CRITICAL REVIEW ON NATURAL GLOBAL AND REGIONAL EMISSIONS OF SIX TRACE METALS TO THE ATMOSPHERE

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Executive Summary

There is on-going regulatory concern for metals in the environment, and numerous regulations have been implemented globally, or are being developed, to control or curtail industrial metal emissions. However, the relative contribution made by natural sources, versus those of anthropogenic origin, is typically ignored in environmental regulation, or dated publications are cited as evidence that natural sources are relatively insignificant. The primary reference cited concerning the contribution made by natural sources to environmental metal contamination remains Nriagu (1989).

There is considerable uncertainty in previously-published estimates of atmospheric metals emissions and uncertainties have gone largely unquantified. Recent data provide an opportunity to update and generate more reliable and precise natural emissions estimates. Also, the advent of computer-assisted uncertainty analysis provides an opportunity to quantify the degree of uncertainty in metals emission estimates from various natural sources.

Presented herein is a critical review and analysis of natural emissions of cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn). Emissions were estimated globally, for Canada, and for continental North America. The natural emission sources considered included wind erosion of soil particulate matter, sea salt spray, volcanic emissions, forest and brush fires, and meteoric dust. For Hg, biogenic emissions from terrestrial vegetation, and evasion of vapour from soil, from the surface of oceans and the surface of lakes were also considered. Statistical methods were employed to derive mean (average) estimates and 5th percentile and 95th percentile emission estimates, the latter statistics providing 90 percent confidence limits for the mean predictions made.

With respect to global emissions, the estimates presented herein are between 1 and 2 orders of magnitude greater than those of Nriagu (1989). Given gains in the volume of available data and literature from which to derive such estimates, the improvements in data collection and analytical methods, and the quantification of fluxes from previously unmeasured or unrecognized sources, it is believed that the estimates presented herein, and their 90% confidence limits, are the most reliable estimates of natural source emissions to date. The omission of biogenic emissions from terrestrial vegetation for all but Hg may have resulted in a significant underestimation of total natural metal fluxes to the atmosphere for those non-volatile metals.

For Cd, Cu, Pb, Ni and Zn, the entrainment of soil dust particles into the air is a predominant source of natural emissions to the atmosphere. For mercury, volcanic emissions of Hg vapour predominate. Total natural emissions estimates for each metal, for Canada, North America and the globe, are presented in Table A.1, along with the global estimates of Nriagu (1989) for comparison.

The most significant data gap identified was the lack of information to quantify biogenic emissions of metals other than Hg. Data are required on the concentrations of non-volatile metals associated with volatile organic substances emitted by terrestrial and marine vegetation to enable the quantification of metal emissions from this natural source. Also, data are required to establish reliable enrichment factors to sea salt spray from sea water for both nickel and zinc.

Table A.1.   Estimated natural emissions of metals to the atmosphere for Canada, continental North
America, and globally.

			MEAN	5th PERCENTILE	50th PERCENTILE	95th PERCENTILE	Median estimates from Nriagu (1989)
CANADA	Flux of Metal (kg/yr)	Cd	5.3×10^4	1.9×10^4	4.8×10^4	1.1×10^5	
		Cu	2.6×10^6	3.5×10^5	1.9×10^6	7.6×10^6	
		Pb	9.7×10^5	2.9×10^5	8.2×10^5	2.2×10^6	
		Hg	1.1×10^6	5.4×10^5	8.2×10^5	2.3×10^6	
		Ni	1.0×10^6	1.7×10^5	8.0×10^5	2.7×10^6	
		Zn	4.6×10^6	1.2×10^6	3.9×10^6	1.0×10^7	
NORTH AMERICA	Flux of Metal (kg/yr)	Cd	7.1×10^5	2.4×10^5	6.3×10^5	1.5×10^6	
		Cu	5.0×10^7	7.4×10^6	3.8×10^7	1.4×10^8	
		Pb	4.5×10^7	6.6×10^6	3.4×10^7	1.3×10^8	
		Hg	5.6×10^6	2.2×10^6	4.7×10^6	1.1×10^7	
		Ni	2.5×10^7	5.2×10^6	2.5×1^7	8.0×10^7	
		Zn	3.8×10^7	1.2×10^7	3.3×10^7	8.5×10^7	
GLOBAL	Flux of Metal (kg/yr)	Cd	4.1×10^7	1.5×10^7	3.6×10^7	8.8×10^7	1.14×10^6
		Cu	2.0×10^9	2.7×10^8	1.5×10^9	5.5×10^9	27.7×10^6
		Pb	1.8×10^9	3.0×10^8	1.3×10^9	5.1×10^9	12×10^6
		Hg	5.8×10^7	2.0×10^7	4.7×10^7	1.2×10^8	2.5×10^6
		Ni	1.8×10^9	2.2×10^8	1.3×10^9	4.9×10^9	30×10^6
		Zn	5.9×10^9	1.2×10^9	4.7×10^9	1.5×10^{10}	45×10^6

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1.0   INTRODUCTION

There is on-going regulatory concern for metals in the environment, and numerous regulations have been implemented globally, or are being developed, to control or curtail industrial emissions to the atmosphere. Of particular concern are metals and metalloids (Sang and Lourie, 1997; Lin and Pehkonen, 1998; among others).   However, the relative impact or contribution made by natural sources, versus those of anthropogenic origin, is typically ignored in environmental regulation.

Metals are released into the environment from natural sources through a variety of processes including volcanic eruption, forest and brush fires, and wind-blown suspension of dust and sea salt spray (Nriagu, 1989; Lin and Pehkonen, 1998; among others).   Metals generally exist within the atmosphere as a component of particulate matter (de Mora et al., 1993). In the case of Hg, however, a significant proportion is also in the vapour phase, due to its volatility at typical ambient temperatures (de Mora et al., 1993; Schroeder et al., 1995; among others).

The primary citation concerning the contribution made by natural sources to environmental metal contamination remains Nriagu (1989), although other authors have also attempted to quantify this phenomenon (discussed and reviewed below). Nriagu (1989) presented an analysis of available data suggesting that natural contributions of metals and metalloids make up generally less than 50% of the total emissions to the atmosphere.

There is considerable uncertainty in previously-published estimates of atmospheric metals emissions; uncertainties that generally go unquantified, and often unmentioned. These uncertainties relate to the application of different quantification methods, to spatial and temporal variation in the data required to predict total atmospheric emissions, and to uncertainties introduced by less than complete knowledge of emission sources, their characteristics, spatial extent and temporal variability.

Regulatory agencies are now preparing to introduce or enact legislative initiatives to reduce industrial metal emissions, with no clear understanding of the relative contributions of anthropogenic and natural sources, and the uncertainties therein. Such legislation has been conceived on the basis of these earlier uncertain estimates of natural source contributions. For example, Canada is developing pollution abatement initiatives for Hg (soil, air and water quality guidelines, phase-out of products containing Hg, emissions reduction targets, etc.) on the assumption that natural and anthropogenic sources contribute approximately equally (50:50) to the environmental Hg problem (L.Trip, Environment Canada, Hull, Quebec, personal communication). Some data indicate that planned reductions in Hg industrial emissions, without consideration for natural sources, will result in no significant decline in levels of biotic contamination (Richardson and Currie, 2000). It is apparent, therefore, that a need exists to update the estimate of natural source contributions with the spate of recent research on the emission of elemental Hg from surface waters, soils, faults and geologic deposits.

In order to evaluate, more rigorously, the sustainable use of metals, it is essential that the contributions of natural releases to the atmosphere be updated to reflect the latest data, and that a statistically rigorous treatment of these data be undertaken to quantify confidence limits and uncertainties in these estimates.

The purpose of this paper was twofold. First, recently-available information was incorporated to estimate natural emissions of six metals to the atmosphere. Those metals were cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn). These emissions have been quantified locally (Canada), regionally (continental North America) and globally. Secondly, variability and uncertainty in the data required to quantitatively estimate emissions were subjected to a statistically-rigorous probabilistic analysis to derive confidence limits on those emission estimates.

2.0 PREVIOUS INVENTORIES OF NATURAL METALS EMISSIONS TO THE ATMOSPHERE

2.1 Particle Flux Estimates

The emissions of metals other than Hg are mainly associated with particulate matter. Therefore, estimates of metal fluxes are closely linked to estimates of primary particle fluxes. Previous emissions inventories for particles are summarized in Table 2.1.

An early inventory of particle fluxes was developed by Hidy and Brock (1970). These estimates were based on studies by other authors, and the particle flux due to forest fires was developed by extrapolating from United States data. Peterson and Junge (1971) independently developed an inventory of total particulate emissions. They also estimated the proportion of the particles that would be less than 5 Fm in diameter. The Study of Man's Impact on Climate (Matthews et al., 1971) presented global particulate emission inventories for particles <20 Fm diameter and particles <6Fm diameter. All of these inventories were based on the limited published data available at the time, and included broad assumptions and extrapolations from regional data (where necessary).

Another inventory of particulate emissions was developed by Lantzy and Mackenzie (1979). This inventory was based on global flux estimates for individual pathways from several other authors. Prospero et al. (1983) compiled emissions inventories from several authors, mainly from the early 1970s. Pacyna (1986) presented ranges of global particulate fluxes based on other authors, including Andren and Nriagu (1979), Peterson and Junge (1971) and Study of Man's Impact on Climate (Matthews et al., 1971). Mosher and Duce (1987) developed an independent particulate emissions inventory for volcanoes, sea salt and fires based on available literature; their estimate for windblown dust was adapted from Prospero et al. (1983).

Regional particulate emission inventories have also been developed. Evans and Cooper (1980) estimated particulate fluxes from windblown dust and fires in the United States, including a breakdown by state. Environment Canada (1981a) published particle flux estimates for Canada, including breakdowns by province, biome and source (i.e., soil dust, sea salts, forest and brush fires, volcanoes, plants and micro-community systems).

The Environment Canada report relied heavily on previous work by Robinson and Robbins (1971), Davis (1974) and Jaenicke (1980), who determined that natural sources contributed 85% to 89% of the particulate mass entrained into the atmosphere.

Windblown soil is one of the largest sources of natural metal emissions to the atmosphere (Pacyna, 1986). Through the process of weathering and erosion, metals that naturally occur in the Earth's crust will also be found in soil. Hagen and Woodruff (1975) suggest that wind erosion is an important source of total particulate mass and high particulate concentrations in the atmosphere. Their estimates place this source of particulate emissions to the atmosphere on par with emissions from anthropogenic sources.

