceans; the extent of that variability is still not well understood.

Forest and Brush Fires

Fires are a source of particulate matter in the atmosphere, containing metals that were naturally occurring within the vegetation before it was burned (Figure 4). Up to 80% of the surface area of certain savannah and grassland ecosystems may be subjected to fire each year; the situation is much less severe for forest ecosystems. However, in terms of total biomass combusted, forest fires generally consume 10 times as much biomass per year as do grassland fires.

The emission rate of smoke and particulate matter can vary over an order of magnitude, depending on fuel type and combustion efficiency. In general, areas with large amounts of brush produce more smoke particles than areas without brush, and fires with a low combustion efficiency produce more particles than fires with a high combustion efficiency. Savannah and grassland fires have lower particulate emissions due to a higher combustion efficiency, since the smoldering component of the burn would be lower.



| Range (kg/yr) | | | |
|---------------|-----------------------|------------------------|-----------------------|
| Metal | Mean | 5th percentile | 95th percentile |
| Cd | 13 x 10 ⁶ | 4.4 x 10 ⁶ | 30 x 10 ⁶ |
| Cu | 4.7 x 10 ⁶ | 1.8 x 10 ⁶ | 9.1 x 10 ⁶ |
| Pb | 83 x 10 ⁶ | 24 x 10 ⁶ | 180 x 10 ⁶ |
| Ni | 2.8 x 10 ⁶ | 0.77 x 10 ⁶ | 6.6 x 10 ⁶ |
| Zn | 68 x 10 ⁶ | 21 x 10 ⁶ | 150 x 10 ⁶ |

Figure 4

Present estimates of global emissions due to forest fires

The emission of particles from fires is highly variable across the globe, due both to variable rates of fires among different regions of the world, and to variation in particulate emission from one type of fire to another. Over 80% of global emissions from biomass burning arise from the tropics, although a large portion of this is caused by human activities. The efficiency of combustion, which affects emissions, is affected by vegetation type, climate, moisture and topography. Emissions also can be affected by other fuel conditions, including physical arrangement and state of decomposition.

The concentration of metals adsorbed to smoke particles from forest fires and grassland fires is different for each metal, just as the concentration of each metal is different in live vegetation. However, metal concentrations generally range between 0.01% and 0.2% (by weight) of the particulate matter emitted. The concentration of metals in smoke from forest fires generally is greater than that from grass fires.

Meteoritic Dust

The Earth is continually intercepting meteorites and interplanetary dust. This phenomenon, known as cosmic flux, is relatively constant over time. Meteorites range in size from sub-micron particles to 1000 tonne or larger rocks. The cosmic flux entering the Earth's atmosphere is dominated by particles between 0.1 mm and 1.0 mm in diameter in most years, with the majority of interplanetary dust entering the atmosphere consisting of particles approximately 200 µm in diameter. Large amounts of interplanetary dust and ablated material from meteorites remain in the atmosphere for prolonged periods of time.

The total mass of meteoritic dust entering Earth's atmosphere cannot be directly measured, so several different methods have been used to make estimates. These methods include geochemical methods measuring specific meteoritic components in deep sea sediments, measuring luminosity caused by particles entering the atmosphere and counting craters on metal panels orbiting the Earth. Cosmic flux estimates have ranged from 4 000 metric tonnes/yr to 800 million metric tonnes/yr, with the most recent and reliable estimates ranging between 40 000 metric tonnes/yr and 400 000 metric tonnes/yr.



| Range (kg/yr) | | | |
|---------------|------|----------------|-----------------|
| Metal | Mean | 5th percentile | 95th percentile |
| Cd | 0.18 | 0.042 | 0.42 |
| Cu | 27 | 9.2 | 55 |
| Pb | 0.22 | 0.049 | 0.54 |
| Ni | 2200 | 780 | 4200 |
| Zn | 62 | 15 | 140 |

Figure 5

Present estimates of global emissions due to meteors

The flux of metals to the atmosphere from meteoritic dust (Figure 5) can be calculated by simply multiplying the concentration of the metals in meteoritic dust by the total annual flux of meteoritic dust entering the atmosphere. The concentrations of metals in interplanetary dust range from hundreds to thousands of parts per million; levels of nickel are particularly high.

