GEOLOGICAL SURVEY OF CANADA
BULLETIN 429

TRACE METALS IN THE ENVIRONMENT: A GEOLOGICAL PERSPECTIVE

P.E. Rasmussen

1996

Natural Resources Canada
Ressources naturelles Canada

Canada

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BULLETIN 429

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Catalogue No. M42/429E
ISBN 0-660-16380-2

Available in Canada from

Geological Survey of Canada offices:

601 Booth Street
Ottawa, Ontario K1A 0E8

3303-33rd Street N.W.
Calgary, Alberta T2L 2A7

100 West Pender Street
Vancouver, B.C. V6B 1R8

or from

Canada Communication Group – Publishing
Ottawa, Ontario K1A 0S9

and through authorized bookstore agents
and other bookstores

A deposit copy of this publication is also available for reference
in public libraries across Canada

Price subject to change without notice

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Original manuscript submitted: 1995-09-22
Final version approved for publication: 1996-01-11

Preface

Environmental geochemistry is an increasingly important scientific activity at the Geological Survey of Canada (GSC). Our involvement stems from concerns, amongst many, about the impact of acid precipitation on weathering processes and the sources and behaviour of metals in the environment. The metals, particularly mercury, lead, and cadmium, for which some compounds have been declared toxic under the Canadian Environmental Protection Act, are a particular focus of attention. The Geological Survey's extensive base line geochemical databases, strong analytical capabilities, and expertise in understanding natural sources of metals and the processes controlling their distribution in the environment, place it advantageously to address these issues.

In the last decade, particular concerns have been raised about sources and pathways of trace metals in remote ecosystems. In response, the United Nations-Economic Commission for Europe (UN-ECE) formed a task group to address the issue of transboundary atmospheric transport of metals, with the aim of developing an international heavy metals protocol. This literature review was initiated to evaluate the scientific basis for the potential protocol, and to contribute information on the global significance of natural sources of metals to the environment for the UN-ECE Science Working Group.

In this report, the author evaluates the evidence presented for significant long-range global atmospheric transport of metals released by anthropogenic processes. The chief lines of evidence are global estimates of natural and anthropogenic metal emissions to the atmosphere, source identification in receptor models, the distribution of metals in remote and rural ecosystems, and regional scale mass balance studies. The author discusses these lines of evidence in terms of the validity of the underlying assumptions, and the challenges in distinguishing between metals of natural and anthropogenic origin at receptor sites. To help resolve the uncertainties that remain possible research directions are suggested.

Marc Denis Everell
Assistant Deputy Minister
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Préface

La géochimie de l'environnement est une activité scientifique de plus en plus importante à la Commission géologique du Canada (CGC). L'engagement de la CGC tient à l'inquiétude suscitée notamment par les répercussions des précipitations acides sur les processus d'altération, de même que sur les sources et le comportement des métaux dans l'environnement. Les métaux, surtout le mercure, le plomb et le cadmium, dont certains composés ont été déclarés toxiques en vertu de la *Loi canadienne sur la protection de l'environnement*, méritent une attention particulière. Forte de ses énormes bases de données géochimiques de référence, de ses grands moyens d'analyse et de ses vastes compétences, la CGC jouit d'un avantage pour traiter des questions relatives aux sources naturelles de métaux et aux processus régissant leur répartition dans l'environnement.

Au cours de la dernière décennie, des préoccupations précises ont fait surface quant aux sources et aux voies de transport des métaux traces dans les écosystèmes éloignés. Pour y répondre, la Commission économique des Nations Unies pour l'Europe (CEE-ONU) a formé un groupe de travail chargé d'étudier la question du transport atmosphérique transfrontalier des métaux, en vue d'élaborer un protocole international concernant les métaux lourds. La présente revue de la documentation a été entreprise pour évaluer la base scientifique d'un éventuel protocole et pour fournir de l'information sur l'importance planétaire des sources naturelles de métaux dans l'environnement au groupe de travail scientifique de la CEE-ONU.

Dans le présent rapport, l'auteur évalue la preuve présentée à l'appui de l'importance du transport atmosphérique planétaire sur de longues distances des métaux d'origine anthropique. Les éléments de la preuve comprennent des estimations à l'échelle planétaire des émissions naturelles et anthropiques de métaux dans l'atmosphère, l'identification de sources dans des modèles de régions réceptrices, la répartition de métaux dans des écosystèmes éloignés et ruraux, ainsi que des études de bilan massique à l'échelle régionale. Ces éléments de preuve sont évalués en termes de la validité des hypothèses sous-jacentes et de la difficulté à distinguer entre les métaux d'origine naturelle et ceux d'origine anthropique dans les régions réceptrices. Des avenues de recherche sont proposées pour aider à lever les incertitudes.

Marc Denis Everell
Sous-ministre adjoint
Secteur des sciences de la Terre

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TRACE METALS IN THE ENVIRONMENT: A GEOLOGICAL PERSPECTIVE

Abstract

This report examines current methods of estimating the relative contribution of anthropogenic and natural sources of metals in the environment, with particular attention to areas distant from industrial point sources. Natural background concentrations and cycling processes must be known in order to assess the extent and impact of anthropogenic releases of metals to the environment. There are, however, critical information gaps and uncertainties associated with attempts to quantify the relative contribution of natural and anthropogenic sources to global, regional, and local scale geochemical cycles. One important issue is the orders-of-magnitude uncertainty associated with global emissions inventories. Another important issue is the uncertainty associated with distinguishing natural accumulation processes from anthropogenic effects in the interpretation of metal distribution in soil, vegetation, and lake sediments. Research is required to obtain robust estimates of annual metal contributions to water bodies and to the atmosphere from natural sources.

Résumé

Le présent rapport traite des méthodes actuelles d'estimation de l'apport relatif des sources anthropiques et naturelles de métaux dans l'environnement, l'accent étant mis sur les régions éloignées des sources industrielles ponctuelles. Il faut connaître les concentrations naturelles de fond et les phénomènes cycliques pour évaluer l'étendue et les répercussions des émissions anthropiques de métaux dans l'environnement. On est toutefois confronté à un manque de données critique et à de grandes incertitudes lorsqu'on tente de mesurer l'apport relatif des sources naturelles et anthropiques aux cycles géochimiques d'échelle planétaire, régionale et locale. L'incertitude de plusieurs ordres de grandeur associée aux inventaires d'émissions planétaires est une question importante, tout comme l'est l'incertitude dans la distinction entre les processus naturels d'accumulation et les effets anthropiques au moment de l'interprétation de la répartition des métaux dans le sol, la végétation et les sédiments lacustres. Il faut faire de la recherche pour obtenir des estimations sérieuses des apports annuels en métaux des sources naturelles, tant dans les étendues d'eau que dans l'atmosphère.

SUMMARY

A number of international agencies, including the International Joint Commission (IJC), the Organisation for Economic Co-operation and Development (OECD), and the United Nations-Economic Commission for Europe (UN-ECE), have formed task groups to address the growing concern about transboundary atmospheric movement of metals from industrial sources. This concern is based on a strong consensus in the environmental literature that trace metal concentrations in rural and remote ecosystems have increased significantly compared to natural background concentrations due to the long-range atmospheric transport of metals from industrial sources. In this context, the term "long-range atmospheric transport" refers to transoceanic or transcontinental atmospheric transport.

This literature review was undertaken to evaluate the evidence in support of the long-range atmospheric transport theory. The lines of evidence include global estimates of natural versus anthropogenic metal emissions, source identification in receptor models, the distribution of metals in remote and rural ecosystems, and regional scale mass

SOMMAIRE

Plusieurs organismes internationaux, dont la Commission mixte internationale (CMI), l'Organisation de coopération et de développement économiques (OCDE) et la Commission économique des Nations Unies pour l'Europe (CEE-ONU), ont mis sur pied des groupes de travail chargés d'étudier la question de plus en plus préoccupante du mouvement atmosphérique transfrontalier des métaux de sources industrielles. Cette préoccupation ressort d'un grand consensus dans la documentation sur l'environnement, selon lequel les concentrations des métaux traces dans les écosystèmes ruraux et éloignés ont augmenté sensiblement par rapport aux concentrations naturelles de fond, à cause du transport atmosphérique sur de longues distances des métaux d'origine industrielle. Dans ce contexte, l'expression «transport atmosphérique sur de longues distances» s'entend du transport atmosphérique transocéanique ou transcontinental.

La présente revue de la documentation a été entreprise pour évaluer la preuve réunie à l'appui de la théorie du transport atmosphérique sur de longues distances. Les éléments de la preuve comprennent des estimations comparatives à l'échelle planétaire des émissions naturelles et anthropiques de métaux, l'identification de sources dans des modèles de régions balance studies. These lines of evidence are evaluated with respect to the quality of the data, the validity of the underlying assumptions, and the uncertainty in distinguishing between metals of natural and anthropogenic origin. In each case, possible research directions to address the uncertainties are suggested.

Emissions of metals to the atmosphere, whether natural or anthropogenic, are among the most important inputs to long-range atmospheric transport models. In current receptor modelling, the anthropogenic component of metals in airborne particulates is estimated on the basis of particle size fraction, elemental ratios, Pb isotope ratios, and atmospheric enrichment factors. Uncertainty arises from the fact that, in remote areas (meaning several hundreds to thousands of kilometres from industrial point sources), these indicators could equally be used as evidence of natural sources. Uncertainties in source apportionment may be addressed through the development of improved geochemical methods of fingerprinting natural and anthropogenic sources.

A critical issue is the lack of representative data on natural metal releases to the atmosphere. Naturally occurring metals are transferred to the air in both particulate and gaseous form. Natural sources of airborne particulates include windblown dust, sea spray, volcanic dust, biogenic particles, and forest fire debris. Natural sources of gaseous metals include passive crustal degassing, volcanic activity, and methylation.

Estimates of the global metal flux from natural sources vary widely, with the result that the estimated ratios of natural to anthropogenic emissions are very uncertain. Discrepancies among estimates are due primarily to the lack of representative data rather than to differences in analytical quality of the data. Uncertainty also arises from differences in the estimation methods and differences in the underlying assumptions about the various sources and metal cycling processes at the Earth's surface.

There are critical information gaps and uncertainties associated with existing theories that long-range atmospheric transport is the chief source of metals in rural and remote ecosystems. The conclusion that regional geochemical variations in metal concentrations of vegetation and soil reflect anthropogenic influences is insupportable unless or until such studies include a quantitative assessment of the natural geochemical base line, and a description of the local geological sources and processes that influence metal distribution. Natural accumulation processes must be understood before any attempt is made to quantify atmospheric fallout based on surface enrichment in soil and lake or marine sediments.

réceptrices, la répartition de métaux dans des écosystèmes éloignés et ruraux, ainsi que des études de bilan massique à l'échelle régionale. Ces éléments de preuve sont évalués en termes de la qualité des données, de la validité des hypothèses sous-jacentes et de l'incertitude dans la distinction entre les métaux d'origine naturelle et ceux d'origine anthropique. Dans chaque cas, des avenues de recherche sont proposées pour aider à lever les incertitudes.

Les émissions de métaux dans l'atmosphère, qu'elles soient naturelles ou anthropiques, sont parmi les intrants les plus importants des modèles de transport atmosphérique sur de longues distances. Dans les modèles actuels de régions réceptrices, la composante anthropique des métaux dans les particules aériennes est évaluée en termes de fraction granulométrique, de proportions élémentaires, de proportions des isotopes du plomb et de facteurs d'enrichissement atmosphérique. L'incertitude tient du fait que, dans les régions éloignées (situées à des distances allant de plusieurs centaines à des milliers de kilomètres de sources industrielles ponctuelles), ces indicateurs pourraient aussi servir de preuve de l'existence de sources naturelles. L'incertitude quant aux apports relatifs des sources pourrait être levée en perfectionnant les méthodes géochimiques de prise d'empreintes des sources naturelles et anthropiques.

Une question critique est celle du manque de données représentatives sur les émissions naturelles de métaux dans l'atmosphère. Les métaux d'origine naturelle sont transportés dans l'air sous forme particulaire et sous forme gazeuse. Les sources naturelles de particules aériennes comprennent la poussière soulevée par le vent, les embruns marins, la poussière volcanique, les particules biogènes et les débris de feux de forêt. Les sources naturelles de métaux gazeux comprennent les émanations passives de la croûte, l'activité volcanique et la méthylation.

Les estimations du flux planétaire de métaux d'origine naturelle sont très variables, de sorte que les estimations des proportions d'émissions naturelles et d'émissions anthropiques sont très incertaines. Les écarts entre les estimations sont surtout associées au manque de données représentatives plutôt qu'à une qualité inconstante d'analyse des données. L'incertitude tient aussi aux différences entres les méthodes d'estimation et entre les hypothèses de départ quant aux divers cycles et sources des métaux à la surface de la Terre.

Il existe un manque de données critique et de grandes incertitudes quant aux théories actuelles selon lesquelles le transport atmosphérique sur de longues distances est la principale source de métaux dans les écosystèmes ruraux et éloignés. Il est inadmissible que des études puissent conclure que les variations géochimiques régionales des concentrations de métaux dans la végétation et le sol sont d'origine anthropique, à moins ou jusqu'à ce que ces études comportent, d'une part, une évaluation quantitative des concentrations de fond de divers métaux et, d'autre part, une description des sources et des processus géologiques locaux qui influent sur la répartition des métaux. Il faut connaître les processus naturels d'accumulation avant d'essayer de mesurer les retombées atmosphériques en fonction de l'enrichissement en métaux dans la partie supérieure du sol et des sédiments marins ou lacustres.