Several authors have estimated the amount of soil that is entrained into the atmosphere via the wind, with the general range of 200-500 x 10^9 kg/yr globally (Nriagu, 1978; Schmidt and Andren, 1980). Nriagu (1989), to estimate metal fluxes to the atmosphere, used a soil flux range from a review paper prepared by Prospero et al. (1983). The maximum value of 500 x 10^9 kg/yr (commonly cited) is also cited in Peterson and Junge (1971) and is based on a value from an unpublished paper. The estimate was extrapolated from a calculation made for the United States including agricultural and natural dust sources. Another source cited in Peterson and Junge (1971) derives the same value of 500 x 10^9 kg/yr based on deep ocean sedimentation rates.

Duce (1995) conducted a review of more recent estimates of global soil flux, ranging from 1000-3000 x 10^9 kg/yr. Duce (1995) suggests that these higher estimates are more accurate than previously published estimates, due to more frequent monitoring and more remote ocean stations monitoring long distance dust flux. Alfaro et al. (1998) cite a value for dust flux from the Sahara alone at 600 x 10^9 kg/yr. Although the Sahara is a large contributor of wind blown dust, there are several other arid areas in the world that produce dust, suggesting that global emissions may be much higher.

2.2 Metal Flux Estimates

Previous metal emission inventories from natural sources are summarized in Tables 2.2 through 2.7. These inventories are generally based on particulate fluxes and estimated metal concentrations in the source particulate material. In some cases, metal concentrations measured directly in airborne particles were employed.

These inventories of natural metal fluxes have not been consistent in the sources considered or in the methods employed to quantify those emissions. However, they generally show windblown dust, volcanic emissions, sea salt spray, fires and biogenic emissions as the main sources of atmospheric aerosols. With a few exceptions, estimated metal fluxes from windblown dust and volcanoes have been relatively consistent between different inventories; estimated metal fluxes from other pathways have often varied by orders of magnitude. Metal fluxes from meteoritic dust were rarely considered in previous inventories.

In the late 1970's and early 1980's (Nriagu, 1978; Nriagu, 1980a,b,c), inventories generally used data obtained by Curtin et al. (1974) for metals in residual ash and ashed plant exudates to calculate fluxes from forest fires and biogenic emissions. However, these data were collected from conifers in areas with

anomalously high metal concentrations in soils or plants, and are not likely representative of typical metals concentrations in those media. Emissions due to sea salt spray were based on concentrations of metals in sea water and published enrichment factors of the metal from sea water to sea salt. However, the enrichment factors appear to have been used incorrectly in many cases (see Section 4.3). Volcanic emissions were based on crustal metal concentrations and published enrichment factors for metal enrichment in fine particulate matter. Zoller (1984) and Pacyna (1986) have summarized emissions inventories from other authors.

Lantzy and Mackenzie (1979) published an inventory of metal fluxes in which the volcanic emissions were based on concentrations in andesites (for volcanic particles) and gases from volcanoes, hot springs and fumaroles (for volcanic gases). The emissions due to fires were based on metal concentrations measured in land plants.

Nriagu (1978) adapted the Hidy and Brock (1970) and Peterson and Junge (1971) particle flux inventories for his metal flux estimates, though he used a lower meteorite dust flux estimated by Hindley (1976). He generally used the same particle fluxes in later publications during the late 1970's and early 1980's, though his inventories for copper (Nriagu, 1980b) and zinc (Nriagu and Davidson, 1980) used a lower flux for volcanogenic particles, and his inventory for Hg used a higher value for the flux from vegetation (Andren and Nriagu, 1979).

Jaworowski et al. (1981) developed natural metal emission inventories using two different approaches. One of these approaches was generally similar to the other inventories discussed above, though the emissions from forest fires, volcanoes and meteoritic dust were based on extrapolations using soil metal concentrations rather than metal concentrations specific to the sources of interest. The second approach was based on a back extrapolation from concentrations of metals and radionuclides in glacier ice; this second method resulted in metal flux estimates orders of magnitude higher than estimates based on particulate flux.

Nriagu (1989) published a revised metal emissions inventory based on particulate fluxes. These estimates, still frequently cited, were based on more recent data than his earlier publications. The basis for his inventory was as follows:

- windblown dust emissions were based on estimates of wind-borne soil particles combined with concentrations of metals in soil;
- sea salt spray emissions were based on estimated global sea salt flux, concentrations of metals in sea water, and enrichment factors for the metals from sea water to sea salt; the enrichment factors used were generally lower than those reported in the source literature;
- volcanic emissions were based on estimated sulphur emissions from volcanoes and published metal : sulphur ratios;
- wild forest fire emissions were based on biomass consumed by forest fires, metal concentrations in plants and assumed burning yields for metals;
- continental biogenic metal emissions were based on particulate organic carbon concentrations, aerosol deposition, and metal concentrations in plants; and

- biogenic emissions of metals complexed with volatiles were based on estimated hydrocarbon fluxes from terrestrial and marine plants and metal concentrations in surface organic microlayers of aquatic ecosystems.

Various data suggest that the natural metal fluxes to the atmosphere may be under-estimated by the Nriagu (1989) study:

- the atmospheric soil flux from the central United States alone (Hagen and Woodruff, 1975) appears to be of the same magnitude as the global flux reported by Nriagu (1989);
- the sea salt enrichment factors used by Nriagu were generally lower than those found in other literature (see Table 4.14); Nriagu (1989) did not specifically present the metal concentrations in sea water employed in his calculations, so those calculations could not be duplicated or confirmed;
- there are now more recent data available on sulphur flux and metal to sulphur ratios (see Tables 4.15 and 4.16) for revised predictions of emissions from volcanic emissions;
- for emissions due to fires, recent studies have measured actual concentrations of metals in smoke particulate (see Table 4.19) (rather than relying on concentrations in non-combusted wood and vegetation); as well, more refined estimates of the quantity of biomass burned (see Table 4.18) and particulate emissions (see Table 4.20) have been published; and
- measurements of Hg vapour emissions from vegetation, and more refined estimates of biogenic emissions of Hg (see Table 4.24), have been recently published.

2.3   Mercury

Additional comment on Hg is warranted given its release from natural sources as both particulate matter and vapour.

To date, two primary approaches have been employed to estimate the relative contributions of anthropogenic and natural sources of Hg to the atmosphere: source inventories and dated lake sediment cores.

2.3.1   *Mercury emissions inventories*

On a global basis, previous source inventories have been used to estimate that anthropogenic sources contribute between 50% and 75% of total annual atmospheric Hg loadings (reviewed by Fitzgerald, 1995; see also Fitzgerald, 1986; Lindqvist et al., 1991; Nriagu, 1989). By difference, natural sources would then contribute between 25% and 50% of total global atmospheric loadings. On a more regional scale, however, available source inventories suggest that natural sources (involving gaseous and particulate emissions from land and water surfaces) can contribute anywhere from only about 13% of total atmospheric loadings (estimated within the province of Ontario, Canada; Innanen, 1998) up to 80% of atmospheric Hg concentrations (for Sweden; Brosset, 1981). Unfortunately, the reliability (quality and quantity) of data upon which natural source Hg emissions estimates are based is far less than that for industrial emissions, the latter having been the subject of quantitative industrial emissions inventories in numerous countries for more than a decade.

Various authors have estimated the annual global Hg flux, or reviewed estimates by other authors, from various natural sources. These authors include Ebinghaus et al. (1999), Rasmussen (1994a), Lindqvist et al. (1991), Nriagu (1989), Pacyna (1986, 1987), Zoller (1984), Jaworowski et al. (1981), and Lantzy and Mackenzie (1979). Regional inventories of natural Hg emissions have been presented by Innanen (1998; for Ontario, Canada) and Vasiliev et al. (1998; for Siberia). These estimates are summarized in Table 2.5.

Since the mid-1980's, quantification of global emissions of Hg to the atmosphere has suggested approximately equal contributions from natural and anthropogenic sources, with the analysis presented by Nriagu (1989) remaining the primary citation on the contributions of natural emissions of Hg to the global atmosphere. For example, the analysis of Nriagu (1989) is the primary basis upon which Environment Canada has assumed that natural sources contribute between 40% and 50% of total annual Hg emissions to the Canadian atmosphere (L. Trip, Environment Canada, personal communication). Unfortunately, previous analyses have not attempted to quantify the uncertainty in these estimates, beyond providing approximate minima and maxima around predicted mean or modal values. The potential range between minimum and maximum natural source emissions can be quite large, however (see Table 2.5).

2.3.2   *Mercury sediment profiles*

Profiles of Hg concentration by depth in sediment cores from remote lakes (lakes not affected by direct industrial discharges or impoundment) have also been put forward as evidence of the significant increase in industrial emissions of Hg in the past century (Fitzgerald et al., 1998). Examination of published data from Ontario lakes (Evans, 1986; Johnson et al., 1986; Johnson, 1987; Rasmussen et al., 1998a) suggests that Hg deposition from the atmosphere to these lakes has increased anywhere from less than 2 times to as much as 10 times over the past 100 to 150 years. This suggests that the natural source component of this atmospheric deposition could range from more than 50% to less than 10%.

Not only does this ratio of surficial (recent) sediment Hg concentration to deep (purported pre-industrial or natural) sediment Hg concentration vary several fold, but it varies several fold between lakes situated in close proximity to one another. The atmospheric deposition of industrial Hg emissions to lakes is known to decline with increasing distance from point sources (EPMAP, 1994). However, lakes in close proximity to one another are also more or less equally distant from significant industrial point sources. Therefore, distance from point sources does not explain all of the inter-lake variation in Hg sedimentation rates. This inter-lake variation in apparent anthropogenic Hg sedimentation indicates that Hg concentration in lake sediments is influenced by factors other than simply atmospheric inputs. One confounding factor may be early diagenesis (Matty and Long, 1995), which is controlled by sediment organic matter content and other chemical and geochemical characteristics that vary from lake to lake. Although the significance, and even the existence, of this phenomenon is debated (Fitzgerald et al., 1998; Rasmussen, 1998a), it is clearly evident that the content of organic matter in sediments explains a great deal of the inter-lake variability in sediment Hg concentrations among lakes in relatively close proximity (Rasmussen et al., 1998a). As a result, it is apparent that Hg sediment profiles provide an inadequate basis for quantifying the relative contributions of natural versus anthropogenic sources of the Hg that is ultimately deposited to lake sediments.

3.0   UNCERTAINTY ANALYSES

As indicated throughout the Methods section (below), variables necessary to calculate natural emissions of metals to the atmosphere were defined in terms of a distribution, spanning values from the likely minimum through the likely maximum. In order to derive confidence limits for estimates of natural emissions to the atmosphere, a statistically rigorous approach to data analysis was required. In order to achieve this, probabilistic (stochastic) methods were employed.