Conclusion

Perhaps the most cited and relied-upon estimates of natural source metal emissions to the atmosphere

are those of Nriagu (1989). Although timely when published, a considerable amount of new research and new data have been produced in the past decade to allow those earlier estimates to be improved and updated. In particular, the contributions from biogenic sources have been previously underestimated, not through a failure to recognize their importance, but rather out of a lack of data to support source emission estimates.

Focusing on the natural sources identified by Nriagu, following his general methods, but incorporating new data and information where available, we have determined that natural source metal emissions have been underestimated; a conclusion also reached by other researchers. Our best estimates of total natural metal emissions are presented in Figure 6, along with those of Nriagu (1989) for comparison.

It is imperative that environmental regulatory agencies recognize the limitations presented by early estimates of natural metal emissions, and investigate their true magnitude before embarking on regulatory initiatives aimed at reducing atmospheric metal levels. Without an accurate determination of natural source emissions, reaching the goal of significantly reducing global atmospheric metal loadings may be impossible.

Estimates such as those presented herein are not free of uncertainty. This was true a decade ago and remains true today. To reflect this uncertainty, we have provided upper and lower confidence limits (90%) about our best (mean) estimate of natural metal emissions. No doubt as more data emerge, particularly on the important and significant role that plants play in the biogenic emission of metals to the atmosphere, these estimates will improve and the confidence limits will narrow.

| Metal | Current Study | | Nriagu (1989) |
|-------|-----------------------------|---|------------------------------|
| Cd | 4.1 x 10 ⁷ kg/yr | (range: 1.5 x 10 ⁷ – 8.8 x 10 ⁷ kg/yr) | 1.14 x 10 ⁶ kg/yr |
| Cu | 2.0 x 10 ⁹ kg/yr | (range: 2.7 x 10 ⁸ – 5.5 x 10 ⁹ kg/yr) | 2.77 x 10 ⁷ kg/yr |
| Pb | 1.8 x 10 ⁹ kg/yr | (range: 3.0 x 10 ⁸ – 5.1 x 10 ⁹ kg/yr) | 1.2 x 10 ⁷ kg/yr |
| Ni | 1.8 x 10 ⁹ kg/yr | (range: 2.2 x 10 ⁸ – 4.9 x 10 ⁹ kg/yr) | 3.0 x 10 ⁷ kg/yr |
| Zn | 5.9 x 10 ⁹ kg/yr | (range: 1.2 x 10 ⁹ – 1.5 x 10 ¹⁰ kg/yr) | 4.5 x 10 ⁷ kg/yr |

Figure 6

Estimated total natural source of global emissions of metals to the atmosphere

Additional Reading

- Nriagu, J. O. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature*, 338: 47-49.
- Richardson, G. M., Garrett, R., Mitchell, I., Mah-Paulson, M. and Hackbarth, T. In press. Critical review on natural global and regional emissions of six trace metals to the atmosphere. GSC Open File, Geological Survey of Canada, Natural Resources Canada, Ottawa.

About the Author

Dr. G. Mark Richardson is founder and director of Risklogic Scientific Services Inc., an environmental consulting company specializing in human health and ecological risk assessment, environmental guidelines, data analysis and biostatistics. Dr. Richardson has conducted numerous risk assessments of metals and other contaminants in the environment for Canadian public sector and private sector clients as well as international companies and agencies. He specializes in support to Canadian environmental regulatory agencies. He earned his Ph.D. in biology from the University of Ottawa, Canada. Prior to entering private sector consulting, Dr. Richardson was Head of Health Canada's Air and Waste Section, developing procedures for and conducting quantitative risk assessments of environmental contaminants, and contributed to the development of risk-based soil quality guidelines under Canada's National Contaminated Sites Remediation Program.

Fact Sheet on Environmental Risk Assessment

This is the eleventh in an occasional series of *Fact Sheets* to be produced by ICMM on metal-specific issues in environmental risk assessment. Authorship selection and editorial review are coordinated by Dr. Anne Fairbrother of Parametrix, Inc. Each *Fact Sheet* is reviewed for technical merit by Dr. Erik Smolders of Katholieke Universiteit (Catholic University) Leuven, Belgium, and by a panel of experts in metal-related regulatory issues. While the *Fact Sheets* reflect the views of the authors, they are intended to provide an objective review of each topic. ICMM hopes these publications provide insights into complex issues in regulatory science, and welcomes questions and comments.

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