To evaluate the significance of trace metal deposition using a mass balance approach, all inputs of a given trace metal must be quantified (i.e., sources and pathways in the geosphere and biosphere, as well as the atmosphere). The mathematical treatment of trace metals is different from that of synthetic substances (e.g. PCBs, DDT, and Mirex), in that trace metal budgets require the quantification of natural loading in order to obtain a realistic estimate of total loading. Moreover, a clear understanding of all local natural and anthropogenic loadings to an ecosystem is required before firm conclusions can be drawn about the relative importance of long-range atmospheric transport.

This report does not discount the potential for long-range airborne transport of metals. However, underestimating the significance and variability of naturally occurring metals in remote areas can result in a systematic overestimation of the anthropogenic component of the global metal cycle. Further research is required to obtain robust estimates of total metal emissions to the atmosphere and to the oceans, in order to determine the relative contribution from anthropogenic sources. Such research must involve a systematic attempt to obtain spatially and temporally representative data on the natural release of metals at the global scale. This information is required to evaluate the significance of anthropogenic metal emissions in the context of the global geochemical cycle.

Pour évaluer l'importance des dépôts de métaux traces dans un bilan massique, il faut mesurer tous les intrants d'un métal trace donné (c'est-à-dire les sources et les voies de transport dans la géosphère et la biosphère, ainsi que dans l'atmosphère). Le traitement mathématique des données sur les métaux traces diffère de celui des données sur les substances synthétiques (par ex. les PCB, le DDT et le Mirex), en ce que, dans les bilans des métaux traces, il faut mesurer la charge naturelle pour obtenir une estimation réaliste de la charge totale. En outre, il faut bien connaître toutes les charges naturelles et anthropiques locales entrant dans un écosystème avant de tirer une conclusion certaine quant à l'importance relative du transport atmosphérique sur de longues distances.

Le présent rapport ne nie pas la possibilité du transport atmosphérique de métaux sur de longues distances, mais il se peut qu'en sous-estimant l'importance et la variabilité des métaux d'origine naturelle dans les régions éloignées, on surestime systématiquement la composante anthropique du cycle planétaire des métaux. Il faut poursuivre la recherche pour obtenir des estimations sérieuses des émissions totales de métaux dans l'atmosphère et dans les océans, afin de déterminer l'apport relatif des sources anthropiques. Une telle recherche doit s'appuyer sur un effort systématique visant à obtenir des données représentatives dans le temps et dans l'espace sur les émissions naturelles de métaux à l'échelle planétaire. Cette information est nécessaire pour évaluer l'importance des émissions anthropiques de métaux dans le contexte du cycle géochimique planétaire.

INTRODUCTION

Background

A number of international agencies, including the International Joint Commission (IJC), the Organisation for Economic Co-operation and Development (OECD), and the United Nations-Economic Commission for Europe (UN-ECE), have formed task groups to address the growing concern about transboundary atmospheric movement of metals from industrial sources. An example is the UN-ECE Convention on Long-Range Transport of Atmospheric Pollutants (LRTAP). This concern is based on a large number of scientific publications which conclude that the mobilization of trace metals by human activity has significantly increased the concentration of these substances all over the globe, to concentrations measurably above natural background levels.

It has long been established in the geoscience literature that trace metals occur naturally in the environment in significant and highly variable concentrations. The interpretation that has gained acceptance in the environmental literature, however, holds that metals observed in remote ecosystems are predominately industrial in origin, arising from long-range atmospheric transport. This review was undertaken to evaluate the evidence for the latter interpretation, from a geoscience perspective. The focus is on methods of identifying natural versus anthropogenic sources of metals in rural and remote areas, meaning areas located several hundreds to thousands of kilometres from industrial point sources (e.g. remote forests of the Precambrian Shield, Greenland glaciers, and the Canadian Arctic).

Purpose

The purpose of this report is to evaluate the evidence in support of the long-range atmospheric transport theory, and to suggest possible research directions to address the uncertainties. The criteria considered include the quality of the environmental data, the study design, and the statistical treatment of the data. The lines of evidence examined include global estimates of natural and anthropogenic metal emissions, source identification in receptor models, the distribution of metals in remote and rural ecosystems, and regional scale mass balance studies. These lines of evidence are discussed in terms of the validity of the underlying assumptions, and the uncertainty in distinguishing between metals of natural and anthropogenic origin.

Scope

The literature examined in this review deals largely with "total" element concentrations, meaning all chemical species of an element combined. A discussion of the behaviour of individual metal species in the environment and their potential effect on health is beyond the scope of this review.

The essential link between this review and the subject of "potential effects" is the underlying fact that large geographic regions of the globe are naturally enriched in certain metals, while other areas are depleted in these same metals. Research into the adaptive response of organisms to the natural enrichment or depletion of bioavailable metals in their environment (that is, on a geological or evolutionary time scale) is outside the scope of this review, but would be of particular significance to the risk assessment process.

Approach and sources of information

The first step in undertaking this review was to identify the global inventories, atmospheric models, and mass balance calculations that have been chosen by international task groups (under the auspices of the OECD, the IJC, and the UN-ECE) as the basis for policy and regulatory decisions. The next step was to search primary materials (journal articles in ecology, earth sciences, agriculture, environmental engineering and related disciplines, and government reports and databases) for the background information needed to evaluate these inventories and models from a geoscience perspective.

This review includes more than 130 references from the peer-reviewed scientific literature, conference proceedings, and government documents published over the past 25 years (1969 to 1994). With few exceptions, the ecological/environmental literature was found to focus on environmental pollution from metals and to contain sparse information on the natural biogeochemical cycling of metals. Information on natural sources and cycling processes was found in primary literature of the earth sciences and soil/agricultural sciences, and from basic textbooks on the geochemistry of metals in the environment.

CRITERIA FOR EVALUATING ENVIRONMENTAL DATA

Introduction

The scientific literature of the past 25 years records a long debate over the relative significance of anthropogenic and natural sources of metals in the environment, particularly in remote areas such as the Arctic. It is not the importance of considering natural sources of trace metals that is under debate. There is general agreement that natural background concentrations must be known in order to assess the extent and impact of anthropogenic sources. Rather, the debate centres on how much of the global metal cycle is from natural sources and how much is anthropogenic.

One underlying cause for the debate appears to be the significant uncertainty associated with attempts to estimate total metal emissions to the atmosphere globally, and the relative contributions to the total load from anthropogenic and natural sources. Another cause is the significant uncertainty associated with attempts to identify and quantify the sources of metals observed in environmental samples collected in remote areas. Existing techniques to estimate the relative contribution of natural and anthropogenic sources, and the uncertainties associated with these techniques, are summarized in Table 1. Each of these techniques is discussed in later sections of this review.

The present section discusses the criteria used in this report to evaluate existing inventories, models and mass balance studies. The criteria considered include (1) the analytical quality of the data (i.e. precision and accuracy), and (2) the representativeness of the data. In this section, "representativeness" is discussed in terms of both the study design and the statistical treatment of the data.

Analytical quality

To enable the reader to assess the validity of a study's conclusions, authors must provide an assessment of the quality of the analytical data. Ideally, such an assessment includes a measure of the precision of the analytical method using appropriate replicate analysis, and a measure of the accuracy through the use of closely matched standard reference materials (Hall, 1993, 1995). Accuracy cannot be easily assessed where standard reference materials are not available. This is a particular problem in the analysis of natural waters for trace metals. In such cases, interlaboratory comparisons can serve to identify a systematic bias in results (Hall, 1993).

The ratio of the metal concentration in the sample relative to the method detection limit is often used as a guide to the uncertainty associated with reported data. This ratio tends to be low in biological samples, such as body fluids, which have a complex matrix containing high concentrations of interfering substances. The ratio also tends to be low in aqueous samples which contain metals in ultratrace concentrations (ppt or ng/L range and lower). Extreme care is required to carry such samples through all stages of the analysis – collection, storage, preconcentration, and determination – without introducing contamination or losses.

A number of handbooks and review articles (e.g. Keith, 1988; Baeyens, 1992) indicate that there has been an overall decrease in "average background concentrations" of trace metals in marine and fresh waters reported in the 1980s literature compared to the 1960s literature. This downward trend over the past decades is not attributed to pollution abatement policies, but rather to the elimination of errors caused by contamination during sampling (Barcelona, 1988) and to lower detection limits resulting from the development of more sensitive instruments (Baeyens, 1992). For example, Fitzgerald and Watras (1988) showed that, as investigators recognized and controlled their sampling errors, background Hg concentrations reported for surface waters of Vandercook Lake (Wisconsin, U.S.A.) decreased from about 241 ng/L in 1983 to 0.5 ng/L in 1986. Similarly, earlier studies of environmental sampling and analysis (e.g. Patterson and Settle, 1976; Bruland and Franks, 1979) concluded that the apparent decrease in average levels of Pb and other trace metals in the oceans was due to improvements in sample collection and handling techniques.

A "rule of thumb" frequently repeated in the environmental literature is that trace metal studies completed prior to the 1980s should be disregarded, on the assumption that older data cannot be considered reliable. While it is true that there have been significant improvements in sampling and analytical methods, as indicated by the reviews quoted above, publication date is not necessarily a valid measure of scientific merit. First, the use of a new instrumental method of detection is not an automatic guarantee of high quality data. The sample collection, preparation, decomposition, and preconcentration steps are just as critical to precision and accuracy as the detection step (Hall, 1995). Second, many researchers who published trace metal work before 1980 carefully monitored and reported their analytical precision and accuracy. On the other hand, there are many post-1980 publications which contain no assessment of data quality whatsoever. It is the ratio of the metal concentration in the sample to the method detection limit that should be used as a general guide to the reliability of the analytical data, rather than the publication date.

Quality of study design

Apart from the analytical quality of the data (precision and accuracy), another important concern is the representativeness of the data. To determine the degree to which a study area is influenced by anthropogenic sources of metals, it is critical that the field survey be designed to adequately characterize the natural background variation in that area. Many studies which attribute regional spatial variations of metals in rural and remote areas to human perturbation of the environment were designed on the assumption that "background" may be taken as a constant value over large geographic regions (discussed further in "Distribution in remote and rural

Table 1. Current tools used to quantify the relative contribution of natural and anthropogenic sources of trace metals in rural and remote areas.

Tool for quantifying anthropogenic vs. natural metals in remote areas	Sample medium	Uncertainties
Global inventories of industrial emissions to the atmosphere Global inventories of natural emissions to the atmosphere	• typically based on production and consumption statistics • typically based on natural particulate emissions (deflated soil and sediment; forest fire debris; sea salt; volcanic dust and volatiles; biogenic particles)	• scarcity of temporally and spatially representative data to calculate emission factors • lack of gaseous flux data • statistical treatment of data • the role of critical non-atmospheric pathways (e.g., seafloor interactions) • nonparallel comparisons of natural and anthropogenic releases
Enrichment in sample relative to average crustal abundance (often normalized to Si or Al) used to identify industrial source	• rain, snow, ice cores • dry deposition (aerosols) • mosses and lichens	• natural organic & inorganic partitioning and enrichment processes cause natural trace metal levels (and elemental ratios) to vary by orders of magnitude
Trace element signatures used to identify industrial sources	• rain, snow, ice cores • dry deposition (aerosols)	• alternate explanations due to the same trace element signatures arising from natural processes
Pb isotope signatures used to distinguish overlapping influence of distant industrial sources	• rain, snow, ice cores • dry deposition (aerosols)	• alternate explanations due to the same Pb isotope signatures arising from natural sources (distant or local)
Particle size to indicate source: • metals on < 2 μm fraction assumed industrial source; • 2-10 μm fraction (and larger) assumed locally derived	• atmospheric aerosols	• particle size not diagnostic as soil dust also contains fine fraction • metals are naturally enriched in the < 2 μm fraction of soil (due to large surface/volume ratio, hydroxides, oxides, organic debris)
Enrichment in modern surface samples compared to samples from deeper, older horizons; used to infer an increase in atmospheric loading of trace metals	• soil • lake sediments • peat bogs	• influence of REDOX gradient, diagenesis, mobility of metal-organic complexes, organic decay • natural metal accumulation due to plant uptake & decay
Regional scale spatial variations in metal concentrations used to infer anthropogenic influences	• soil • mosses • sediments	• background variation due to geology ignored or oversimplified • regional differences due to organic matter and climate
Mass balances (input-output budgets) used to quantify anthropogenic loadings	• local and regional scale watershed models • global reservoirs	• natural inputs are needed to calculate total loading; i.e., the annual flux to water and air from natural sources of metals

ecosystems"). The assumption of a "constant average background" is not supported by worldwide geochemical survey data, which indicate that the natural abundance of trace elements in many sample media can vary by 2 to 3 orders of magnitude over short distances, and up to 5 or 6 orders if samples from rare types of high-grade mineral deposits are included (Darnley, 1995).

The importance of obtaining representative data has been emphasized in the estimation of Pb emissions from natural sources (discussed further in "Global inventories of natural and anthropogenic emissions"). For example, Nriagu's (1989) estimate of the global Pb flux from volcanoes ranges over four orders of magnitude from 540 kg/a to 6000 t/a. This 10 000-fold uncertainty was attributed to the difficulty in obtaining temporally representative data due to the episodic nature of volcanoes (Nriagu, 1989). Jaworowski et al. (1981, 1983) observed that orders-of-magnitude variation in natural atmospheric Pb concentrations also occur spatially, depending on proximity to volcanoes and other geological anomalies. Jaworowski's study design was based on the premise that to obtain globally representative emissions data using glacier ice and snow cores, one must sample from various parts of the Earth, and not only from Greenland and Antarctica as had been the practice of other workers (e.g. Murozumi et al., 1969; Ng and Patterson, 1981).