Probabilistic uncertainty analyses were carried out in order to evaluate the influence of simultaneous, independent variations in several equation variables. Data such as concentrations of metals in soil particulate matter, sea salt, etc. are not constant, but range over several orders of magnitude, depending on geographic setting and numerous other factors. The ranges of possible values are best represented by distributions or probability density functions.

The exact form of the probability distribution for many of the parameters is not known. Therefore, triangular distributions have been assigned to most of the variables, defined in terms of the upper and lower limits and the modal or most likely value. Triangular distributions are recommended when data are insufficient to define the true data distribution, or when the underlying distribution type is known (log-normal, say) but data are insufficient to accurately quantify all distributional characteristics and parameters (Finley et al., 1994).

Using a form of Monte Carlo simulation, multiple iterations of flux calculations were conducted while randomly sampling from the distributions of input variables. A population of equation solutions was thereby generated, resulting in a probability distribution for the calculated fluxes from which the mean value and the 5th, 50th (median) and 95th percentiles of the flux distributions were estimated. The 5th and 95th percentile statistics represent robust estimates of the upper and lower 90% confidence limits for the estimated mean and median flux values. For each simulation, a Latin hypercube sampling method was used and 20 000 iterations were performed using Microsoft Excel97® (Microsoft Corp., 1996) and Crystal Ball ® (Decisioneering Inc., 1996), software.

4.0   GENERAL METHODS

Consistent with the earlier work of Nriagu (1989), five natural sources of metals emissions to the atmosphere were considered herein for Cd, Cu, Pb, Ni and Zn:

- wind-borne soil particles;
- sea salt spray;
- volcanoes;
- forest and brush fires;
- meteoritic (extra-terrestrial) dust.

The atmospheric emissions of Cd, Cu, Pb, Ni and Zn due to biogenic processes could not be calculated due to insufficient data on metal concentrations in volatile plant exudates. This is discussed further in section 8 (Discussion).

In addition to particulate-borne emissions of Hg, direct evasion of vapour also occurs from surface waters, soil, geologic deposits and vegetation. Therefore, nine natural sources of Hg emission to the atmosphere were considered:

- Hg vapour (Hg^0) flux from soils and bedrock;
- Hg^0 flux from surface marine waters;
- Hg^0 flux from surface fresh waters;
- volcanic emissions (both gaseous and particulate Hg);
- wind-induced entrainment of surficial soil and dust particles;
- wind-induced entrainment of sea salt spray;
- forest and brush fires;
- meteoritic (extra-terrestrial) dust;
- Hg^0 flux directly from vegetation (biogenic emissions).

Nriagu (1989) recognized the potential biogenic emission of Hg vapour from vegetation. However, no data existed at that time to directly quantify such emissions. Therefore, Nriagu (1989) necessarily extrapolated from published data on hydrocarbon emissions from plants, combined with measured fluxes of methylated Hg compounds and available data on the ratio of Hg vapour concentration and hydrocarbon concentration as reported for urban, rural and remote air samples. Recent advances in the measurement of vegetative Hg emissions has lead to speculation that natural emissions of Hg may be under-estimated by as much as 100% (Lindberg et al., 1998).

Also, the accurate quantification of Hg vapour flux from soils and bedrock is a recent (< 5 years) development and that recent research permits the direct quantification of Hg flux to the atmosphere as a function of soil Hg concentration (see Rassmussen et al., 1998b, for example).

Nriagu (1989) did not specifically quantify Hg emissions emanating from bodies of fresh water. However, recent research permits the quantification of this flux, accounting for seasonal variability due to the influence of ambient temperature.

Specific equations and data reviewed to quantify natural emissions are outlined in greater detail below. The first step, however, was to divide the regions under consideration (Canada, continental North America, Globe) into specific biomes or ecoregions, each of which has unique vegetative characteristics, leading to unique atmospheric particle flux rates, unique fire frequency, etc.

4.1   Ecoregions

The total areas of Canada, continental North America and the globe that encompass nine prescribed ecoregions are presented in Tables 4.1 through 4.3. General descriptions of the different ecoregions are provided below.

For Canada, two sources of information were used to define ecoregions - Environment Canada (1981a) and Clayton et al. (1977). The ecoregion areas in both reports were quite similar. Therefore, they were averaged together to obtain mean values for surface area covered. In the case of the grassland ecoregion, that defined by Clayton et al. (1977) comprised 3 of Environment Canada's ecoregions - Eastern Canada Grassland, Agricultural Grassland (Prairies and BC) and Aspen Parkland. To simplify the proposed ecoregion scheme, the grassland scheme of Clayton et al. (1977) was used.

For continental North America, data from Leenhouts (1998) provided detailed information on vegetation cover in the United States. That information was reviewed in conjunction with an ecoregion map prepared by the United States Geological Survey (Eastern Energy and Land Use Team, 1982) which used ecoregions as described by Bailey (1998). These two sources were used to define ecoregions in the United States. The nine ecoregions defined for Canada and the U.S. were simply added to derive total areas for each ecoregion in continental North America.

Different researchers have used varying criteria in categorizing the global land surface into ecoregions (Guenther et al., 1995; Bailey, 1998; Hannah et al., 1995; and Pears, 1985). Categories defined by Bailey (1998) most closely resemble the ecoregion scheme used herein. In addition, Bailey (1998) provides a detailed map by which to gain a geographical understanding of the ecoregions. Therefore, Bailey's (1998) data were used herein to estimate world ecoregion areas.

The estimated total surface area of each ecoregion changes temporally due to changing climatic factors, deforestation, etc. Also, the estimation of ecoregion surface area varies from one author to another due to varying estimation methods and data employed. However, for the purpose of the analysis presented herein, the area of each ecoregion was assumed to be constant (fixed) so as not to unduly influence the uncertainty analysis.

4.1.1   Tundra

The tundra region occupies the northernmost regions of the northern hemisphere and southernmost regions of the southern hemisphere. It is characterized by a cold climate, general absence of trees, and an intermittent ground covering of lichens, mosses, and sedges (Clayton et al.,1977). For the purposes of this study, it also includes areas classified as arctic deserts. It includes 14.1×10^6 km^2 of ice covered areas such as Greenland and the Antarctic, and the islands in northern Canada (Bailey, 1998).

4.1.2   Boreal barrens

The boreal barrens refers to the transition zone between the tundra and the boreal forest consisting of open, stunted coniferous forests, interspersed with tundra vegetation (Clayton et al., 1977). It includes areas such as northwest Siberia, northwest Canada and Alaska (Bailey, 1998).

4.1.3   Boreal forest

The boreal forest ecoregion refers to the cool forest zone of mainly coniferous trees (dominated by spruce species) that occurs south of the tundra ecoregion (Clayton et al., 1977). It covers a wide band across Canada from coast to coast and into Alaska, and for this study includes the taiga regions across most of Russia (Bailey, 1998).

4.1.4   Grassland

The grassland ecoregion is characterized by ground cover of a variety of grasses and sparse trees (Clayton et al., 1977). It covers agricultural areas, savannas, steppes and prairies. For the purposes of this report, groundcover dominated by grasses was the criteria for placing an area in this category. It was assumed that similar ground cover would allow similar soil exposure to wind, and similar fire conditions. Also included in this category were the humid savannas of central South America, south central Africa, India and the Carribean. These latter areas are dominated by grasses, but may be somewhat more humid than grasslands in North America. Aspen Parkland areas have been included in the grassland ecoregion because they are largely fescue prairie (Clayton et al., 1977) and they were not segregated by Bailey (1998).

4.1.5   Coastal/mountain forests

The coastal/mountain ecoregion is characterized by a dominance of coniferous forests (mainly pine, cedar and fir species) in montane and coastal regions (Clayton et al., 1977). It includes areas in western North America including the Rocky Mountains, mountainous regions in the southern portions of South America, and portions of Europe, the United Kingdom, New Zealand and Australia (Bailey, 1998).

4.1.6   Mixed forest

In Canada, the mixed forest ecoregion is comprised of the mixed forests surrounding the Great Lakes region and the Acadian forest in the Maritimes. These forests consist of a mixture of deciduous and coniferous trees (Clayton et al., 1977). In North America, this region includes the Great Lakes forests, the mixed forests in the northeastern United States and the mixed and deciduous forests in the southeastern United States. Deciduous forests are included in this category based on the assumption that amount and type of vegetation cover is quite similar.

4.1.7 Rainforest

Rainforests are areas that receive significant annual rainfall and have a closed canopy of diverse evergreen trees with a lower layer of vines, palms and epiphytes (Brown and Gibson, 1983). Regions in this category include the Amazon Rainforest, Zaire and several smaller countries in west/central Africa along the coast, and Indonesia (Bailey, 1998).

4.1.8 Shrubland

This area is a mix between grassland, forest and desert. It is characterized by dry areas with Mediterranean climate, and includes chaparral, shrubland and dry woodlands. These areas have a dense mass of shrubs covering the ground and often have hot, dry summers (Brown and Gibson, 1983). Regions in this category include areas of the southwestern United States, central Africa, parts of Australia, and central/southwest Asia (Bailey, 1998).

4.1.9 Desert

Deserts are in the most arid parts of the world and receive little and/or sporadic rainfall. Vegetation is quite sparse and consists of scattered shrubs (Brown and Gibson, 1983). Desert areas are found in north Africa, the Middle East, Australia, south central Asia/northern China and in the southwestern United States (Bailey, 1998).

4.2 Atmospheric Metal Emissions due to Soil Particle Flux

The flux of each element to the atmosphere due to suspension of soil particles was calculated as:

$$\text{MF (kg/year)} = \sum [A_{ERi} \times PF_{ERi} \times C_{Si} \times 10^{-6} \text{ kg/mg}]$$

where, MF = metal flux to atmosphere (kg/yr)
  AER_i = the area of ecoregion i (km^2)
  PF_{ERi} = particulate flux to atmosphere from ecoregion i (kg/km^2/yr)
  C_{Si} = concentration of metal in soil of ecoregion i (mg/kg)

Based on an extensive review of available literature, only the shrubland ecoregion had published data quantifying the soil particulate flux to the atmosphere. Several studies have been conducted on particle movement during dust storms in the Great Plains of the central United States (Hagen and Woodruff, 1973, 1975; Gillette et al.,1978).

The flux data reported by Hagen and Woodruff (1975) for the south central United States (Texas, Oklahoma, New Mexico, Kansas and Colorado) were selected to represent the shrubland ecoregion for the following reasons:

1. Flux data were available for the south central United States for 2 decades (the 1950s and the 1960s) while only 1950s data were available for the north central United States.

2. The Environment Canada (1981a) report suggests that the 1950s were an exceptionally dry decade. Therefore, using the flux data recorded over 2 decades (including the 1950s)would encompass the range of climate variability.

3. The land surface encompassed by the south central United States most closely resembles the shrubland ecoregion.

It should be noted that the values reported by Hagen and Woodruff (1975) are based on soil flux during dusty hours only. A previous study by Hagen and Woodruff (1973) calculated that the south central United States was dusty 45 hours per year. Therefore, the Hagen and Woodruff (1975) soil fluxes were adjusted (multiplied by 0.005; i.e., [45 hours]/[8760 hours per year]) to obtain an annual soil flux in units of $kg/km^2/yr$ for the shrubland ecoregion.

For the uncertainty analysis and determination of confidence limits of estimated emissions, variability in the element concentrations in soil and the atmospheric flux of the soil particles for the different ecoregions were considered.

For the uncertainty analysis, a triangular distribution was assigned to the particle flux value for the shrubland ecoregion with the 1960s minimum value as the overall minimum value (526 $kg/km^2/yr$), the 1950s maximum value as the overall maximum value (431 225 $kg/km^2/yr$) and the mean of the 1950s and 1960s data as the most likely value (61015 $kg/km^2/yr$).

A study by Gillette et al. (1978) confirms the range of soil fluxes selected for the shrubland ecoregion. Gillette et al. (1978) measured dust flux during dust storms in Texas, reporting 0.3 to 0.5 million metric tons of soil entrained per dust storm (measured at an altitude of 2.7 km and over an area of 5.7×10^{11} m^2) which results in 527 to 877 kg/km^2 dust particles released per storm. Assuming 3 storms per year (as per Gillette et al., 1978), the annual soil flux would be 1578 to 2631 $kg/km^2/yr$ which falls within the low end of the range of fluxes calculated using the Hagen and Woodruff (1975) data. It should be noted that the Gillette et al. (1978) data were measured at an altitude of 2.7 km which implies that their flux excludes those particles with shorter atmospheric residence times.

4.2.1 *Dustiness of ecoregions relative to shrubland*

To quantify the atmospheric soil flux for the other ecoregions, a flux ratio, relative to shrubland, was determined based on published dust storm day frequency data (see Table 4.4). It was assumed that the flux of soil particulate matter to the atmosphere in any given ecoregion was directly proportional to the frequency of dust storms in that area. Therefore:

$$F_{DS\text{-}shrubland}/F_{DS\text{-}ecoregion i} = PF_{shrubland}/PF_{ecoregion i}$$

OR

$$PF_{ecoregion\,i} = PF_{shrubland} \times F_{DS\text{-}ecoregion\,i}/F_{DS\text{-}shrubland}$$

where, $F_{DS\text{-}shrubland}$ = frequency of dust storms on shrubland
         $F_{DS\text{-}ecoregion\,i}$ = frequency of dust storms on ecoregion i
         $PF_{shrubland}$ = particle flux from shrubland
         $PF_{ecoregion\,i}$ = particle flux from ecoregion i

Minimum, maximum and most likely values for the ratio $F_{DS\text{-}ecoregion\,i}/F_{DS\text{-}shrubland}$ were calculated for each ecoregion from available data and are presented in Table 4.4.

There is very little information available on soil flux or frequency of dust storms for forested areas. Estimates by Middleton (1984) were used to evaluate the forested parts of Australia and data from Orgill and Sehmel (1976) were used to evaluate the forested parts of the United States. Estimates of dusty day frequency for forested areas predicted herein are much higher than those predicted by Environment Canada (1981a). Although Environment Canada (1981a) also used data from Orgill and Sehmel (1976), it remains unclear as to how Environment Canada (1981a) arrived at their reported relative dust frequency for forested areas.

One problem with using dusty day frequencies as a basis for soil flux is that these data give no estimate of the volume of dust raised, the length of the storm nor the altitude to which the dust is raised (Middleton et al., 1986). As well, the dust observed in an area does not necessarily originate in that area. Orgill and Sehmel (1976) suggest that much of the dust observed in mountainous areas and mixed forest areas in the United States originated elsewhere. Therefore, the estimated dustiness values for the coastal/mountain region, mixed forest, and rainforest were arbitrarily reduced by a factor of 2, as done by Environment Canada (1981a) in their calculations. There was no other information in the reviewed literature to suggest a different correction factor.

Based on the dust storm day data, a higher soil flux was calculated for the mixed forest ecoregion than for the mountain/coastal forest ecoregion. Support for this conclusion comes from the Wind Erosion Research Unit (1999) which mapped the areas in the United States with wind erosion problems. The Pacific coastal and mountain areas showed very little erosion, while a large section in the southeastern United States (part of the mixed forest ecoregion) was subject to wind erosion.

For the rainforest ecoregion, a value of 0.077 dusty days/yr, relative to shrubland, was calculated from the maps of Australia (Middleton, 1984). This value is high due to the influence of one data location that had a much higher dust storm day frequency than the others. The only other data available for rainforests is a value of 0 from Middleton (1986b) from a map showing the southern tip of India. Choosing a most probable value of 0.039 (0.077/2) relative to shrubland would indicate that rainforests are dustier than mountain/coastal forests and mixed forests, which is unlikely. It is more likely there is hardly any dust flux emitted from rainforests. Therefore, a triangular distribution was selected herein for the rainforest ecoregion with minimum and most likely relative values of 0 and a maximum value of 0.039.

Estimates for dusty days on tundra were not found in the literature. In the tundra region, limited ground cover and trees will allow wind erosion to occur. However, much of this erosion can be attributed to blowing snow (Fristrup, 1952). Ashwell (1986) reports that dust storms do occur in central Iceland. It seems reasonable that, due to lack of vegetation, and reports of dust storms, that tundra would be dustier than mountain/coastal areas. However, over half of the estimated tundra area is permanently ice covered from which there should be no dust emissions. Therefore, the tundra region dustiness was arbitrarily estimated to be ½ of the value for the mountain/coastal ecoregion.

Estimates from minerogenic dust storm frequencies for boreal barrens and boreal forest were not found in the literature. Nickling (1978) shows that dust storms do occur in boreal barrens areas, specifically in a river valley delta in the Yukon Territory. However, the National Climate Data Center in the United States (NCDC, 2000) indicates 0 recorded dust storms from January 1, 1993 to June 30, 2000 for Alaska (also boreal barrens). This suggests that dust storms are possible in boreal barrens and boreal forest, but that they are not frequent. Boreal forest and boreal barrens have a similar coniferous type forest to the mountain regions and, therefore, were assigned the same dusty day frequency as mountain regions (i.e., 0.01 relative to shrubland). Boreal barrens and boreal forest likely have a longer snow cover (especially when compared to the coastal portion of the mountain/coastal region) and thus will likely have a maximum dustiness less than the maximum for the mountain/coastal ecoregion. A uniform distribution was chosen for boreal barrens and boreal forest with 0 as the minimum and 0.01 as the maximum.

Mountainous, coastal and forested areas do not often experience dust storms (Orgill and Sehmel, 1976). In forested areas, the vegetation cover acts as a protective barrier against winds to prevent aeolian erosion and suspension of soil materials (Orgill and Sehmel, 1976). Brazel and Nickling (1987) report that vegetation cover alters the aerodynamics of the air movement over the land and it requires a higher wind speed to raise dust. A large portion of the coastal mountains and rocky mountains in the northeastern United States have very low dust frequencies, with much of that dust originating elsewhere (Orgill and Sehmel, 1976). The non-erosive materials of mountainous and other similar areas also leads to a minimal amount of soil suspension (Hagen and Woodruff, 1975).

4.2.2   Metals concentrations in soil

Data used herein on concentrations of metals in soils are summarized in Tables 4.5 through 4.10. Metal concentrations in soil entrained into the atmosphere are equivalent to those found in surface soil (Eltayeb et al., 1993). Canadian average concentrations for each metal were calculated by averaging all tabulated data for Canada. North American values were obtained by taking a weighted average of the Canadian and United States data based on land area. Estimates for global metal concentrations in soil were calculated by taking a weighted average of available data from various continents. In cases where data for a continent were missing, average concentration data from other continents were assumed to be representative. The values calculated for the world were comparable with world estimates made by various other sources. Average concentrations derived as described above were used as most likely values in triangular distributions employed for uncertainty analysis. Minimum, maximum and most likely metals concentrations used herein are detailed in Tables 4.5 through 4.10.

Data for the South Pacific were omitted from calculations for Ni concentrations because of anomalously high values (see Table 4.9). Hg data for Africa were also omitted due to anomalously low values (see Table 4.8).

4.3   Atmospheric Metal Emissions Due to Sea Salt Spray

The flux of each element to the atmosphere through suspension of sea salt spray was calculated as:

$$MF \text{ (kg/year)} = A_{Ocean} \text{ x } SF_{Ocean} \text{ x } [C_{SW}/C_{Na}] \text{ x } EF_{Sea} \text{ x } SS_{Na}$$

where, MF = metal flux to atmosphere (kg/yr)

A_{Ocean} = surface area of ocean (km^2)

SF_{Ocean} = sea salt spray flux to atmosphere from the ocean area considered (kg/km^2-yr)

C_{SW} = concentration of metal in sea water (ng/L)

C_{Na} = concentration of sodium in sea water (ng/L)

EF_{Sea} = enrichment factor for the concentration of the metal in sea water versus sea salt, relative to the enrichment of sodium in sea water versus sea salt

SS_{Na} = concentration of sodium in sea salt (kg/kg)

Note: EF_{Sea} is not simply the relative concentration of the metal in sea salt versus sea water (discussed below).

In order to estimate the emission of Cd, Cu, Pb, Hg, Ni and Zn to the atmosphere in sea salt, the following assumptions were employed:

- For the Canadian and North American estimates, the ocean surface area was considered to be defined by international territorial limits (200 nautical miles from the coast). These areas were prorated for seasonal ice cover to obtain annual average ice-free surface areas.

- The sea salt flux per unit ice-free area for Canada, North America and globally was assumed to be equivalent, on a kg/km^2/yr basis, although variation due to average wind speed, storms, etc. were considered within the uncertainty analysis.

- The concentrations of metals in the sea near Canada and North America were based on data collected adjacent to North America, whereas all reviewed data were used for global average concentrations.

- Data from areas clearly polluted by anthropogenic effects (i.e., located near major industrial sources) were excluded.