The issue of representative data has been the subject of considerable debate in the literature. Patterson (1983) countered the views of Jaworowski et al. (1981, 1983) with the assertion that "*there is no 1000-fold uncertainty concerning the natural emission flux of lead to the atmosphere from volcanoes*". The sampling scheme of Patterson and colleagues had been based on the assumption that spatial and temporal variations in atmospheric Pb concentrations previously reported by Jaworowski and others were simply an artifact of sample contamination (i.e. poor analytical quality) during the collection and handling of snow and ice cores.

It is true that the avoidance of sample contamination is of extreme importance (see "Analytical quality") but it is also true that orders-of-magnitude variation in atmospheric Pb concentrations can arise for reasons other than erroneous data. The analytical quality of data used in a global estimate can be excellent, but if the data are not spatially and temporally representative (usually because there are too few sampling sites and/or too short a sampling period), then a global estimate based on that data may be either too high or too low. Sources of natural variation are discussed further in "Global inventories of natural and anthropogenic emissions" and "Source apportionment in receptor models".

Although this review deals primarily with long-range atmospheric transport studies, it may be added that it is equally important to characterize background in field surveys close to industrial sources. A recent humus and till survey in Manitoba, Canada (Henderson and McMartin, 1995) is an example of a mapping study designed to account for atmospheric fallout in the context of the natural geological background variation. A lack of attention due to background variation can lead to erroneous conclusions. For example, a US-EPA study (Crockett and Kinnison, 1979) investigated the concentration gradient of Hg in soil around a major coal-fired power plant. Previous studies using the same sample type (soil) in the same location had concluded that Hg concentrations were significantly higher in the vicinity of the power plant due to local atmospheric fallout. The US-EPA study, on the other hand, concluded that Hg concentrations around the plant were not significantly elevated above background. It was explained by the authors (Crockett and Kinnison, 1979) that the earlier investigations had limited usefulness due to the small number of samples involved, inadequate statistical treatment of the data, and lack of attention to confounding factors such as terrain and natural background levels of Hg.

Statistical treatment of data

Trace metal concentrations in natural earth materials vary by orders of magnitude and tend to display frequency distributions that are positively skewed (i.e., having a long right tail) or bimodal (Skinner, 1976). Talbot and Simpson (1983) noted that ecologists and biologists tend to base their interpretation of environmental data on the *a priori* assumption that samples are taken from a normally distributed population. These authors warn against the serious errors that may arise out of this assumption. Talbot and Simpson (1983) join many exploration geochemists (Miesch, 1976; Rose et al., 1979; Garrett and Goss, 1979; Brooks, 1995) in recommending that a sound statistical approach is to carefully examine the spread of the data before assuming a normal population, and to report median and modal values, or geometric means.

The importance of evaluating statistical methodologies can be illustrated using existing inventories of anthropogenic metal emissions. Assessing regional variability was considered by Voldner and Smith (1989) to be the overriding priority in calculating emission inventories. Their survey of coal burned in North America, for example, indicated that Hg concentrations in coal range from 0.10 to 0.24 ppm (g/t), depending on the type of coal being burned and the geological origin of the coal (Voldner and Smith, 1989). In contrast, a widely-cited global Hg inventory (Nriagu and Pacyna, 1988) was calculated using emission factors of 0.5 to 3.0 g/t for industrial and domestic coal combustion. That is, the lowest emission factor used in the global inventory (0.5 g/t) was higher than the highest concentration reported for North American coal (0.24 g/t). Even if 100% of the Hg in North American coal were emitted to the global atmospheric cycle (which is not the case), the global emission factors could not be considered representative of North American emissions.

Nriagu and Pacyna (1988) indicated that median concentration values for each source category (e.g. ore smelting, coal combustion) were used to estimate the global anthropogenic emission of each element. Their estimated median values appear to be equivalent to values calculated using

$$\frac{\text{min} + \text{max}}{2}$$

where min and max are the lowest and highest values given in their data tables. This equivalence would be expected if the observations came from a symmetrical distribution function

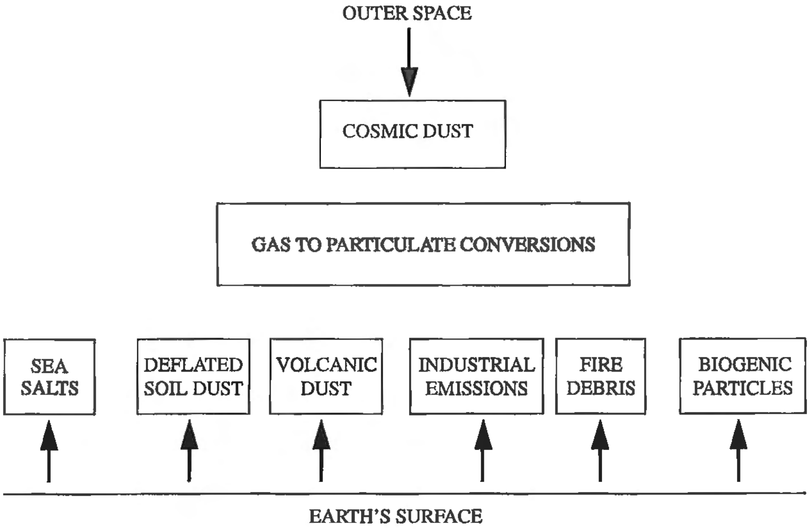

Figure 1.

Sources of atmospheric particulates (adapted from Pye, 1987).

such as a normal distribution. However, normally distributed metal concentration data for raw materials such as ore and coal are the exception rather than the rule, pointing to uncertainty in these emission estimates. To further evaluate these estimates would require additional information, in particular a sample distribution function. Nevertheless, emission estimates which are calculated using the highest and lowest values for each source category are not considered "robust" in a statistical sense (see Andrews et al., 1972). Such estimates are inordinately sensitive to the choice of the highest value due to the fact that the skewness tends to be positive (i.e. a long right tail). Significant errors in global estimates may result, because of the importance attached to a few extreme values (3.0 g/t in the case of Hg in coal[1]). This example underscores the importance of examining the spread of data before assuming a symmetrical distribution (Talbot and Simpson, 1983).

GLOBAL INVENTORIES OF NATURAL AND ANTHROPOGENIC EMISSIONS

Emissions of metals to the atmosphere, whether natural or anthropogenic, are the most important inputs to long range atmospheric transport models (Royal Society of Canada, 1984). Emission inventories have historically been used as air quality planning tools, but limited research has been performed to quantify emission inventory uncertainties. The Royal Society of Canada (1984) emphasized the need for a strategy to evaluate such uncertainties, and to determine how these uncertainties affect conclusions based on long range atmospheric transport models. By identifying the difficulties in distinguishing between natural and anthropogenic sources of metals in the environment, this report is a first step in addressing that need. Ultimately, a strategy is required to formally quantify the uncertainties in global inventories and source apportionment models.

The significance of natural emissions to the atmosphere

Estimates of the global flux of metals from natural sources are commonly obtained by multiplying the annual particulate flux from a given source (in tonnes/year) by a metal "emission factor" representative of that source (in grams/tonne). Most existing global inventories are generated from literature surveys, using emission factors derived from reported measurements of metal concentrations in particulate materials and gases[2].

Natural sources of airborne particulates include windblown dust, sea spray, volcanic emissions, biogenic material, and forest fire debris (Fig. 1). Natural gaseous metal emissions (not shown in Fig. 1) include crustal degassing, volcanic gas emissions, and the methylation of certain metals to volatile forms (e.g. Hg, Se, As). Methylation occurs through both biologically mediated and abiotic reactions.

Estimates of the global primary particulate flux vary widely, but indicate that natural sources account for at least 93% of the total (Table 2). Not included in Table 2 are estimates of gas-to-particulate phase conversions in the atmosphere. Conversions of industrial gases to particulates are estimated to contribute up to 248 x 10^6 t/a, and conversions of natural gases to particulates are estimated to contribute 478-2113 x 10^6 t/a of particulates (references cited by Pye, 1987). Other estimates cited by Chester (1986) for particulate emissions from industrial sources range from 30 x 10^6 t/a

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[1] For example, Hg emissions from industrial and domestic coal combustion sources are estimated at 495 to 2970 t/a (Nriagu and Pacyna, 1988). This is equivalent to the lowest and highest emission factors (0.5 g/t and 3.0 g/t respectively) multiplied by a global production/consumption figure of 990 x 10^6 t/a (using data provided). Adding all other source categories results in a total emission estimate of 910 to 6200 t/a. The total estimate is 3560 t/a, approximately the average of the low and high values.

[2] The term "aerosol" is generally used to refer to the particulate phase alone, although some references apply the term to both the gas and particulate phases of a system.

Table 2. Global estimates of particulate emissions from natural and anthropogenic sources.

Source of airborne particulates	Annual production estimates (cited by Pye, 1987; units in t/a)	Comments (from Pye, 1987)	Annual production estimates (from Nriagu, 1989; units in t/a)
Wind deflation of sediments and soils	$61 - 366 \times 10^6$	not including short-range, low level dust transport; if included estimates range up to 5000×10^6	$60 - 500 \times 10^6$
Sea salts	$508 - 1113 \times 10^6$	relative importance declines toward continental interiors	$1000 - 10\,000 \times 10^6$
Fire debris	148×10^6	5 t/a estimated for <5 µm fraction	$200 - 1500 \times 10^6$
Volcanic dust	$4 - 25 \times 10^6$	dust from explosive eruptions can extend worldwide in 3 weeks	* 10×10^6
Cosmic dust	$0.02 - 0.2 \times 10^6$	difficult to distinguish from industrial fly ash	not given
Industrial emissions	$38 - 112 \times 10^6$	main sources: smoke stacks, stockpiles, waste dumps, open-cast pits and quarries	not given
Biogenic particulates (e.g. pollen, spores, waxes, leaf and needle fragments, fungi, algae, etc.)	not included		$100 - 500 \times 10^6$
total natural particulate production (from above estimates)	$721 - 1652 \times 10^6$		$1370 - 12\,510 \times 10^6$
total particulate production (natural + industrial)	$759 - 1764 \times 10^6$		not calculated
proportion of global particulate production from industrial sources	5 - 6 %		not calculated

* Nriagu, 1979

Table 3. Uncertainty in estimated ratios of anthropogenic to natural Pb emissions to the atmosphere. The estimate by Kownacka et al. (1990) was based on long-term stratospheric and tropospheric measurements over Europe, while that of Nriagu (1989) was based on a literature survey. Estimated proportion of the natural and anthropogenic particulate flux included for comparison.

Global emissions to the atmosphere	Annual flux of primary particulates	Annual flux of Pb to the atmosphere	
Anthropogenic sources	**7%**	**96%** (3.32×10^5 t/a)	**9.7%** (3.6×10^5 t/a)
Natural sources	**93%**	**4%** (1.2×10^4 t/a)	**90.3%** (3.34×10^6 t/a)
Reference	Strauss (1978)	Nriagu (1989)	Kownacka et al. (1990)

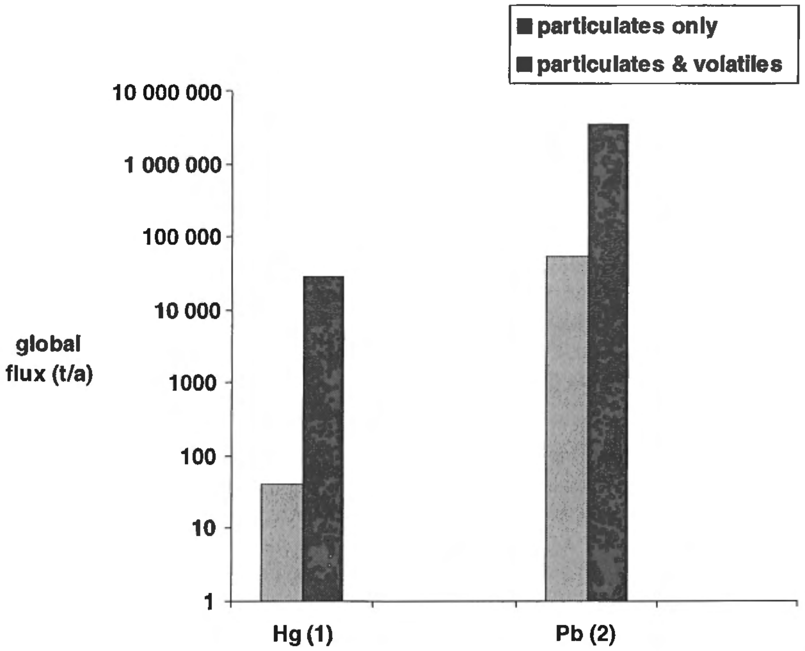

Figure 2.

Different estimates of natural global emissions based on different methods of calculation by the same authors. (1) Hg estimate by Lantzy and Mackenzie (1979), and (2) Pb estimate by Kownacka et al. (1990). Note the logarithmic scale.

(direct particulate flux only) to 200 x 10^6 t/a (including direct particulate flux and gas-to-particulate conversion flux combined).

Ratios of natural versus anthropogenic emissions

Global inventories are commonly used to compare the relative contribution of natural and anthropogenic emissions to the atmosphere. Inventories by Nriagu and Pacyna (1988) and Nriagu (1989) estimated that, on a global scale, industrial emissions of many trace metals equal or exceed natural emissions. For example, worldwide emissions of Ni, Cr, Cd, and Pb from natural sources were estimated to be 30 000, 44 000, 1300, and 12 000 metric tonnes per year (t/a) respectively (Nriagu, 1989). In comparison, worldwide emissions of Ni, Cr, Cd, and Pb from anthropogenic sources were estimated to be 56 000, 30 000, 7600, and 332 000 t/a respectively (Nriagu and Pacyna, 1988; Nriagu, 1989). Thus, the proportion of the global atmospheric load of Ni, Cr, Cd, and Pb arising from industrial sources were estimated at 65%, 41%, 85%, and 96% respectively (Nriagu, 1989).