For the uncertainty analysis, variability in element concentrations in sea water, sea water to sea salt enrichment factors and ocean surface emission rates of sea salt spray (as affected by storms, variation in

annual average wind speeds, etc.) were considered. The estimates of sea salt flux (as sodium) to the atmosphere was summarized by a triangular distribution defined from the minimum, modal and maximum values published in the literature. The enrichment factor was represented by a triangular distribution, with the minimum enrichment factor of 1 (assumes that the ratio of the concentrations of the metal and sodium (Na) was the same in sea water and sea salt); the 'most probable' enrichment factors were taken as the median of all published values (on a metal-by-metal basis) (see discussion below); and the maximum enrichment factor was taken as the maximum reported value in the literature. Triangular distributions were developed for metal concentration data, using published values for Canadian, North American and global average metal concentrations in sea water.

4.3.1   Metal concentrations in sea water

Measurements of metal concentrations in sea water are summarized in Table 4.11. Data suspected of being affected by nearby anthropogenic sources were excluded. Median values were used to represent "most probable" concentrations instead of mean values, since the data were not normally distributed.

4.3.2   Mass of sea salt emitted to the atmosphere

Available estimates of global sea salt flux are summarized in Table 4.12. Based on these estimates a triangular distribution (minimum, mode and maximum values) was developed to represent the global sea salt flux from the oceans on a $kg/km^2/yr$ basis. Sea salt is emitted to the atmosphere through bursting bubbles at the water surface, and the rate of sea salt production is highly dependent on wind speed (Monahan, 1986). The salt is emitted from a thin microlayer at the ocean surface, which contains elevated concentrations of many metals when compared with the near-surface water (Duce et al., 1976).

The sea salt fluxes for Canadian and North American marine territories (defined by the international territory boundaries) were calculated by multiplying published global fluxes by the ratio of the ocean area in the territorial boundaries to the total ocean area. Adjustment was also made in Canadian calculations to account for areas of ice cover, from which salt spray is not expected. This was done by multiplying the actual area defined by the territorial boundaries by ice cover factors adapted from Environment Canada (1981a): 0.25 for the Arctic Ocean, 0.58 for the Atlantic Ocean north and east of Newfoundland and 0.83 for the Canadian portion of the Atlantic Ocean south and west of Newfoundland.

4.3.3   Enrichment of metals in sea salt

Previous estimates of the contribution of sea salt flux to global metals emissions were calculated by Nriagu (1980a,b,c). In those papers, the metal flux due to sea salt spray was determined as:

$$MF = C_{SW} \times EF \times F_{SS}$$

where, MF = metal flux to the atmosphere (kg/yr)
C_{SW} = concentration of metal in sea water (mg/kg)
EF = enrichment factor for metal between sea water and sea salt (mg/kg salt/mg/L water)

F_{SS} = flux of sea salt to the atmosphere (kg/yr)

However, in those papers, the enrichment factors obtained from Duce et al. (1976) appeared to be mistakenly represented as $[C_{M\text{-atm}}]/[C_{M\text{-water}}]$, where $C_{M\text{-atm}}$ is the concentration of the metal in the atmosphere and $C_{M\text{-water}}$ is the concentration of the metal in sea water. The enrichment factors are actually meant to represent the ratio of the concentrations of the metal to that of sodium in sea salt aerosol divided by the ratio of the concentrations of the metal to that of sodium in sea water:

$$EF_{sea} = \frac{[X_{atm}]\Big/[Na_{atm}]}{[X_{water}]\Big/[Na_{water}]}$$

Studies have shown that the concentrations of many metals are greater in the ocean surface microlayer compared to bulk sea water (Buat-Ménard, 1984; Duce et al., 1976; Hardy, 1997). Surface microlayer metal concentration data are summarized in Table 4.13 (for comparison to data in Table 4.11). Therefore, the enrichment of metals in sea salt reflects, in part, their higher concentration in this surface microlayer from which sea salts are emitted. Enrichment may also be partly due to the surface bubbles (which generate sea salt) scavenging materials from the ocean (Weisel et al., 1984; Heaton, 1986). The amount of material scavenged is affected by biological activity. Also, anthropogenic metals deposited to the ocean surface may be bound to organic particles contained in the surface microlayer (Hardy, 1997).

As a result of this enrichment, the composition of sea salt particles is different than the composition of bulk sea water. An enrichment factor can be estimated to account for this effect; this factor is based on the assumption that all sodium measured in sea salt aerosol is from the ocean. These factors have been derived under controlled conditions in order to ensure that the enrichment is due to the bubble generation, and not due to other sources (such as windblown dust or anthropogenic sources), as described by Duce et al. (1976), Weisel et al. (1984) and Heaton (1986).

Values of enrichment factors reported in the literature (for Cd, Cu, Pb and Zn) are summarized in Table 4.14. The published values date from 1986 or earlier. Dr. Robert Duce, one of the principal authors of the published research on enrichment factors, reported that, to his knowledge, no subsequent data on sea water to sea salt enrichment factors have been published or collected (R. Duce, personal communication). He also indicated that enrichment factors have not been published for Hg and Ni.

For purposes of the analysis presented herein, reported concentrations of metals in bulk seawater were employed to estimate atmospheric emissions from the ocean surface. Published salt spray enrichment factors were considered to indirectly account for the surface microlayer enrichment phenomenon.

Work by Fitzgerald (1976) suggested that Hg concentrations are not enriched in the ocean surface microlayer. Therefore, it was assumed herein that Hg is not enriched in sea salt aerosols. In the case of Ni, the EF_{sea} was conservatively assigned minimum and modal values of 1 (i.e., no enrichment) and a

maximum value of 10, the value used by Nriagu (1989). The assumed maximum value of 10 is still much lower than the measured EF_{sea} values for other metals (see Table 4.14).

For purposes of calculating the metal fluxes, it was assumed herein that the mean concentration of sodium in sea water was 10.6 g/L, and the concentration of sodium in sea salt was assumed to be 35% by weight (based on Duce et al., 1976, and Weisel et al., 1984).

Sea salt flux is highly dependent on wind speed, among other factors (Monahan, 1986). The estimates of sea salt flux used herein were, of necessity, global averages. In addition to the variability in sea salt flux, there is also spatial variability in the concentrations of metals in seawater, and in the enrichment of metals in sea salt. The latter is likely due to variable biological activity in the ocean; the extent of the variability is still not well understood (Weisel et al., 1984). Unfortunately, there were insufficient data to permit a more detailed and precise treatment of this variability.

4.4   Volcanoes

The flux of each element to the atmosphere due to volcanic emissions was calculated as:

$$MF \text{ (kg/yr)} = ER_{SO2} \ x \ R_{M\text{-}SO2}$$

where, MF = metal flux to atmosphere (kg/yr)
ER_{SO2} = sulphur dioxide emission rate (kg/yr)
$R_{M\text{-}SO2}$ = metal to sulphur dioxide ratio

The quantification of metal emissions from volcanoes could not be determined based on direct measurements of particulate emissions and metal concentrations in that particulate matter. There are only a few estimates of global particulate emissions from volcanoes, most of which are dated. Although several publications exist on the concentration of metals in volcanic particulate matter, most of these reported data in units of mass/volume. Unfortunately, only one publication (Abramovskiy et al. , 1977) provides data on the mass of dust in the plume of a volcano (3-4 mg/m^3) and the general representativeness of this figure is unknown.

Volcanic metal emissions based on limited and possibly outdated studies was not considered a reliable representation of the present state of emissions. Therefore, atmospheric metal emissions from volcanic activity were determined using metal:sulphur dioxide emission ratios.   Several recent studies have used metal:sulphur ratios as a method for estimating metal emissions (Le Cloarec et al. 1992; Hinkley et al. 1999; Dedeurwaerder et al. 1982; Varekamp and Buseck 1986; Patterson and Settle 1987; Ballantine et al. 1982; Stoiber et al. 1982; Nriagu 1989; Phelan et al. 1982; Buat-Menard and Arnold 1978) and, in our opinion, remains the most valid approach until sufficient direct measurements are made. Using metal to sulphur dioxide ratios also accounts for emissions during both passive and active periods; sulphur dioxide release has been measured from volcanoes at different stages of volcanic activity.

In order to estimate the emission of Cd, Cu, Pb, Hg, Ni and Zn to the atmosphere, which are contained in or adsorbed to ejected particulate matter, the following assumptions were employed:

- Metals are released from volcanoes proportionally to sulphur dioxide.

- Globally, the annual average emission of sulphur dioxide is approximately 4.5×10^6 - 5.0×10^7 t/yr. The ratio of metals to sulphur dioxide was used along with the annual global sulphur dioxide emissions to determine metal emissions from volcanoes.

- The continental United States (including Alaska and the Aleutian Islands) contains approximately 10% of the world's active volcanoes. Lacking more precise data, it was assumed that the emission of sulphur dioxide to the atmosphere of continental North America was, therefore, 10% of the annual average global emission (this equates to 4.5×10^5 - 5.0×10^6 t/yr).

- In Canada there are no active volcanoes and, therefore, this source is not considered in estimates of natural emissions of metals to the atmosphere of that country.

For the uncertainty analysis, variability in sulphur dioxide emissions between different years and variation in element concentrations emitted to the atmosphere (which can vary widely from one volcano to another) were considered.

4.4.1   *Sulphur dioxide released to the atmosphere*

Various estimates of volcanic sulphur dioxide emissions are presented in Table 4.15. There have been several estimates of volcanic sulphur dioxide emissions as it is a frequently measured compound. Berresheim and Jaeschke (1983) estimated that 1.52×10^7 t of sulphur dioxide are released each year from volcanoes globally. This value is used commonly by others in their estimates of emissions, and was chosen as the "most probable" value for this study. As well, it is very similar to the values mentioned in the studies by Hinkley et al. (1999) and Varekamp and Buseck (1986). A larger value of 5.0×10^7 t/yr was estimated by Lambert et al. (1988) using a different measurement technique. This larger value was used as the maximum value for the sulphur dioxide emission distribution.

Hinkley et al. (1999) reported a global sulphur dioxide emission value of 1.3×10^7 t/yr, but chose to use a smaller value of 4.5×10^6 t/yr in their calculations of worldwide volcanic metal emissions. This value represents the emissions from quiescently degassing volcanoes. The value of 4.5×10^6 t/yr sulphur dioxide release was chosen as a minimum value for the emission distribution. Due to temporal variability of volcanic eruptions and the variation in the quantity of emissions during eruptions, a baseline amount of emissions from passive volcanoes is assumed to be released during these non-eruptive periods. During a period without any major volcanic eruptions, volcanoes would still be degassing passively and it is assumed that this value would adequately represent emissions during those times.