In fact, global estimates of natural emissions vary widely, with the result that estimated ratios of natural to anthropogenic emissions are very uncertain (Environment Canada, 1987). Compare, for example, two recent estimates of the natural to anthropogenic Pb flux ratio (Table 3). The large difference between these estimated proportions (Table 3) is due mainly to uncertainty in the estimate of the global natural flux, as both estimates were based on a similar value for the anthropogenic flux.[3]

The above example demonstrates the importance of obtaining accurate information on global natural sources. However, significant uncertainty is also associated with existing global anthropogenic emission estimates. Data compilations by the International Lead and Zinc Study Group (1990) and the OECD (1993) indicate that the above estimates of the global Pb flux from anthropogenic sources should be revised.

A major source of uncertainty in global natural flux estimates is the magnitude of gaseous metal emissions (Jaworowski et al., 1981). Estimates based on the particulate flux alone are generally much lower than those based on the total flux (gaseous flux plus particulate flux). For example, Lantzy and Mackenzie (1979) included both estimation methods to calculate the global Hg flux (Fig. 2). When crustal degassing was included along with the particulate flux, the total flux estimate was three orders of magnitude higher than the estimate based on particulate flux alone (displayed on a logarithmic scale in Fig. 2). Similarly, global Pb flux estimates based on particulate emissions alone by Kownacka et al. (1990) are about two orders of magnitude lower than estimates based on their measurements of the total atmospheric burden (Fig. 2). To address these uncertainties in the global metal cycle, globally representative data describing the gaseous metal flux from natural sources are needed.

Estimates of the global natural emissions of Hg range over two orders of magnitude, as illustrated in Figure 3. A similarly wide range of estimates, from 2500 to 125 000 t/a, was cited by the OECD (1994). Using a global anthropogenic estimate[4] of 3600 t/a (from Nriagu and Pacyna, 1988), these estimates suggest that the natural proportion of the total global Hg flux could range anywhere from >97% to 41%. In Canada, the natural proportion of the total annual Hg flux may be estimated at about 98% based on a ratio of 3500 t/a from natural sources (Environment Canada, 1987, citing EPS, 1981) to 46 t/a from anthropogenic sources (Environment Canada, 1995).

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[3] Existing global anthropogenic estimates are subject to revision in light of recent advances in emission source monitoring.

[4] Uncertainties associated with the anthropogenic estimate are discussed in "Statistical treatment of data".

Natural emission estimates which are based on the total atmospheric metal burden (e.g. Weiss et al., 1971; Kownacka et al., 1990) tend to be orders of magnitude higher than estimates which are based on source emission factors (e.g. Nriagu, 1989). For example, Weiss et al. (1971; Fig. 3) based their total Hg flux estimate of 150 000 t/a on average atmospheric elemental mercury (Hg^0) concentrations measured in unpolluted air (1 ng/m^3). On the other hand, Nriagu (1989; Fig. 3) arrived at a much lower flux estimate of 2500 t/a (ranging from 100 to 4900 t/a) using the particulate flux estimates listed in Table 2 and emission factors derived from the literature for each source category (discussed further in "Natural sources of aerosols").

Although there have been significant improvements in environmental sampling and analysis over the past 25 years (see "Analytical quality") there is no evidence that these improvements account for discrepancies among existing global inventories (Table 3, Fig. 3) as has been suggested by some reviewers. For example, the background value of 1 ng/m^3 used in the estimate by Weiss et al. (1971) is in agreement with measurements of background concentrations of Hg in air (1-4 ng/m^3) cited by Lindqvist et al. (1991). Thus, it is differences in the methods of estimation rather than differences in analytical quality that have created the discrepancy between the more recent Hg flux estimate by Lindqvist et al. (1991, Fig. 3) and the earlier estimate by Weiss et al. (1971, Fig. 3). Similarly, the natural emissions inventory published by Nriagu (1989) was based on a survey of previously published literature.

In summary, the large discrepancies among estimates of the global metal flux from natural sources (Table 3; Fig. 2, 3) appear to be due primarily to the lack of representative data rather than to differences in analytical quality of the data. Other causes are the differences in estimation methods, and differences in the underlying assumptions about metal cycling processes at the Earth's surface. A critical issue is the lack of data on natural gaseous emissions of metals from volcanic activity, passive crustal degassing, and methylation.

Natural sources of aerosols

Deflated soil and sediment

Uncertainties in estimating global metal fluxes from deflated soil and sediment (windblown dust) arise from the orders-of-magnitude variation in metal concentrations of unconsolidated surface materials (Darnley, 1995), the fact that such geochemical data do not tend to be normally distributed (Darnley, 1995), and the difficulties in estimating the global annual terrigenous dust flux (Pye, 1987). The latter is reflected by the variation in global dust flux estimates cited in the literature, which range from 61 x 10^6 t/a to 5000 x 10^6 t/a (Pye, 1987).

It is difficult to choose a meaningful and representative global emission factor to account for unconsolidated surface materials subject to wind deflation. The uncertainty is illustrated by the orders-of-magnitude variability in the global range of metal concentrations in natural soils (Table 4). The use of average crustal abundances is an unsatisfactory method of calculating emission factors because metal concentrations in sediments and soils are often 2 to 3 times higher than the crystalline bedrock from which they are derived, with maximum levels up to 20 times higher (Ledin et al., 1989). The emission factors for Ni, Cr, and Pb chosen by Nriagu (1989) are similar to or lower than average crustal abundances, and are at the low end of the global range in natural soils (Table 4).

A further source of uncertainty is the question of size fraction used in the determination of metal concentrations in soil and sediment samples. "Typical global ranges" of metal concentrations of soils (Table 4) provide conservative estimates as these values are based on the <2 mm fraction, which is the sieve aperture used in the soil and agricultural sciences. A large number of geochemical maps included in the Global Mapping Project (Darnley, 1995) are based on finer fractions (e.g. the < 177 µm, <63 µm, or <2 µm fractions).

In most soils, the finer fractions tend to have higher concentrations of trace metals than the coarser fractions (Rose et al., 1979; Forstner and Wittman, 1983). The <2 µm fraction

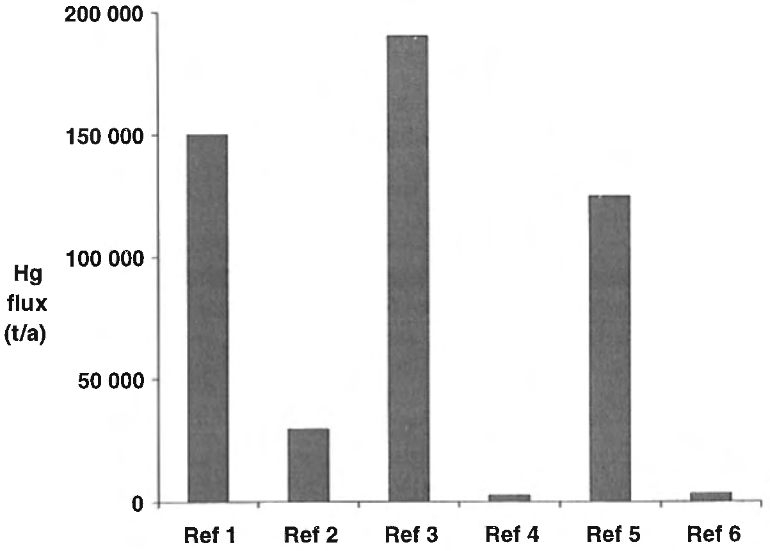

Figure 3.

Variation in estimates of the natural global Hg flux arising from different methods of calculation. (1) Weiss et al., 1971; (2) Lantzy and Mackenzie, 1979; (3) Jaworowski et al., 1981; (4) Nriagu, 1989; (5) IPCS, 1989; (6) Lindqvist et al., 1991. The 1989 estimate by IPCS (Ref 5) ranges from 25 000 to 125 000 t/a, and refers to "crustal degassing" only.

Table 4. Uncertainty in estimates of natural Ni, Cr, and Pb emissions to the atmosphere from soil deflation

Database	Ni	Cr	Pb	Reference
global range in natural soils (g/t or ppm)	5-500	5-1000	2-200	Trudinger et al. (1979); Bowie and Thornton (1984) citing Levinson (1974)
average crustal abundance (g/t or ppm)	75	100	12.5	Bowie and Thornton (1984)
range (g/t or ppm) used to calculate soil emission factors	30-40	60-100	5.0-15	basis for estimate of global flux from wind-borne soil particles (Nriagu, 1989)

of soil and surficial sediments is particularly enriched in metals because fine particles have a large surface area per unit mass and because the fine fraction is enriched in substances active in metal bonding, including hydrous oxides and hydroxides, organic substances, and other weathering products (Forstner and Wittman, 1983). Fine sieve fractions are often used in the earth sciences (e.g. Bell and Franklin, 1993; Kettles and Shilts, 1994) and have direct relevance to the calculation of emission factors because most dust that is carried by long-range atmospheric transport is less than 10 μm and much is less than 2 μm (Pye, 1987).

Volcanic emissions

At present, there is a lack of globally representative data on metal emissions from volcanic activity. As a result, existing global estimates for this source category have relied on a sparse data set compiled from the literature, most of which is derived from studies having unrelated purposes. This procedure for generating natural emission inventories has been criticized as a totally inadequate substitute for continuous monitoring data (Royal Society of Canada, 1984).

The uncertainty introduced by the lack of representative data is illustrated by the wide discrepancies among global estimates of volcanic emissions, which vary by orders of magnitude. For example, estimates of the volcanic Pb flux based on Pb/S ratios and particulate emissions are generally 10-fold to 100-fold lower than estimates based on measured changes in Pb concentrations in the upper atmosphere following volcanic eruptions. This discrepancy is due in part to the lack of globally representative gaseous flux data (Kownacka et al., 1990). However, even estimates based on the same calculation method, for example the Pb/S ratio method, vary by over four orders of magnitude, from 0.540 t/a to 6000 t/a (Environment Canada, 1987; Nriagu, 1989).

Global estimates of volcanic Hg emissions also vary by orders of magnitude. As in the case of Pb flux estimates, Hg flux estimates based on Hg/S ratios are significantly lower than Hg flux estimates based on the continuous monitoring of Hg vapour emissions in volcanic zones (Varekamp and Buseck, 1986; Siegel and Siegel, 1987; Ferrara and Maserti, 1990).

Uncertainties in estimating global metal fluxes from volcanic sources arise from the technical difficulty of making field measurements (Varekamp and Buseck, 1986), the lack of spatial and temporal representativeness of the limited data that do exist (Le Cloarec and Marty, 1990), and lack of agreement between the very different estimation methods being used (see Ng and Patterson, 1981; Jaworowski et al., 1981, 1983; Patterson, 1983; Kownacka et al., 1990). Extrapolations from isolated, short term measurements are imprecise due to significant variations in the composition of emissions from one volcano to another, and from one event to another in the same volcano (Le Cloarec and Marty, 1990).

Research necessary to understand the global significance of volcanic metal emissions includes 1) the development of the capability to monitor volcanic metal emissions, with particular attention to metal partitioning between condensed (particulate) and gaseous phases (Taran, 1989; Hinkley, 1991; Symonds, 1994), 2) measurement of the passive flux of volatile metals between volcanic events (Siegel and Siegel, 1987; Ferrara and Maserti, 1990), and 3) quantification of the transfer of metals from the oceanic crust to seawater (Le Cloarec and Marty, 1990).

Forest fire debris

The sources of uncertainty associated with calculating metal emissions from forest fires include regional variations in the geochemistry of forest soils (see "Deflated soil and sediment"), the significant variation in the metal accumulation behaviour between different forest species, and variations in estimates of the particulate flux from forest fires. According to Nriagu (1989), estimates of the particulate flux from forest fires vary by about an order of magnitude, from 200 - 1500 x 10^6 t/a.

No attempt to evaluate the first two sources of uncertainty could be found in existing inventories. Ashed samples of the volatile components of trees (foliage and twigs) typically contain 50-100 g/t Pb, but ashed samples of some species contain concentrations up to 19 000 g/t Pb (Dunn, 1995). Chromium and nickel concentrations in ashed plant samples typically range up to about 180 g/t (Dunn, 1995). Of significance to local studies is the report by Peterson (1986) that much higher metal values (e.g. Ni in % range, Cr in mg/g range) may be found in certain accumulator species.

Much lower emission factors for forest fire particulates (0-0.12 g/t for Cr; 0.5 -3.5 g/t for Ni; 0.1-2.5 g/t for Pb) were calculated by Nriagu (1989) using an alternate estimation method. The wide variation among methods of estimating emission factors suggests an uncertainty of at least 3 to 4 orders of magnitude for this source category.

Biogenic emissions

The biogenic emissions category includes airborne particulates (e.g. pollen, spores, waxes, leaf and needle fragments, fungi, algae) and biologically mediated volatilization processes (Nriagu, 1989). Evidence of the long-range transport capability of airborne biogenic particles is provided by the discovery of tree pollen in snows of the high Arctic (Bourgeois et al., 1985).

Biogenic emissions have been identified as playing a dominant role in transferring metals to the atmosphere on a global scale, and are considered by some to be at least as significant as nonbiogenic sources (100-500 x 10^6 t/a; Nriagu, 1989). The Royal Society of Canada (1984) emphasized the need for continuous monitoring data to estimate natural metal emissions. This research need is particularly apparent in the evaluation of biogenic emissions of metals to the atmosphere. Nriagu (1989) and others have indicated that this category has been ignored or badly underestimated in most natural source inventories.

Oceanic emissions

There is a scarcity of accurate data on metal transfer across the air-sea interface for trace elements such as As, Cd, Hg, and Pb (Buat-Menard and Duce, 1987). These data are difficult to obtain, due to the significant spatial and temporal variability of trace metal concentrations in the air over the ocean, the difficulty in analyzing trace metals in seawater, and the theoretical and experimental difficulties in calculating the net flux (Patterson, 1974; Buat-Menard and Duce, 1987). Buat-Menard and Duce (1987) emphasized that one of the major mysteries in this field of research is the lack of knowledge of all the natural sources of these metals.

Recent attempts to model the global Hg cycle provide an example of the importance of understanding the significance of the natural metal content of the ocean. Global Hg budgets reviewed by Mason et al. (1994) suggest that oceanic emissions account for 30% of the total global Hg flux to the atmosphere. Emission inventories (e.g. Lantzy and Mackenzie, 1979; Nriagu, 1989) have previously classified oceanic Hg emissions as a natural source. In contrast, a recent budget (Mason et al., 1994) attributes the oceanic evasion of Hg to an increased oceanic Hg burden that has resulted from human activities. This new budget attributes 70 to 80% of the oceanic Hg flux to anthropogenic origins (Mason et al., 1994). Reinterpretations of existing Hg emission data are discussed further in "New interpretations of previously collected data".

A drawback of the global Hg budget of Mason et al. (1994) is the omission of the potential contribution of Hg to seawater from submarine volcanic activity and other seafloor hydrothermal systems. This pathway is also missing from the global budget of Lindqvist et al. (1991). Preliminary estimates based on Hg/heat ratios suggest that the annual Hg flux from the oceanic crust to the oceanic reservoir is sufficient to account for the annual flux of Hg from the oceans to the atmosphere (Rasmussen, 1994). These calculations indicate that consideration of seafloor hydrothermal systems would significantly decrease the proportion of the oceanic flux attributed to anthropogenic sources in the current global budgets.

The study of seafloor hydrothermal systems is a relatively new field of research (two decades) which has led to a major re-assessment of the Earth's geochemical budgets for a number of other trace elements, including Pb, As, Cu, Zn, and Co (Baker et al., 1993; Lowell et al., 1995). The state of understanding of the global impact of hydrothermal heat and chemical flux through the Earth's crust, the upper ocean and biosphere, and the variation of this flux through time is summarized in the Final Report of the RIDGE/VENTS Workshop (1994). This report indicates that the influence of submarine hydrothermal systems on the chemistry of mid-depth and surface waters partly depends on the efficiency of vertical transport processes. Vertical transport mechanisms include both physical and biological processes, as illustrated in Figure 4.

Limitations and assumptions involved in modelling the global influence of submarine hydrothermal systems were discussed by Baker et al. (1993) and Lowell et al. (1995). Li (1991) summarized current progress in modelling the partitioning of elements between marine solid phases and seawater, and explained how this partitioning behaviour influences seawater composition and oceanic residence times of different minor and trace elements.

The concept of a "mobilization factor"

A "mobilization factor" is generally defined as the ratio of the total mass of an element released to the environment from all anthropogenic sources to the total mass released from all natural sources. Mobilization factors are often based on global atmospheric inventories in which metal emissions from natural and anthropogenic sources are expressed in tonnes/year (see Lantzy and Mackenzie, 1979; Galloway et al., 1982). The estimated proportions of anthropogenic and natural emissions of Ni, Cr, Cd, and Pb listed previously (see "Ratios of natural versus anthropogenic emissions") are examples of mobilization factors.

Caution is advised in the use of mobilization factors because there are significant uncertainties associated with the data used in calculating them, as discussed below. Anthropogenic emission inventories are often constructed using metal production and consumption statistics, emission factors derived from literature surveys, and "professional guesswork" (Voldner and Smith, 1989). Unless there are actual measurements of anthropogenic emissions (i.e. source tests), it is not known what percentage of waste metals actually escapes to the atmosphere and what percentage is released to the environment by other routes, such as liquid discharges and solid waste disposal. Voldner and Smith (1989) provided an example of the uncertainty associated with emission estimates by comparing three North American inventories of Cd emissions (US-EPA, 1981; Radian Corporation, 1984; and Mead et al., 1986). Their comparison indicated that emission factors in one inventory (US-EPA, 1981) were consistently higher than in the others, especially oil combustion factors which were seven times higher.

Before firm conclusions can be made on the basis of "mobilization factors", the representativeness of the values used to calculate existing anthropogenic and natural inventories should be evaluated. First, the statistical reduction of data used in making estimations must properly account for the regional variability of the metal content of raw material in each source category (Voldner and Smith, 1989). Second, global estimates calculated by averaging highest and lowest values for each source category are inordinately sensitive to the choice of the high value (see "Statistical treatment of data"). Thus, the magnitude of emissions may be either overestimated or underestimated depending on the choice of the high value. Finally, natural emission estimates vary by orders of magnitude as discussed previously, with the result that the estimated "mobilization factors" are very uncertain.

Discrepancies among existing emission inventories illustrate the need for refinement and standardization of methods of estimating anthropogenic metal emissions. An example is provided in Table 5, which compares local, regional, and global inventories of selenium (Se) emissions from the nonferrous metal smelting sector. A regional inventory (EPS, 1977) estimated total Se emissions from all Canadian Cu-Ni mining and processing sources at 138 t/a. Except to say that the estimates were based on source testing and literature reviews, this inventory did not detail the method of calculation. For a single Canadian location (Sudbury, Ontario), Nriagu and Wong (1983) estimated that the total release of Se to the environment is 630 t/a, of which 50 t/a is dispersed through the atmosphere and the remainder (580 t/a) is released as liquid or solid waste. This estimate was based on 1977 production and recovery figures and an estimated average Se concentration of 40 g/t in the ore (Nriagu and Wong, 1983). In a global inventory, however, emission factors used for this source category were significantly higher, ranging from 50 to 150 g/t (Nriagu and Pacyna, 1988). The resulting final estimate was then increased by an additional factor of 1.67 to account for "volatile Se", and additional factors were applied to account for emissions from "mining and secondary production" (Table 5).

Finally, the "mobilization factor" should be based on natural and anthropogenic estimates that have been calculated using parallel estimation methods - that is, using analogous types of information to compare natural and anthropogenic emissions. This has not generally been the practice. Natural

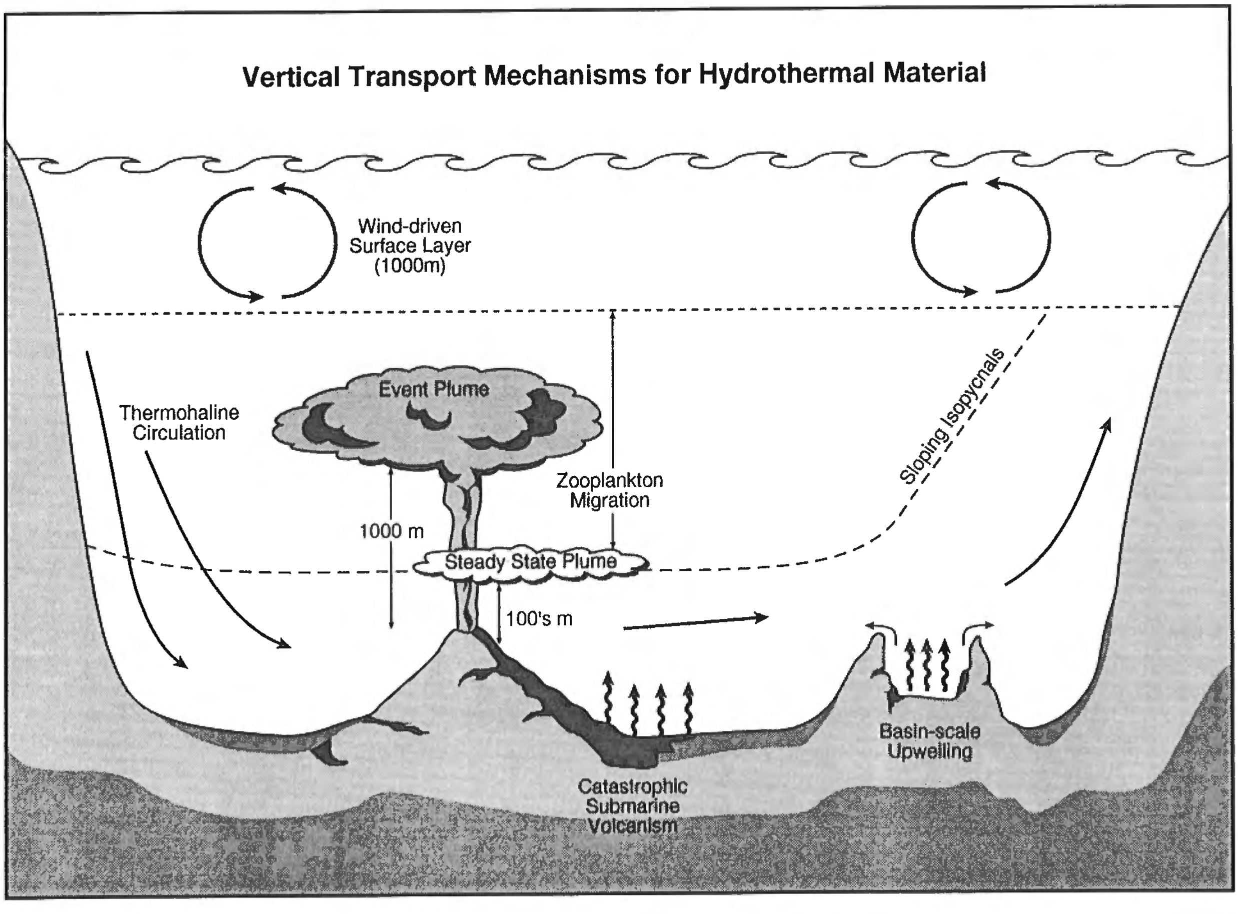

Figure 4. The influence of submarine hydrothermal systems on seawater chemistry: summary of vertical transport mechanisms (reproduced with permission from RIDGE/VENTS Workshop, 1994).

emissions are most often calculated on the basis of particulate flux estimates (as in Table 2) while, in contrast, anthropogenic emissions are most often calculated on the basis of production and consumption figures (as in Table 5). This problem is illustrated by Table 3 which contrasts two methods of calculating mobilization factors to account for the presence of Pb in the atmosphere. Anthropogenic sources of Pb are estimated to account for 10% of the total Pb in the atmosphere according to the study in which the natural Pb flux estimate is based on atmospheric measurements (Table 3). In contrast, anthropogenic sources of Pb are estimated to account for 96% of the total Pb in the atmosphere where the natural Pb flux estimate is based on particulate flux estimates (Table 3). The inconsistencies are largely due to the different methods of calculating natural emissions, as the two anthropogenic Pb emission estimates were very close.

An assessment of the mobilization of metals from natural sources must also consider factors other than atmospheric emissions, including the release of metals to the environment by chemical and physical weathering processes, mobilization along aqueous pathways, the role of biogeochemical cycling, and chemical interactions between seawater and the seafloor. A comparison of natural and anthropogenic sources based solely on emissions to the atmosphere may be misleading. In other words, if production figures are used for calculating the mobilization of metals by human activity, then it may be argued that some equivalent to production figures should also be used to account for the mobilization of metals in the natural global cycle. For example, terrestrial volcanic lava production is a significant natural contributor of metals to the environment. The total production rate for subaerial volcanic lavas has been estimated to be in the order of 6 km^3/a (Le Cloarec and Marty, 1990). While substantial, this amount is less than half of the production rate for submarine volcanism (Le Cloarec and Marty, 1990). Submarine volcanism, which has been omitted from some recent global budgets (see "Oceanic emissions") is thus a significant natural contributor of metals to the ocean that should be included in global cycling models.

An additional point should be made regarding the common practice of using generalized metal/S ratios to estimate volcanic metal emissions. There is some disagreement regarding the validity of this approach, due to the complexity of metal partitioning between gaseous and particulate phases (see "Volcanic emissions"). However, metal/S ratios appear to be a currently accepted method of estimating volcanic metal emissions for certain elements. For these elements it may be appropriate to apply the metal/S ratio method to the estimation of anthropogenic emissions as well. The use of metal/S ratios to estimate emissions from anthropogenic sources may have an advantage in that such ratios would help account for reductions in metal emissions due to the installation of SOx emission control technologies. For example, it is probable that the installation of SOx emission controls in the Sudbury facility (Table 5) also resulted in a decrease in Se emissions due to the similarity in behaviour between Se and S. Not only does Se substitute for S in sulphide minerals, but it also forms volatile compounds in the environment that are analogous to volatile S compounds (Rasmussen, 1987).

SOURCE APPORTIONMENT IN RECEPTOR MODELS

In the context of this report, "source apportionment" means determining the relative contribution of natural and anthropogenic sources to the metal content of an environmental sample collected at a given sampling site. While there have been major advances in the measurement of ultratrace

Table 5. Emission of Se from Cu-Ni production: differences between local, regional, and global estimates.