4.4.2 Metal to sulphur dioxide ratios

Metal concentrations are often measured in parallel with sulphur dioxide concentrations in volcanic plumes. The metal concentrations are measured through filtration and collection of the volcanic dust and gases in the plume or at vents or fumeroles depending on the eruptive state of the volcano. From these data, the ratio of metal concentration to sulphur dioxide concentration can be calculated (Hinkley et al., 1999). For the analysis presented herein, it was assumed that particulate adsorbed metals and sulphur dioxide are always released at the same time.

Data published on metal to sulphur dioxide ratios are presented in Table 4.16 and the values employed herein are indicated in Table 4.17. The "most probable" value used for the distribution of metal to sulphur dioxide ratios was the mean of the values presented (see Appendix 1 for the detailed data). The minimum and maximum values are the lowest and highest published values, respectively. Most of the values were calculated by the authors, however, some values were calculated from their raw data for use in this study.

Some authors distinguish between passively degassing volcanoes and active volcanoes. Varekamp and Buseck (1986), for example, suggest that $Hg:SO_2$ ratios were higher in active volcanoes. However, the summarized data suggest that the values for Hg vary over 3 orders of magnitude and that the mean Hg to sulphur ratio for active volcanoes is very similar to the ratio from passive volcanoes. For other metals, insufficient data were available to derive separate metal to sulphur ratios for passive and active volcanoes. Therefore, the mean of the metal to sulphur ratios from all volcano types was used as the typical or most likely value for both active and passive states.

4.5 Forest and Brush Fires

The flux of each element to the atmosphere due to natural forest and brush fires was calculated as:

$$MF \text{ (kg/year)} = \sum [A_{Burned\text{-}i} \times B \times R_{PE} \times C_{Smoke} \times 10^{-6} \text{ kg/mg}]$$

where, MF = metal flux to atmosphere (kg/yr)
$A_{Burned\text{-}i}$ = the area burned in ecoregion i per year(ha/yr)
B = biomass consumed per area burned (tonnes/ha)
R_{PE} = rate of particulate emission per biomass consumed (kg/tonne)
C_{Ash} = concentration of metal in emitted ash, soot and other particulate (mg/kg)

For the uncertainty analysis, variability in the amount of biomass consumed by fire, variability in the mass of particulate emissions emitted between different years, and variability in element concentrations in the smoke particulate were considered.

Due to limitations in the available data, ecoregions were grouped into three categories: forest, grassland/shrubland and other. The forest category included the boreal forest, boreal barrens, coastal/mountain forest and mixed forest ecoregions described in Section 4.1. The grassland/shrubland category included grassland and shrubland. The "other" category included desert, tundra and rainforest.

This latter category was assumed to have a negligible contribution to fire emissions and was, therefore, omitted from further analysis. Rainforest was also omitted from analysis of fire-related metal emissions because natural fires in this ecoregion are rare (Goldammer, 1991, 1993).

Biome-specific data on fires and biomass burnt are presented in Table 4.18. The ecoregion with the most reliable biomass burning data is the boreal forest ecoregion. This is largely explained by the lack of fire statistics kept by many countries, particularly developing countries (Levine et al., 1999). Furthermore, fire statistics are usually based on administrative jurisdictions, not forest types. However, the data presented by Andreae (1991), Stocks (1991) and Hao and Ward (1993) indicate that boreal forest burning accounts for approximately 50% of the total particulate emissions from forest fires. Therefore, particulate emissions from forest fires were modelled using the boreal forest data, and the resultant particulate emissions were doubled. Metal concentrations measured in particulate emissions from forest fires (Table 4.19) were used with the estimated particulate emissions (Table 4.20) to quantify the metal fluxes from forest fires.

Likewise, the data reported in Tables 4.18 through 4.20 generally do not distinguish between grassland and shrubland ecoregions, and is usually reported as "savanna burning." Therefore, these two ecoregions were combined. Nearly all of the available data is from Africa and South America. Metal concentrations measured in particulate emissions from grassland and chaparral fires (Table 4.19) were used with the estimated particulate emissions to estimate the metal fluxes from grassland/shrubland fires.

The global, North America and Canada metal flux estimates from fires were calculated by multiplying the metal fluxes from forests and grassland/shrublands (per km^2) by the areas of the respective ecoregions (see Tables 4.1 through 4.3).

Fires are a source of both fine and coarse particulate matter in the atmosphere. They are, however, variable both spatially and temporally. To further complicate matters, many fires ("prescribed fires") are deliberately set in order to burn areas under optimal weather conditions (U.S.EPA, 1996), rather than waiting for natural fires, and many other fires are used for agriculture or forest clearing. Therefore, it is difficult to separate emissions from deliberate fires from those of natural fires.

Fires in wild lands (land not used for urban or agricultural purposes) can be divided into three categories (McMahon, 1999):

- Prescribed fires: fires which are intentionally ignited for land management purposes, with predetermined boundaries and under optimum weather conditions (to control the fire and reduce emissions). These fires are frequently lit in areas with a high probability of fire in order to have the burning done under controlled conditions. Fires used for agriculture or forest clearing are also included in this category.

- Wildland fires: fires which are ignited naturally in an area where prescribed fires are used; they are managed just like prescribed fires.

- Wildfires: unwanted and unplanned wild land fires.

For the estimation of the emissions of Cd, Cu, Pb, Hg, Ni and Zn to the atmosphere, wild fires, wildland fires and prescribed fires (including agricultural burning) were considered. However, deforestation fires, burning of agricultural waste, burning of logging waste and burning of fuel wood were not considered herein. Prescribed fires are included in the estimate since these are often set to burn areas under controlled conditions that would otherwise be subject to wildfires (McMahon, 1999). Agricultural fires were included since wild fires in these areas would likely be common in the absence of human interference (Goldammer, 1991). Tropical deforestation burns are not included because the fire frequency in the absence of human interference is most likely quite low, especially in rainforests (Goldammer, 1993).

4.5.1 *Frequency of fire and anthropogenic interference*

The area burned by fires globally is not well known, especially for forests, since statistics are often not kept by developing countries (Levine et al., 1999). Recently, satellite data has been used for some estimates, though these estimates still provide only limited information (Levine et al., 1999). Charcoal records indicate that fires have occurred in most biomes, including rainforests and savanna, since before human habitation. However, the 'natural' frequency of fires is not known for most areas (Clark and Robinson, 1993). The 'fire return interval', which is the average number of years between fires at a given location, is highly variable between different areas; the fire return interval is not known with great confidence in many areas due to limited or biased sampling data (Johnson and Gutsell, 1994).

In present times, many fires are started by humans, particularly in tropical regions where fires for agricultural purposes are common (Hao and Ward, 1993). However, fire management has played a large role in reducing natural biomass burning. In many locations, the number of fires started is higher than in pre-industrial times, but the total area burned is lower (Trabaud et al., 1993). In the United States and Canada, emissions from biomass burning are much lower now than in pre-industrial times (Leenhouts, 1998; Taylor and Sherman, 1996). Some of the fires that do occur are prescribed burns, often started to ensure that the fires occur under optimum weather and wind conditions. Prescribed fires typically have lower particulate emissions than wild fires (Ward et al., 1976).

Studies by Leenhouts (1998) for the United States (excluding Alaska and Hawaii) and Taylor and Sherman (1996) for British Columbia have attempted to estimate the emissions from biomass burning during pre-industrial times. Leenhouts (1998) carried this one step further and estimated emissions based on current wildlands having historical fire return intervals. Trabaud et al. (1993) estimated that historic fire return intervals were at least 5 to 7 years for a garrigue (a type of French shrubland), 10 to 15 years for maquis (Mediterranean shrubland), and 30 to 50 years for forests. In Australia, current fire return intervals have been estimated at 10 to 50 years for arid shrublands, 5 to 20 years for grassy woodlands, and 3 to 15 years for forests (Trabaud et al., 1993).

In the tropics, current average fire return intervals are typically about 1 to 5 years for deciduous forests, pine forests, and savanna/grassland. However, these return intervals are largely due to agricultural burning and forest clearing (Goldammer, 1991). Historically, fire was likely common in dry or montane forests, savannas and grasslands, though the return intervals are not known. The natural fire return intervals in

lowland and humid rain forests are probably on the order of hundreds of years or more (Goldammer, 1991, 1993).

The proportion of fires caused by humans versus natural causes varies from area to area. In modern times, up to 90% of all fires may be caused by humans, especially in tropical savannas (Levine et al., 1999). A study in Kruger National Park in South Africa (Trollope, 1996) indicated that 47% of fires were controlled burns, 10% were caused by lightning, 23% were caused by refugees, and 20% by other causes. In boreal forests, however, natural causes may dominate; Alberta Environment (2000) statistics indicate that 61% of all forest fires occurring in Alberta from 1990 to 1999 were caused by lightning, and these fires were responsible for over 90% of the area burned. Cofer et al. (1996) reported that approximately 90% of the area of boreal forest burned globally is due to wild fires. At present, only 2% of the land area is burned annually in lightning-caused fires in the Mediterranean, partly due to barriers to fire such as roads and fields (Trabaud et al., 1993)

4.5.2 *Relevant particle emissions size*

Over 90% of the particles that are capable of remaining airborne and thus traveling long distances are less than 2 to 3 Fm in diameter (Ward et al., 1976); the average particle size has been reported as 0.1 Fm (McMahon and Ryan, 1976). Particulate emissions are produced by fires through two different processes. Particles can be produced chemically, from gaseous organic compounds, or mechanically, by small pieces of fuel material being released. The mechanically produced particles are larger, but also fewer in number (McMahon and Ryan, 1976).

4.5.3 *Quantity of biomass consumed by fires*

Estimates of the total biomass consumed by wild fires each year are summarized in Table 4.18. These estimates were used to develop triangular distributions (minimum, mode and maximum) to represent the total biomass consumed by fires in forests (all types) and grassland, shrubland and savanna. In the absence of detailed data for other forest types, the forest estimate assumes that boreal forests account for 50% of all forest biomass burning, consistent with forest biomass burning estimated by Andreae (1991), Stocks (1991) and Hao and Ward (1993). It was conservatively assumed that the contributions of biomass burning in tundra and desert were negligible.

4.5.4 *Mass of particulate matter emitted to the atmosphere*

Several estimates of regional and global fire-related particulate emissions are summarized in Table 4.20. The emission of particles from fires is highly variable. The emission rate (g particles emitted per kg biomass consumed) can vary over an order of magnitude, depending on fuel type and combustion efficiency. In general, areas with large amounts of brush produce more smoke particles than areas without brush, and fires with a low combustion efficiency produce more particles than fires with a high combustion efficiency (Ward and Hardy, 1991). Savanna and grassland fires are expected to have lower particulate emissions due to a higher combustion efficiency, since the smoldering component of the burn would be lower (Ward and Hardy, 1991).