Estimated Se emission	Method of calculation	Emission factor (g/t)	Reference
LOCAL			
50 t/a to the atmosphere out of an estimated total of 630 t/a released to environment (Sudbury, Canada)	Method for estimating that >90% of selenium content of ore produced enters environment based on average Se content of total Cu-Ni ore produced in 1977 (40 g/t) = subtotal 680 t/a, subtract amount Se recovered: (50 t/a) = 630 t/a. Method for determining atmospheric proportion (50 t/a) not given.	Total release: 630/ 680 = 90% of average Se content of ore produced (40g/t) Atmospheric release 50/680 = 7.4% of Se in ore produced	Nriagu and Wong (1983)
NATIONAL			
138 t/a Se emitted from all operations in Canada	not given, except to say that the figure refers to all Cu-Ni mining and processing sources across Canada, based on literature reviews/source testing	not given	National Inventory of Sources and Emissions of Selenium (EPS, 1977)
GLOBAL			
713-2137 t/a to global atmosphere (for 1983)	emission factor multiplied by total Cu-Ni produced, increased by factor of 1.67 to account for volatile forms	50-150 (x 1.67)	Nriagu and Pacyna (1988)
plus a component of the following:	additional emission factors applied to account for:	plus additional	
18-176 t/a to global atmosphere	mining nonferrous metal ore	1-2.5	
3.8-19 t/a to global atmosphere	secondary nonferrous metal production	1-5	

concentrations of metals in environmental samples (Boutron et al., 1994), the literature indicates a need for further development of methods to distinguish metals that are of anthropogenic rather than natural origin. At present, the problem of nonuniqueness occurs in air parcel back trajectory models where geochemical evidence for an anthropogenic source could equally be used as evidence for a natural source.

The term "nonuniqueness" is used in numerical modelling to describe a model which has two different solutions (Oreskes et al., 1994). This is a particular problem in the interpretation of metals observed in aerosol samples, rain, snow, and ice cores. The lack of methods to uniquely identify metals of anthropogenic origin has resulted in a long debate over the validity of source apportionment models based on snow and ice core evidence (e.g. Murozumi et al., 1969; Weiss et al., 1971; Landy et al., 1980; Ng and Patterson, 1981; Jaworowski et al., 1981, 1983; Patterson, 1983). This section explains some of the uncertainties associated with current source apportionment techniques and suggests possible methods to address these uncertainties.

Elemental tracers

Certain trace elements in aerosol samples are used as characteristic indicators of anthropogenic sources in air parcel back trajectory models. For example, selenium and arsenic are used as characteristic tracers of coal combustion, and their presence in aerosols collected at eastern U.S.A. sampling sites is interpreted as evidence of air contamination by stack emissions in the Ohio Valley (Keeler and Samson, 1989). Similarly, Zn has been used as a characteristic anthropogenic tracer in Canada, indicating contamination from either coal combustion or iron and steel manufacturing (Environment Canada, 1994).

The use of elemental associations as anthropogenic indicators is complicated by the fact that elemental associations typical of coal and ore are also found in common rock types, and may be reflected in the organic soil, sediment, and vegetation overlying these rocks (Levinson, 1974). If natural elemental associations at the receptor site can be well constrained and are known to be distinct from those of the anthropogenic source, such a technique has potential usefulness in distinguishing overlapping anthropogenic and natural influences at the local scale. Attempts to extrapolate such findings to a broader regional scale, however, may introduce unacceptable uncertainties, arising from

1) the fact that elements used as anthropogenic tracers (such as Se, As, and Zn) also occur naturally in unconsolidated earth materials in significant and highly variable concentrations (Darnley, 1995), and
2) the probability that windblown dust and biogenic debris transport these elements in the same air masses that are affected by stack emissions.

For example, soil geochemical maps (Shacklette and Boerngen, 1984) indicate that large areas of central U.S.A. are naturally enriched in selenium and arsenic. It is likely that windblown dust originating in these areas would also be naturally enriched in selenium and arsenic, raising serious questions about the validity of using these elements as characteristic tracers of coal combustion in central U.S.A. In total, about 19% of the world's land surface has some multi-element data available in the form of geochemical maps (Darnley, 1995). Where available, these spatial data could help atmospheric modellers evaluate uncertainties associated with their source terms.

Atmospheric enrichment factors

The enrichment of metals in atmospheric particles relative to the average crustal abundance (normalized against a reference element such as Si or Al) is commonly used as an indicator of anthropogenic sources (Rahn, 1976; Chester, 1986). The enrichment factor technique was used by Murozumi et al. (1969) to calculate the natural component of Pb in Greenland ice cores, a study that is viewed as the classic proof that anthropogenic emissions have caused a 200-fold increase in the global atmospheric Pb burden since 800 B.C. (Forstner and Wittman, 1983). The assumptions made by Murozumi et al. (1969) were

1) chronological changes in Pb/Si ratios in polar snows reflect parallel chronological changes of this ratio in the atmosphere,
2) enrichment in Pb/Si ratios above average crustal abundance solely reflects industrial sources of Pb (Ng and Patterson, 1981), and
3) volcanoes make no significant contribution to enriched Pb/Si ratios in atmospheric aerosols on a global scale (Ng and Patterson, 1981).

Although current source apportionment studies continue to rely on these assumptions (Boutron et al., 1991, 1994; Hong et al., 1994), there is substantial geochemical evidence to suggest that the latter two assumptions are not valid. Studies of volcanic rocks and continent-forming processes have established that Pb is anomalously enriched in the Earth's continental crust, due to its partitioning behaviour in both magmatic and nonmagmatic (e.g. hydrothermal) processes (Miller et al., 1994). As discussed previously (see "Global inventories of natural and anthropogenic emissions") enrichment of a metal relative to Al and Si can be expected in

1) gaseous emissions of metals caused by volcanic activity, crustal degassing, and methylation;
2) airborne dust from rock types which are enriched in the metal of interest relative to the reference elements Al and Si;
3) products of chemical weathering processes in surficial materials (soils and sediments) which result in a gradual depletion of metals from aluminosilicate compounds and an enrichment of metals in organic matter, oxides, and hydroxides; and
4) naturally high metal concentrations in biogenic particles.

Uncertainties in source apportionment should be addressed through the development of improved geochemical methods of fingerprinting natural sources, such as Hinkley (1992) used to investigate the variation of rock-forming metals in subannual increments of modern Greenland snow. Merefield et al. (1994) used a combination of fingerprinting methods in the vicinity of an opencast coal mine, in South Wales, U.K. The methods involved analyzing the mineral content by XRD, and the particle size, shape, and geochemistry by scanning electron microscopy with energy dispersive X-ray analysis (EDAX). Using these methods the authors were able to distinguish dust arising 1) on-site from the coal workings, 2) immediately off-site, and 3) from regional sources.

Isotopic signatures

In the earth sciences, Pb isotopic studies have played a major role in improving our understanding of the evolution of the Earth's crust (Faure, 1986). Earth scientists have also applied Pb isotopic techniques to environmental problems, specifically to distinguish between natural and anthropogenic pathways of Pb in mining areas, where the signatures of the various contributing sources can be well constrained (Gulson et al., 1994; Church, 1994). Recent studies address the physical and chemical weathering and transport processes affecting Pb isotopic signatures in glacial till and soil (Bell and Franklin, 1993; Erel et al., 1994). Such studies of metal distribution in earth materials have direct relevance to atmospheric models, as indicated in the discussion on windblown dust (see "Deflated soil and sediment").

A number of studies have estimated the relative contribution of different anthropogenic sources of Pb in atmospheric samples on the basis of Pb isotopic ratios (e.g. Sturges and Barrie, 1987, 1989; Rosman et al., 1993, 1994). Each of these studies attributed the Pb content of atmospheric samples to various anthropogenic sources without considering the potential natural component of Pb in the samples. It is important to recognize that the range of isotopic signatures of Pb in natural earth materials (i.e., not exposed to anthropogenic Pb) varies at least as widely as the Pb isotopic signatures of lead additives, fossil fuel, and smelter products. The degree of uncertainty that arises from ignoring the natural component is significant, in light of the fact that natural sources may account for at least 93% of atmospheric particulates on a global average (Environment Canada, 1994, citing Strauss, 1978).

Certain studies have concluded that there is significant transboundary atmospheric transport of trace metal pollution into Canada from industrial sources in the U.S.A., on the basis of $^{206}Pb/^{207}Pb$ isotopic ratios observed in samples of airborne particulates, and in samples of surface waters of the Great Lakes (Sturges and Barrie, 1987, 1989; Flegal et al., 1989). These authors all concluded that there are three main sources of atmospheric Pb in this area that can be distinguished on the basis of Pb isotopic ratios: United States automobile exhaust emissions, Canadian automobile exhaust emissions, and Canadian industrial sources (mainly smelters). These studies estimated that about 30 to 50% of the airborne lead in southern Ontario is imported from anthropogenic sources in the United States. None of the studies corrected for the natural component of Pb in the atmosphere or surface waters.

This source interpretation would have been strengthened had the authors demonstrated that the anthropogenic components of Pb in the samples have unique and distinctly separate isotopic signatures from possible natural components. In fact, there are alternative interpretations for these data that remain unaddressed. For example, comparatively low $^{206}Pb/^{207}Pb$ ratios (1.05-1.15; from Fig. 3 and 5 in Sturges and Barrie, 1989) observed in the Dorset sampling area were attributed to long-range atmospheric transport of Pb from smelters in either Noranda, Quebec or Sudbury, Ontario, depending on the wind direction at the time of sampling (Sturges and Barrie, 1989). However, similarly low $^{206}Pb/^{207}Pb$ ratios (1.05-1.12) have been reported in bedrock samples collected in the vicinity of the atmospheric sampling site (from Table 1 in DeWolf and Mezger, 1994). The Pb occurs naturally in these rock samples due to the substitution of Pb for K in common minerals (feldspars and micas). Thus, local windblown dust should have been investigated as an alternate explanation for the observed Pb isotopic signatures that were attributed to the northern smelters by Sturges and Barrie (1989).

Based on $^{206}Pb/^{207}Pb$ ratios, Flegal et al. (1993) attributed the Pb content of Antarctic seawater to a mixture of natural sources and anthropogenic sources. Low $^{206}Pb/^{207}Pb$ ratios were considered indicative of the dispersal of anthropogenic Pb in the form of atmospheric aerosols, from industrial sources in the Southern Hemisphere (Flegal et al., 1993). However, a review of published Pb isotopic data in Antarctica (K.D. Collerson, pers. comm., 1993) showed that the observed low $^{206}Pb/^{207}Pb$ ratios could equally indicate erosion and transport of natural crustal materials. In other words, an alternate explanation for the data presented by Flegal et al. (1993) is that the Pb isotopic composition of Antarctic seawater represents a mixture of Pb derived from the wide range of potential natural end-member Pb isotopic compositions (K.D. Collerson, pers. comm., 1993).

To aid in source apportionment, additional information may be obtained using isotopic signatures of other elements in the same sample. For example, $^{87}Sr/^{86}Sr$ ratios were used to determine the varying influence of marine and calcareous soil sources in wet deposition from northern to southern Sweden (Wickman and Jacks, 1991). Measurements of the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotopic ratios of dusts in the Antarctic served to define sources and place constraints on southern hemispheric circulation models (Grousset et al., 1992). Chlorine isotopes also have potential as an additional tool to aid in atmospheric source apportionment (Tanaka and Rye, 1991). Since the early 1980s, it has been possible to determine Cl isotopic ratios with a precision smaller than the natural variations (Eggenkamp, 1994).

Particle size

Atmospheric modelling often relies on the particle size spectrum of an element in an aerosol sample to evaluate the source (Ng and Patterson, 1981; Chester, 1986). In a number of studies (Barrie, 1988; Schichtel and Husar, 1991; Environment Canada, 1994), elements in the fine particle fraction (<2.5 µm) have been apportioned to various industrial sources, while elements found in the coarse fraction (generally 8-15 μm) have been apportioned to either natural or industrial sources. This technique is based on the observation that 1) low temperature, mechanically-generated, crustal (and sea-salt) particles tend to be coarser than particles generated from high-temperature processes, such as smelting and fossil fuel burning; and 2) metals released from high temperature processes tend to be associated with the sub-micrometre particle size range (Chester, 1986).

It has also been observed that higher concentrations of trace metals such as Pb, Ni, and Cr tend to be associated with the fine fraction of aerosol samples collected in remote or rural areas (several hundreds to thousands of kilometres from industrial sources) and thus it is generally assumed that metals in the fine fraction are anthropogenic in origin (Barrie, 1988). For example, Sturges and Barrie (1989) discounted the possibility of a natural component of Pb in atmospheric particulates in a rural sampling site in eastern Canada (Dorset, Ontario) based on a previous size-segregated sampling study in the same area (Barrie, 1988). The earlier study revealed that the dominant proportion of Pb was present in the fine fraction (<2.5 μm). From this it was assumed that the coarse fraction (from 2.5 μm to 10 μm) contained windblown dust plus anthropogenic sources, while the fine fraction contained only the anthropogenic component (Barrie, 1988).

Uncertainty arises from the fact that 1) at least 93% of particulate material collected in remote and rural areas can be expected to arise from natural sources, such as soil dust, fire debris, biogenic particles, etc. (Table 2); 2) particles smaller than 2 μm are abundant in natural soil and sediment; and 3) metals are naturally enriched in the fine fraction (<2 μm) of soil and sediment, a reason why this size fraction is commonly used in geochemical surveys (Rose et al., 1979; Forstner and Wittman, 1983). It is therefore very likely that windblown dust and particulate organic matter, carried from local or distant sources, contribute a significant portion of the metals observed in the fine aerosol fraction.

More definitive lines of evidence are required to address the uncertainty associated with this currently accepted technique of identifying anthropogenic sources of metals in aerosols. Unfortunately, current methods of correcting for the natural component of K, Ca, Mg, Si, and Al in the fine fraction of airborne particulates (reviewed by Schichtel and Husar, 1991) overlook the need to correct for the natural component of Pb and other potentially toxic trace metals.

The widely accepted assumption that fine particle size is a unique identifier of anthropogenic sources may have resulted in a systematic overestimation of the anthropogenic component of aerosols. Metals become concentrated in the fine fraction of dust, soils, and sediments whether the source is anthropogenic or natural. A major reason for the association of metals with fine grained particles is the relatively large surface area of the fine particles available for adsorption and other metal bonding mechanisms. Furthermore, the fine fraction (<2 μm) of soil and sediment tends to be enriched in substances active in metal bonding, including hydrous oxides and hydroxides, organic substances, and other weathering products (Forstner and Wittman, 1983).

Assumptions about the source of fine particles are important in the interpretation of metals in wet deposition as well as dry deposition, as the most important mechanism of fine particle deposition is washout by rain or snow (Pye, 1987). For example, fallout of dust storms in Australia and New Zealand as precipitation, and similar fallout of Saharan dust in central and northern Europe, is commonly referred to as "red rain" or "blood rain" (Pye, 1987).

Chemical extractions

Chemical extraction techniques are used widely to determine mechanisms of trace metal accumulation in sediments and soils, to compare mechanisms of trace metal transport, and to estimate the biological availability of trace metals. A limited number of studies have used chemical extractions for the purpose of distinguishing natural and anthropogenic sources. Most use extraction techniques in combination with other techniques (e.g. physical separation techniques and electron microprobe studies) to establish identities of individual particles on the basis of characteristic morphologies and chemical composition (Kersten and Forstner, 1989). A description of extraction techniques and their limitations in the context of source assessment is provided by Kersten and Forstner (1989).

Before attempting to distinguish natural and anthropogenic inputs on the basis of chemical extractions, it is important to understand the complexity of natural partitioning behaviour. Sequential extraction studies of natural environments have shown that trace metals are partitioned among several substrates in soils and sediments, and that partitioning behaviour is strongly influenced by the concentrations of the different substrates in the sediment (Kersten and Forstner, 1989). Interpretation errors arise from the misconception that the "natural component" is confined to the mineral fraction of soil and sediments, and is nonreactive, immobile, and biologically unavailable. Two common errors arise from this oversimplification of natural processes: 1) the assumption that metals found in the weakly-bound or water-soluble phases must have an anthropogenic origin, and 2) the assumption that metals associated with the organic fraction must be derived solely from atmospheric deposition. These issues are discussed further in "Distribution in remote and rural ecosystems".

DISTRIBUTION IN REMOTE AND RURAL ECOSYSTEMS

Interpretation of regional spatial variations

Historical increases in atmospheric metal loading have been inferred from observed spatial variations in metal concentrations in vegetation and humic matter in remote areas surveyed at a regional or continental scale (e.g. Glooshenko, 1989; Steinnes, 1990; Lindqvist et al., 1991; Nater and Grigal, 1992). A conclusion that regional geochemical variations in metal contents reflect anthropogenic influences is insupportable unless or until such studies include a quantitative assessment of the natural geochemical base line. Instead, some spatial studies rely on the assumption that metals derived from geological sources are negligible compared to anthropogenic sources (e.g. Steinnes, 1990). Others assume that metals from geological sources are confined to the mineral fraction of soil and sediments, and that metals associated with humic matter are derived solely from atmospheric deposition (e.g. Nater and Grigal, 1992).

The concept of a "critical load"

The "critical load" concept is based on the assumption that the metal content of surface soils in remote forest ecosystems (i.e. several hundreds to thousands of kilometres from industrial sources) is derived chiefly from atmospheric fallout. The term "critical load" was defined in the context of the Hg cycle by Lindqvist et al. (1991) as "the atmospheric load where the input to the forest soils is less than the output and, consequently, where the Hg content in the top soil layers and the transport of Hg to the surface waters starts to decrease."

The assumption that the metal content of surface soil in remote regions is derived chiefly from atmospheric fallout is inconsistent with data derived from the application of established mineral exploration techniques (Fig. 5). These techniques use plants and humic matter as indicators of metal concentrations in underlying bedrock and glacial drift (Brooks, 1995; Dunn, 1995), and are based on an understanding of the natural biogeochemical metal cycle (Levinson, 1974; Rose et al., 1979). The term "biogeochemical cycle" indicates the interaction of biology, geology, and chemistry, and is defined by O'Neill (1985) as "the breakdown of rock to form soils, the uptake of the mobilized chemicals by plants, and the return of the dead plant material to the soil ready for further uptake".

A quantitative estimate of anthropogenic loading in a remote landscape requires the definition of all inputs and outputs in that location, natural as well as anthropogenic. The critical load concept and similar input-output models should be re-evaluated in the context of our current understanding of the biogeochemical cycle (Fig. 5).

The assumption of a "constant background"

The assumption that "background" may be taken as a constant value is common in atmospheric models which attribute regional spatial variations of metals in rural and remote areas to human perturbation of the environment. The concept of a "constant background" is not supported by worldwide survey data, which indicate that the natural abundance of trace

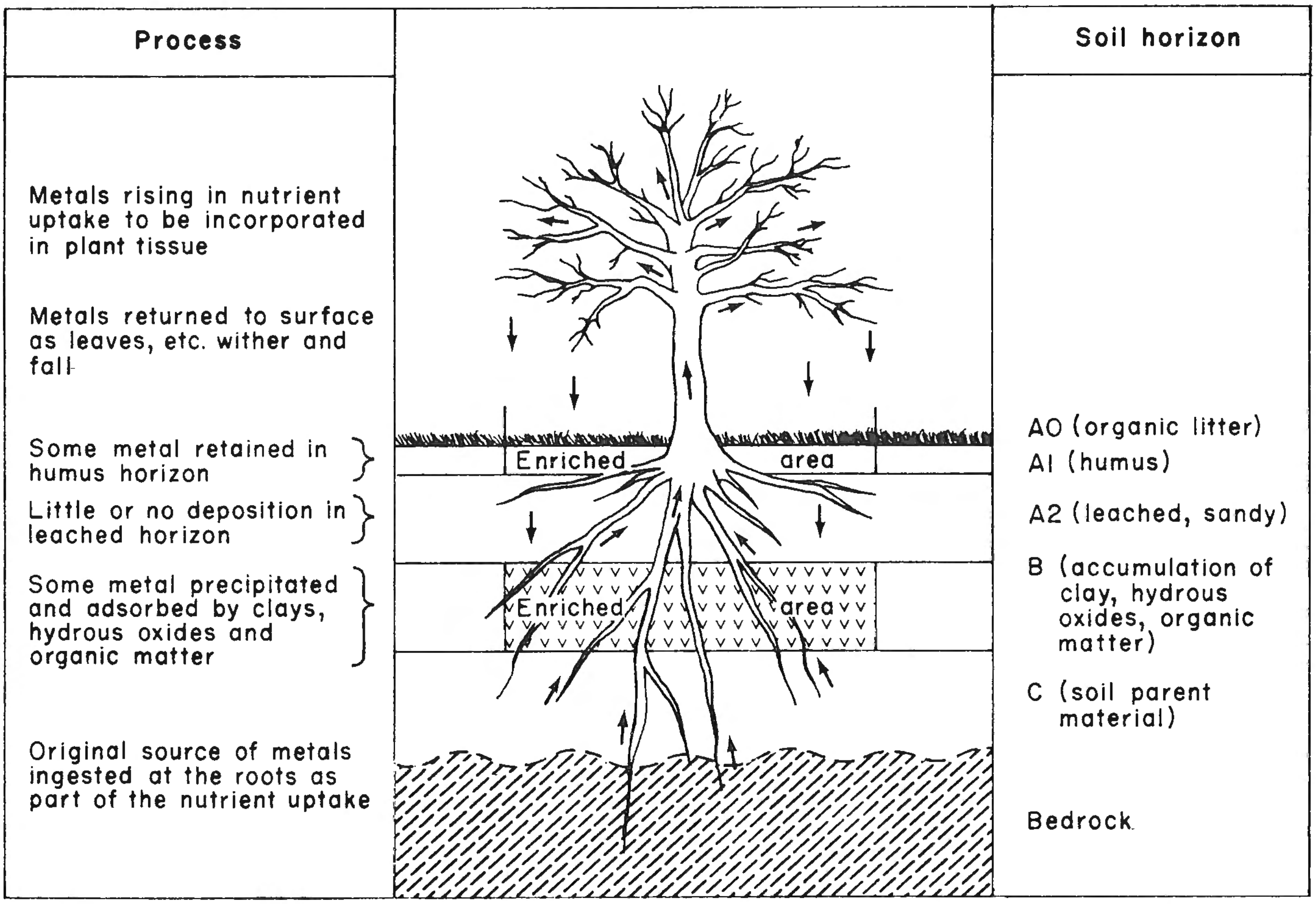

***Figure 5.** The biogeochemical cycle (reproduced with permission from Rose et al., 1979).*

elements in many surface sample media can vary by 2 to 3 orders of magnitude over short distances, and up to 5 or 6 orders of magnitude if samples from rare types of high-grade mineral deposits are included (Darnley, 1995). In Canada, large geographic areas are characterized by naturally elevated trace metal concentrations (e.g. As, Cd, Cu, Hg, Ni, Pb, Zn) that exceed guidelines and clean-up criteria designed to protect the environment (Painter et al., 1994).

Ledin et al. (1989) stated that the use of a single average background value in the interpretation of environmental media can be entirely misleading. This comment is supported by their study of metals in pristine groundwater, monitored at 126 stations across Sweden during 1985-1987, which indicates that natural metal concentrations in groundwater vary by at least an order of magnitude in relation to local geology (e.g. Pb varies from 0.02 to 0.30 μg/L).

Interpretation of the natural background variation of metal concentrations must consider both geological variation and climatic/topographic variation. First, the degree to which bedrock and drift geochemistry influences spatial variation in metal contents needs to be assessed. For example, a till survey in southeastern Sweden by Andersson and Nilsson (1992) indicated that elevated Cu, Cr, Co, Ni, and V concentrations are characteristic of till derived from one Precambrian sequence while elevated Pb and Zr concentrations are characteristic of till derived from another Precambrian sequence. Quantification of the contribution of Pb and other metals from till to the surface environment would thus be required in order to evaluate the relative contribution from atmospheric sources affecting southeastern Sweden.

Second, the degree to which organic carbon influences spatial variations in metal contents needs to be assessed. Metals have an affinity for organic matter in soils (Levinson, 1974; Rose et al., 1979; Jeffrey, 1987), in lake sediments (Coker et al., 1979), and in marine sediments (Rashid, 1985). The variation in organic matter with variation in climate and geographical setting is thus a governing influence on the regional distribution of metals in the environment (Garrett and Hornbrook, 1976; Garrett et al., 1990). Lindqvist et al. (1991) illustrated the importance of considering organic matter in the interpretation of latitudinal variations of Hg in Swedish forest soils. The interpretation that anthropogenic sources account for the north-south variation in Hg contents of Swedish humus was based on the assumption that a single average background value per unit area was valid for the entire country (Lindqvist et al., 1991). However, if the increased bulk density and thicker humus layer in southern Sweden were considered, the "background" Hg value would be three times higher in the south than in the north (Lindqvist et al., 1991).

Vertical enrichment in sediments and soils

A large number of studies use changes in the metal content of natural samples of varying age (e.g. organic lake sediments, organic forest soils) to infer changes in atmospheric input to the ecosystems where these samples are collected. Unless such studies address the accumulation processes which cause metals to become naturally enriched in surface soil and organic sediments, it is difficult to verify their conclusions. Natural enrichment processes in a wide geographic and latitudinal range of environments must be understood before an attempt is made to quantify the anthropogenic component of metals in organic soil and sediment samples.

Surface enrichment in soil

Uncertainty in the interpretation of metal enrichment in organic forest soil arises from the fact that naturally occurring metals such as Pb typically become concentrated in the upper few centimeters of undisturbed soils, due to their incorporation in living plants and accumulation in the decomposing remains in the humus layer (Fig. 5). Once in the surface layer, Pb and other metals tend to be held strongly by organic matter (Rose et al., 1979; O'Neill, 1985; Nuorteva, 1990). A number of studies have misinterpreted these natural biogeochemical concentrating effects as surface contamination by atmospheric fallout (O'Neill, 1985; Ter Haar, 1986).

Surface enrichment in lake and marine sediments

Organic lake sediments are commonly used as a historical record of atmospheric loading in lakes remote from industrial point sources (e.g. Ouellet and Jones, 1983; Lindqvist et al., 1991). In this technique, the sediment layers are dated, and metal concentrations in each layer are assumed to reflect atmospheric deposition at the time of sedimentation. However, it has been established that natural processes (diagenesis and remobilization) can also lead to the enrichment of metals at the top of the sediment column (Cline and Upchurch, 1973; Carlson et al., 1978; Coker et al., 1979; Farmer, 1991). Thus, there is uncertainty in the use of surface enrichment in remote lake sediments as a monitor of atmospheric loading (Cornwell, 1987; Farmer, 1991; Rasmussen, 1994).

Kersten and Forstner (1989) emphasized the need for research to improve knowledge of diagenetic processes and remobilization of metals in sediment. The processes which lead to the remobilization of trace metals in sediments were listed by Kersten and Forstner (1989) as follows:

1) Postdepositional remobilization by oxidation and decomposition of organic matter, mediated by microbiological activities.
2) Control of the solid/solution partitioning by early diagenetic effects such as changing the surface chemistry of oxyhydroxide mineral coatings.
3) Authigenic production/dissolution of metal precipitates.
4) Desorption from clay minerals and other substrates due to formation of soluble organic and inorganic complexes.