Triangular distributions were developed from the data in Table 4.20 to represent particulate emissions from fires occurring in forests or in grassland, shrubland and savanna.

4.5.5   Spatial variability in wild fires

Fires are variable among different regions of the world, both in terms of biomass burned and the emissions from the burning. Over 80% of emissions from biomass burning occur in the tropics, though a large portion of this is anthropogenic (Allen and Miguel, 1995). The efficiency of combustion, which affects emissions, is affected by vegetation type, moisture, and topography (Lobert and Warnatz, 1993). Emissions can also be affected by other fuel conditions, including physical arrangement and state of decomposition (McMahon, 1983).

4.5.6   Temporal variability in fires

Wild fires and prescribed fires are seasonal in many areas of the world. In Canada and the northern United States, for example, fires occur mainly over the summer months; in the southern United States, fires occur mainly in the winter (Ward et al., 1976). Savanna and grassland fires in the tropics normally occur during the dry season (Lacaux et al., 1993). Yearly variations can also be significant, with order of magnitude differences between different years, particularly in forests. For example, the estimated areas of boreal forest burned have ranged from 2 million ha in 1992 to 22 million ha in 1987 (Cofer et al., 1996).

The emissions from fires are affected by weather conditions, including wind, humidity and drying conditions prior to the fire (McMahon, 1983).

Long-term trends have been observed in fire occurrence, particularly in boreal forests. Over the past 50 years, the number of fires has been observed to increase due to increased road access and area use causing more fires. However, in some areas the total area burned has actually decreased since the same access enables quicker detection and response (Stocks, 1991).

4.5.7   Metals in fire emissions

Metals naturally present in vegetation are emitted with particulate matter during fires, though the quantity varies depending on the type of fire and the location. Sanhueza (1991) concluded that fire was not a major source of Cd, Pb or Zn in the atmosphere above a Venezuelan savanna. Maenhaut et al. (1996a), however, found fire to be a major contributor of Cu, Pb and Zn in the atmosphere above savannas and brushlands in Brazil, though fire was not deemed to be a significant source of atmospheric Ni in that study.

Data on metal concentrations in plants and residual ash are summarized in Table 4.21. Several previous emissions inventories (Nriagu, 1978, 1980a,b,c; Schmidt and Andren, 1980) used metal contents in conifer needle and twig ash from Curtin et al. (1974). However, the samples analyzed by Curtin et al. (1974) were collected from areas where previous testing had revealed anomalously high concentrations of metals in vegetation ash, mull ash and soil, including elevated Cd and Pb concentrations at 2 of the sampling sites.

Recent work has been conducted on metal concentrations in the particulate matter emitted by fires. These data are summarized in Table 4.19. Metal emission rates are affected by fuel type; chaparral fires have been shown to have generally higher metal emissions than conifer logging slash fires, for example (Ward and Hardy, 1991; see also Table 4.19). Triangular distributions were developed using the minimum, mean and maximum measured values for Cd, Cu, Pb, Ni and Zn concentrations in smoke as reported in Table 4.19. Separate distributions were used for fires in forests and in grassland, shrubland and savanna.

As shown in Table 4.19, Hg was investigated in only one of the cited studies, and in that case it was present below the analytical detection limit (approximately 0.1% by weight). However, due to its volatile nature, Hg is expected to be emitted in gaseous form, since the temperatures encountered in fires exceed the volatilization temperatures of most Hg compounds (Veiga et al., undated). Veiga predicted that 90% of Hg would be lost from above-ground biomass burned, based on loss of Hg from burnt fossil fuels. Therefore, Hg emissions were calculated using measured concentrations of Hg in plants and the estimated biomass burned, and by assuming that 90% of the Hg in the biomass burned is emitted to the atmosphere.

4.6   Meteoritic Dust

The flux of each element to the atmosphere due to meteoric and interplanetary dust was calculated as:

$$MF \text{ (kg/year)} = F_{MD} \times A_{Region}/A_{Globe} \times C_{MD} \times 10^{-6} \text{ kg/mg}$$

where, MF = metal flux to atmosphere (kg/yr)
          F_{MD} = flux of meteoric dust (kg/yr)
          A_{Region} = area of the region being considered (Canada, North America, globe) (km^2)
          A_{Globe} = area of the globe (km^2)
          C_{MD} = concentration of metal in meteoric dust (mg/kg)

The Earth is continually intercepting meteorites and interplanetary dust. This phenomenon, known as cosmic flux, is relatively constant over time (Bruns, 1999). Meteorites and interplanetary dust are classified based on chemical composition and physical structure; a commonly used classification scheme is detailed by Mason (1971). According to Mason (1971), the most common class is the chondrites, which are believed to represent undifferentiated (i.e., background) interstellar material. These are further divided into groups based largely on the iron content and oxidation state. Other classes of meteorites include achondrites, stony-irons and irons, all of which also have several groups. Over 80% of all meteorite falls are chondrites (Mason, 1971).

In order to estimate the emission of Cd, Cu, Pb, Hg, Ni and Zn to the atmosphere from meteorites and interplanetary dust, the following assumptions were employed:

•   The rate of cosmic flux is constant (i.e., no major meteor impacts).

•   The rate of cosmic flux is spatially uniform (i.e., not dependent on geographic location).

The flux of metals to the atmosphere from meteoritic dust was calculated by simply multiplying the concentration of the metal in meteoritic dust by the total flux of meteoritic dust into the atmosphere. Meteoritic dust inputs to Canada and North America were based on their surface areas relative to that of the globe.

For the uncertainty analysis, variability in the following parameters was considered:

- flux of meteoritic dust entering the atmosphere
- concentrations of metals in meteorites.
-

4.6.1 Relevant meteoritic particle size

Meteorites range in size from sub-micron particles to 1000 tonne or larger rocks. The cosmic flux entering Earth's atmosphere is dominated by particles between 0.1 mm and 1.0 mm in diameter in most years, though the impacts of large (1000 tonne or greater) bodies may dominate over the long term (Love and Brownlee, 1993). Large amounts of interplanetary dust and ablated material from meteorites remain in the atmosphere (McNeil et al., 1998; Jessberger et al., submitted).

4.6.2 Mass of extraterrestrial dust entering the atmosphere

The total mass of meteoritic dust entering earth's atmosphere ("cosmic flux") cannot be directly measured, so several different methods have been utilized to estimate the cosmic flux:

- geochemical methods measuring specific meteoritic components in deep sea sediments;
- measuring luminosity caused by particles entering the atmosphere;
- counting craters on metal panels orbiting the earth.

Bruns (1999) summarized several estimates of cosmic flux; these and others are presented in Table 4.22. The relative accuracies of the different methods of measuring the cosmic flux are not known, but the highest estimated values were determined based on luminosity, while the majority of early estimates were based on geochemical methods. Recent measurements seem to support the luminosity-based estimates, but the geochemical estimates may better reflect the amounts of heavy metals entering the atmosphere (Bruns, 1999).

It is expected that recent estimates of the cosmic flux will generally be more accurate than older measurements due to improved methods and technology. Therefore, measurements made prior to 1980 were excluded from the cosmic flux estimation used herein. A triangular distribution was used to represent the flux of cosmic dust, using the minimum, median and maximum values estimated since 1980 (see Table 4.22). Since the geochemical estimates are believed to better reflect the heavy metals entering the atmosphere, and the luminosity estimate of cosmic flux (7.8×10^8 tonnes/year) was several orders of magnitude higher than these other estimates, this luminosity-based measurement was not considered herein.

4.6.3   Concentrations of metals in meteorites and interplanetary dust

The concentrations of metals in interplanetary dust are generally believed to resemble those found in CI carbonaceous chondrites, which are the most basic class of chondrites and are thought to resemble the background cosmic material (Lebedinets and Kurbanmuradov, 1992; Mason, 1971). This is supported by measured metal concentrations in numerous interplanetary dust particles (summarized in Table 4.23). Uncertainties are present in the data, due to different types of particles having different probabilities of being captured by the Earth, surviving atmospheric entry, or being collected, as well as biassed sampling by researchers (Jessberger et al., submitted). Furthermore, due to the limited technology for capturing larger interplanetary dust particles during atmospheric entry, most analyzed particles have diameters ranging from 0.005 mm to 0.025 mm, or are larger meteorites collected from the Earth's surface where they may have been altered or contaminated, while the mass of interplanetary dust entering the atmosphere is dominated by particles approximately 0.2 mm in diameter (Jessberger et al., submitted).

A triangular distribution was used to represent the concentrations of metals in meteorites and interplanetary dust. The modal value of the distribution was based on the mean of the reported values for typical CI carbonaceous chondrites. The minimum and maximum values were the minimum and maximum average values reported for the various types of chondrites (see Table 4.23).

4.7   Mercury Vapour Emissions

Unlike other metals, which are primarily found in the atmosphere associated with particulate matter, Hg is volatile and exists in the atmosphere primarily as vapour (Schroeder and Munthe, 1998). It has been shown that 95% of the Hg in the atmosphere, and 99% over the oceans, is in the vapour phase (Lindqvist et al., 1991; Fitzgerald et al, 1983). While gaseous Hg can occur as a variety of organic and inorganic compounds, it is mainly released as elemental Hg (Hg^0) (Schroeder and Munthe, 1998).

The following sources of Hg vapour were considered:

- soils;
- freshwater surfaces (lakes, rivers and other areas of open fresh water);
- ocean surfaces;
- vegetation.

Gaseous Hg may also be emitted through volcanic eruptions and geothermal activity; these processes were considered in Section 4.3. Large quantities of Hg are also emitted from the Earth's subsurface crust (Ebinghaus et al., 1999). This Hg must pass through surface soil, freshwater or the ocean to reach the atmosphere. Therefore, this process is not considered directly herein; emissions from ocean surface, from surface soil, from lake surface water, etc. are considered to indirectly address subsurface Hg contributions.

Emission of Hg vapours is not a unidirectional process; all of the sources considered can also act as Hg sinks (Ebinghaus et al., 1999). Studies have indicated that there may be "compensation points", which are

source Hg concentrations relative to atmospheric Hg concentrations below which the source will absorb Hg and above which the source will emit Hg (Kim et al., 1995; Hanson et al., 1995).

Measured Hg vapour fluxes from soil, surface waters and vegetation are summarized in Table 4.24. All Hg vapour flux and concentration data prior to 1985 were excluded, since this data is suspect due to outdated sampling and analytical practices (Leonard et al., 1998a). For purposes of these calculations, only positive fluxes were considered.