Evidence for natural causes of surface enrichment is provided by analyses of the trace metal content of Fe-Mn nodules in lake and ocean bottoms (Table 6). Nodule formation is attributed to the diagenetic remobilization of Fe^{2+}, Mn^{2+}, and other elements in buried sediments under reducing conditions, and their subsequent oxidation and incorporation into nodules or encrustations at the surface. Most of the literature on Fe-Mn nodules is a result of their economic

Table 6. Enrichment of trace metals in naturally occurring Fe-Mn nodules found in marine and freshwater surface sediments.

	Fe (%)	Mn (%)	Cu (µg/g)	Ni (µg/g)	Zn (µg/g)	Pb (µg/g)
Pacific Ocean (1)	2.4-26.6	8.2-50.1	280-16 000	1600-20 000	400-800	200-3600
Canadian lakes (1)	11.7-40.2	15.7-35.9	6-16	95-373	250-1940	10-29
Fennoscandian lakes (2)	8.6-36.9	16.6-33.9	15-35	330-410	355-1651	33-60
English lakes (1)	5.9-39	1.4-13	5-20	10-40	0.03-3000	30-8000

References: (1) cited in Lundgren and Dean (1979)
(2) Carlson et al. (1978)

potential, not only as ores of iron and manganese, but also certain other trace elements (especially Co, Ni, and Cu). For example, UNESCO (1994) reported elevated concentrations of nickel (up to 1 wt.%), cobalt (up to 2 wt.%) and copper (up to 2 wt.%) in sedimentary Fe-Mn deposits of marine basins.

Any theories which attempt to explain the surface enrichment of metals in freshwater sediments should take into consideration the fact that diagenetic processes also lead to the enrichment of metals at the surface of deep marine sediments (Lundgren and Dean, 1979). An important difference between freshwater and deep marine Fe-Mn nodules is that metal concentrations in marine nodules are commonly orders of magnitude higher than concentrations found in freshwater nodules. It is thought that freshwater nodules do not have the time to adsorb transition metals to such high concentrations because they form at rates at least three orders of magnitude faster than deep sea nodules (Lundgren and Dean, 1979). The natural enrichment of metals in sediments of the marine environment is a highly significant phenomenon in the context of the global geochemical cycle (Duke, 1980; Rashid, 1985).

New interpretations of previously collected data

Uncertainty arises from recent reinterpretations of existing data on natural sources of metals in remote areas. For example, the US-EPA (1994) suggested that emissions of Hg previously classified as natural may in fact be re-emissions of anthropogenic Hg.

Actual field data are required to determine the degree to which emissions of trace metals previously classified as natural should be reclassified as anthropogenic. As it stands, the US-EPA (1994) suggestion runs contrary to the original long-range atmospheric modelling work of Lockeretz (1974), which concluded that the natural Hg cycle dominates in remote areas. The Lockeretz (1974) model cannot be easily disregarded, as it was based on empirical geological evidence collected during the preceding decades and reported in the literature of the time (e.g. see Jonasson and Boyle, 1972). Recent geochemical studies (listed in Rasmussen, 1994) have reinforced rather than disproved the Lockeretz (1974) model. The conclusion that natural sources of Hg dominate in remote areas was also supported by the International Programme on Chemical Safety (IPCS, 1989), and by a separate US-EPA study (Gubala et al., 1995). The latter study estimated that Hg from anthropogenic sources accounted for less than 10% of background concentrations in two remote lakes in Arctic Alaska, but the authors commented that the high background concentrations made it impossible to distinguish possible effects of long-range atmospheric transport with any certainty.

As noted in "Oceanic emissions" the new interpretation that Hg volatilization in remote areas (such as the open ocean) originates from the recycling of anthropogenic Hg cannot be substantiated until the significance and variability of natural sources has been properly established.

REGIONAL SCALE MASS BALANCE STUDIES

Introduction

Mass balances (input-output budgets) are commonly used to evaluate the relative significance of anthropogenic loading of substances to a waterbody. The mathematical treatment of geochemical mass balances in watershed systems is conceptually identical to that of an individual reservoir in global geochemical cycles (Velber, 1986). That is, the mass balance input and output terms are generally treated as functions of the flux of water and the concentration of the substance of interest (Velber, 1986). It is a major undertaking to obtain a realistic estimate of total loadings to a water body, as all the sources and pathways in the geosphere and biosphere, as well as the atmosphere, need to be included (Forstner and Wittman, 1983).

Example: mass balancing the Great Lakes

An important example of a regional scale mass balance is that of the Great Lakes watershed system, located in eastern North America on the border between Canada and the U.S.A. Both the US-EPA (1994) and the International Joint Commission (IJC, 1988) have concluded that the atmosphere is the dominant pathway for Pb and Hg in the Great Lakes region. The IJC (1988) estimated that, on average, 83% of the total Pb loading to the Great Lakes is derived from the atmosphere, based on individual estimates for each lake shown in Table 7. The US-EPA (1994) estimated similar proportions for lakes Superior, Michigan, and Huron (Table 7). Although it is reported that the best trace metal information available is for Pb, an examination of the calculations in Table 7 indicates that there are significant discrepancies between the input and output data (IJC, 1988).

Table 7. Annual lead inputs and outputs for the Great Lakes and the fractions attributed to atmospheric pathways (from IJC, 1988; US-EPA, 1994).

Lake	Total input (kg/a)	Total output (kg/a)	Net flux (kg/a)	% of total input that is attributed to atmospheric loading (direct + indirect)	
				IJC (1988)	US-EPA (1994)
Superior	241	828	-587	97	95
Michigan	543	472	71	99.5	95
Huron	430	496	-66	98	95
Erie	567	2010	-1440	46	not calculated
Ontario	428	490	-64	73	not calculated

One area of uncertainty is the quantification of metal inputs from local anthropogenic sources compared to long-range atmospheric influences. Major source categories in the Great Lakes region include the production of electricity and heat, combustion of fuels in industrial, commercial, and residential units, including wood combustion, manufacturing and use of various industrial goods, mobile source emissions, incineration of municipal and industrial wastes, and incineration of sewage sludge (Keeler et al., 1993). A recent evaluation of available data on anthropogenic sources of airborne metals in the Great Lakes region (Keeler et al., 1993) indicates that there are significant uncertainties in the existing estimates of inputs from these sources, and emphasizes the difficulty in obtaining quantitative information.

With respect to the natural component of the Great Lakes mass balance, the US-EPA (1994) commented that, at present, there is a limited understanding about the natural sources of trace metals. Indeed, in the existing IJC (1988) budget, it appears that the same assumptions underlying the modelling of synthetic pollutants (e.g. PCBs, DDT, and Mirex) have been applied to the modelling of trace metals. Unlike models of synthetic substances, however, trace metal mass balances require an understanding of natural loading through both aqueous and atmospheric pathways. There is no indication that the estimate of total inputs in Table 7 included any attempt to quantify natural rates of weathering of bedrock and till sources, the subsequent movement of released metals through surface and groundwater, or the important role of the biogeochemical cycle.

Until the necessary input data are obtained for the Great Lakes and other impacted regions, no firm conclusions can be drawn about the relative importance of atmospheric deposition. Key areas of uncertainty are 1) the relative importance of long-range atmospheric transport compared to short-range atmospheric transport, 2) the relative importance of aqueous loading compared to atmospheric loading, and 3) the relative importance of natural loading compared to anthropogenic loading through all aqueous and atmospheric pathways. To address the latter research need, studies will have to be specifically designed to quantify the annual contribution of trace metals from natural sources to the air and to the major watercourses in the Great Lakes watershed.

Estimation of natural inputs

In the 1980s, a large number of mass balance studies were undertaken to quantify the release of naturally occurring metals in forest ecosystems due to chemical and physical weathering processes (Colman and Dethier, 1986). One purpose of these studies was to predict the long-term effects of acid precipitation on natural weathering and release rates. Field and laboratory experiments were designed to quantify and compare pre-industrial weathering rates with modern weathering rates, using a variety of approaches. Most field studies dealt with relatively small catchment areas (e.g. Paces, 1986), but a few dealt with larger, regional scale watersheds (e.g. Ohlander et al., 1991).

Advances in determining natural metal release rates that resulted from acid rain research have direct relevance to the current need to evaluate the relative significance of natural and anthropogenic metal loadings to water bodies. An example is the study of the relatively pristine Kalix river system of northern Sweden (23 600 km^2) by Ohlander et al. (1991). The authors calculated a mean annual weathering rate of 2.4 g/m^2/a during postglacial time for the Kalix watershed, which occupies about 5% of Sweden's total land area. Based on the calculated weathering rate, Ohlander et al. (1991) estimated the natural annual release rate to be in the order of tonnes per year for many metals (V, 7.4 t/a; Ni, 3.1 t/a; Cu, 7.0 t/a; Cr, 3.0 t/a from the Kalix watershed area). In the case of Hg and Pb, however, a net gain was estimated in the terrestrial part of the Kalix watershed (14 kg/a and 237 kg/a respectively). The authors were unsure whether the estimated net gain was due to contamination from anthropogenic sources, or if the results were an artifact of analytical or methodological problems (Ohlander et al., 1991).

Velber (1986) summarized a number of methodological problems regarding the estimation of weathering rates, including 1) difficulties in estimating the reactive mineral surface area in natural systems, and 2) discrepancies between natural weathering rates and rates derived from artificially-treated mineral surfaces in laboratory experiments.

The biogeochemical cycling of metals (Fig. 5) is another extremely important issue which is often overlooked in the calculation of input-output metal budgets. One factor to be considered is the significant effect of humic acid leaching on metal release rates (Rashid, 1985). Another factor is the accumulation of metals in soils due to plant uptake and subsequent decay and the affinity of metals for soil organic matter (discussed in "Distribution in remote and rural ecosystems"). Velber (1986) also indicated that the common assumption that the biomass is constant and therefore need not be included in mass balance calculations "almost certainly causes erroneous estimates of weathering rates."

Consideration of natural accumulation processes is particularly important in the interpretation of the cycling of metals such as Pb and Hg which are strongly retained by organic matter in the surface environment. These considerations may shed light on the above-mentioned uncertainty in estimating net release rates of metals in the Kalix watershed system (Ohlander et al., 1991). The role of biogeochemical cycling must be taken into account not only in the calculation of regional scale mass balances, but in all natural budgets from the local watershed scale to the global scale.

CONCLUSIONS

1) There are significant uncertainties in comparing natural and anthropogenic metal emissions to the atmosphere at the local, regional, and global scale. Natural emission estimates vary by orders of magnitude, with the result that the estimated ratios of anthropogenic to natural emissions ("mobilization factors") are very uncertain.
2) Natural emission estimates are extrapolated from a very sparse data set. Most recent estimates were calculated using literature data originally collected for other purposes. The uncertainty introduced by the lack of representative data is illustrated by the wide discrepancy between existing estimates of the global volcanic Pb and Hg fluxes, which are the two most studied metals.
3) Uncertainty in source apportionment models is caused by the difficulty in distinguishing airborne metals that are of anthropogenic rather than natural origin. Air parcel back trajectory models suffer from the problem of "non-uniqueness"; that is, chemical indicators of anthropogenic sources could equally be used as indicators of natural sources. It is estimated that, globally, the annual emission of primary particulate matter from natural sources exceeds that of anthropogenic sources by a ratio of at least 93% (natural) to 7% (anthropogenic). These estimates underscore the importance of considering natural sources of airborne particulate matter.
4) There are critical information gaps and uncertainties associated with attempts to quantify the natural and anthropogenic components of metals in soil, vegetation, and lake sediment samples, particularly where these samples have been collected in rural and remote ecosystems. An understanding of natural accumulation processes is particularly important in the interpretation of the cycling of metals such as Pb and Hg which are strongly retained by organic matter in the surface environment.
5) To evaluate the significance of atmospheric deposition using a mass balance approach, all inputs and outputs of a given trace metal, both natural and anthropogenic, must be considered. Quantification of local natural and anthropogenic loadings to an ecosystem is required before firm conclusions can be drawn about the relative importance of long-range atmospheric transport.
6) Methods are required to routinely quantify uncertainty in the estimates of relative proportions of natural and anthropogenic emissions to the atmosphere and to aqueous systems.
7) Further research is required to obtain robust estimates of total metal emissions to the atmosphere globally, and to determine the relative contribution from anthropogenic and natural sources. This research is critical if "mobilization factors" are used to evaluate the global significance of anthropogenic metal emissions. A well co-ordinated, systematic effort to collect spatially and temporally representative data is required for the development of a global database on natural metal emissions.

ACKNOWLEDGMENTS

The assistance of M. Berry, W. Coker, A. Darnley, M. Duke, J. Franklin, R. Garrett, R. Koerner, and R. Macqueen in reviewing drafts of the material was especially appreciated. Special thanks go to A. Ignatow for initiating this project. Advice from L. Anglin, C. Boreiko, C.-J. Chung, E. Dorward-King, G. Ethier, G. Hall, M. Shaw, and B. Taylor was also appreciated. Thanks go to Helena Karam and to the staff of the GSC Main Library (CGIC) for their assistance. Partial funding from the International Council on Metals and the Environment is gratefully acknowledged. Parts of this review have appeared elsewhere as "***The Significance of Natural Sources of Metals in the Environment***", UN-ECE Science Working Group on LRTAP (HM) Invited Report, 1995 and as "***Methods of Partitioning Net Exposure Amongst Different Sources***" in The Ecological Risk Assessment - Guidance Manual, Chemical Evaluation Division, Environment Canada Report (under review).

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