4.7.1 Mercury vapour flux from soils

A series of recent studies have now clearly demonstrated the net flux of Hg vapour out of soil (Rasmussen et al., 1998b; Kim et al., 1995; Carpi and Lindberg, 1998; Poissant and Casimir, 1998; Meyers et al., 1996) with the flux being proportional to substrate concentrations of total Hg (Rasmussen et al., 1998b) as well as soil temperature, incident solar radiation, wind speed and turbulence (Carpi and Lindberg, 1998; Kim et al., 1995; Lindberg et al., 1995; Gustin et al., 1997; Poissant and Casimir, 1998).

Data presented by Rasmussen et al. (1998b) showed a strong correlation between the log of the soil Hg concentration and the log of the Hg flux from soil. All additional data on soil Hg flux from studies identified in Table 4.24 (for which both the soil Hg concentration and the soil Hg flux were available) were combined with the Rasmussen data, and it was found that this relationship still held. Therefore, a regression equation was developed relating the soil Hg concentration and the Hg flux from soil ($r^2 = 0.87$). The Y intercept and slope of the equation were modelled as normal distributions defined by the predicted (mean) intercept and slope and the standard errors of the slope and intercept. The minimum, mean and maximum soil Hg concentrations used earlier for soil erosion calculations were used here.

4.7.2 Mercury vapour flux from fresh water surfaces

Hg^0 plays a key role in the aquatic Hg cycle and may represent 10% to 30% of the dissolved Hg content of lake water (Amyot et al., 1997a,b). Its relatively low solubility, and relatively high volatility subsequently favour the evasion of Hg^0 from lake surfaces to the atmosphere under appropriate conditions of temperature, solar radiation, relative humidity, wind speed and turbulence, lake water chemistry and possibly other factors (Amyot et al., 1995, 1997a,b; Poissant and Casimir, 1998).

A variety of recent studies have attempted to quantify the flux of volatile Hg from lake water to the atmosphere using different approaches. These approaches include a predictive (indirect) method employing the thin film gas exchange model (Amyot et al., 1997a,b; Vandal et al., 1993), the modified Bowen ratio method (Lindberg et al., 1996; Meyers et al., 1996) and using a flux chamber for direct measurement of evasive Hg flux (Xiao et al., 1991; Schroeder, 1995; Poissant and Casimir, 1998). All methods demonstrate a net flux of Hg^0 from lake surfaces to the atmosphere during the periods of measurement (ice-free conditions during spring, summer, and/or fall). However, the flux rates derived from these different studies and methods span two orders of magnitude, suggesting significant uncertainty in the quantification of this phenomenon. It is also apparent from evaluations of the influence of solar radiation, temperature and other factors that the flux of Hg^0 from lakes to the atmosphere would be negligible at temperatures $\#0^oC$,

and when ice cover prevents solar irradiation of the lake surface, as well as limiting direct atmosphere-water interaction.

Annual Hg^0 evasion has been predicted for Lake Ontario (Schroeder, 1996). Other, less certain methods have been employed to estimate total Hg emission from all freshwater surface areas in the province of Ontario (Innanen, 1998).

Hg evasion from rivers has also been observed. However, the data available for this phenomenon are extremely limited at present (Ebinghaus et al., 1999) and, therefore, rivers were not differentiated from lakes or other freshwater surfaces for purposes of estimating Hg^0 flux.

The minimum, mean and maximum measured Hg fluxes from freshwater sources (presented in Table 4.24) were used to define triangular distributions. All available data were used for the global estimate; only data from the United States and the Arctic were used for the Canada and North America estimates. It should be noted that the available data is all from the Arctic, the United States and Sweden; therefore, these data may not be truly reflective of global Hg evasion from freshwater. The data were based on measurements taken during the spring, summer and fall; the Arctic data was assumed to be reflective of winter conditions elsewhere.

4.7.3 *Mercury vapour flux from ocean surfaces*

Much like freshwater, the oceans have been shown to emit gaseous Hg to the atmosphere (Fitzgerald et al., 1984; Fitzgerald, 1986; Kim and Fitzgerald, 1986). The flux is caused by seawater that is supersaturated with dissolved Hg^0 (Kim and Fitzgerald, 1986). The highest dissolved Hg^0 concentrations were measured in cooler, nutrient-rich waters with high biological productivity, indicating that the Hg flux may be related to biological productivity (Kim and Fitzgerald, 1986). Pongratz and Heumann (1998, 1999) demonstrated that methylated Hg compounds are released to the atmosphere by marine algae and bacteria in the Arctic and North Atlantic.

The only data reviewed on marine Hg vapour flux were equatorial Pacific Ocean data (Fitzgerald, 1986; Kim and Fitzgerald, 1986) and methylated Hg compound data (Pongratz and Heumann, 1999). Since the latter estimate assumed that all methylated Hg in the marine atmosphere was produced by marine organisms, these data were excluded from the calculations.

Global estimates of Hg flux were derived by Fitzgerald (1986) and Kim and Fitzgerald (1986) of 2.3 x 10^6 kg and 2.9 ± 1.8 x 10^6 kg per year based on data from the equatorial regions of the Pacific Ocean and assuming that the Hg flux is directly proportional to primary production.

The global marine Hg vapour flux was modelled using a normal distribution, defined by the mean and standard deviation of the global Hg vapour flux estimated by Kim and Fitzgerald (1986). For the North America and Canada estimates, the marine flux was calculated by subtracting the equatorial Pacific flux from the global flux presented in Kim and Fitzgerald (1986), and further adjusting for the proportion of

ocean surface prescribed by the 200 nautical mile territorial limit. The equatorial Pacific data were removed from these estimates to reflect the dependence of Hg flux on biological activity.

4.7.4   *Mercury vapour flux from vegetation*

Research by Lindberg and coworkers (Lindberg et al., 1998; Hanson et al., 1995, 1997) and others (Siegel and Siegel, 1988; Kama and Siegel, 1980; Siegel et al., 1980; Leonard et al., 1998a, b) have directly quantified the flux of Hg vapour from plants. Although there is a bi-direction flow of Hg vapour, there is a net evasion of Hg^0 out of vegetation (Lindberg et al., 1998). Factors influencing the flux of Hg from vegetation include canopy area (total leaf surface area), temperature, solar radiation and wind turbulence (Lindberg et al., 1998; Siegel and Siegel, 1988; Leonard et al., 1998a,b). This flux is also indirectly influenced by soil Hg concentration as Hg content in plants is a function of both direct root uptake from soil and vegetal absorption of Hg vapour evolving from underlying soils with subsequent re-emission (Lindberg et al., 1998; Leonard et al., 1998a,b).

Recent data on Hg vapour flux from plants comprises mainly studies performed on forest canopy emissions, as shown in Table 4.24. Leonard et al. (1998b) compiled the available data and developed a linear regression equation relating Hg flux from plants to the soil Hg concentration ($r^2 = 0.97$). Therefore, Hg^0 evasion from vegetation was derived from this regression equation employing the soil Hg data presented earlier in Table 4.8 Since the majority of the reliable data summarized in this review were included in the development of the regression equation, it was used directly herein to estimate the Hg vapour flux from forests. The Hg vapour flux from grassland and brushland areas was assumed to be the same as forests per m^2 of exposed plant surface in the absence of specific data from these ecoregions. The grassland and brushland areas were assumed to have an exposed plant surface area equal to the ground surface area; the forest exposed plant surface area was assumed to be 5.5 to 9.5 times greater, as per Hanson et al. (1997). Therefore, the Hg flux per km^2 from grasslands and brushlands was 5.5 to 9.5 times less than that from forests. Plants in ecoregions with low vegetation density (desert and tundra) were assumed to have a negligible contribution to the total Hg vapour flux from plants.

5.0   RESULTS OF THE REAPPRAISAL OF NATURAL EMISSIONS TO THE ATMOSPHERE

The calculated natural metal fluxes associated with air-borne soil particles, sea salt spray, volcanic activity, forest and brush fires, and cosmic dust are presented Tables 5.1 through 5.5, respectively. Tables 5.6 through 5.9 present estimated emissions of Hg vapour from soil, fresh surface waters, marine surface waters and terrestrial vegetation, respectively. Table 5.10 summarizes total emissions for each metal from all natural sources combined, and also presents the estimates of Nriagu (1989) for global natural emissions for comparison.

The analyses presented herein are believed to be the first comprehensive assessments of natural emissions of Cd, Cu, Pb, Hg, Ni and Zn in Canada and continental North America. A previous assessment undertaken for natural Hg emissions in Canada (Environment Canada, 1981b) is considered inaccurate (L.Trip, Environment Canada, personal communication). For all metals but Hg, the primary natural source

for Canada and North America appears to be soil particulate matter entrained into the air due to wind erosion. The contribution from entrained soil particulate ranges from about 51% (Cd - Canada) of total natural emissions to nearly 100% (Cu, Ni, Pb - both Canada and continental N.A.). In the case of Hg, suspension of soil particulate matter is a minor source, representing 2% or less of total atmospheric emissions. For Canada, emissions of Hg vapour from soil and from terrestrial vegetation are the two primary sources, constituting about 94% of total natural Hg emissions to the atmosphere in Canada. For continental N.A., Hg vapour emission from soil and terrestrial vegetation is also important (29% and 21% of total Hg emissions, respectively), however, the contribution from volcanic activity is the single greatest natural source, representing 46% of total Hg emissions to the atmosphere of continental North America.

Globally, natural fluxes due to soil erosion represent from 46% (Zn) to virtually 100% (Cu, Ni) of natural emissions of the non-volatile metals, while this source constitutes only about 9% of total Hg emissions. Consistent with earlier global evaluations of Hg emissions from natural sources, volcanic emissions provide the single greatest source of Hg to the global atmosphere; about 45% of total emissions. Evasion of Hg vapour from soil is the next most significant source globally at about 33% of total natural emissions.

The global estimates of natural source emissions of all metals were between 1 and 2 orders of magnitude greater than those of Nriagu (1989) (see Table 5.10). This is despite the fact that the analysis conducted herein omitted biogenic emissions for all metals but Hg. Emissions of metals from all natural sources but volcanic activity were higher than those of Nriagu (1989); the natural flux from volcanoes was approximately equivalent (i.e., similar order of magnitude) to that predicted by Nriagu (1989).

6.0   DISCUSSION

6.1   Omission of biogenic sources

Unfortunately, the atmospheric emissions of Cd, Cu, Ni, Pb and Zn due to biogenic emissions could not be calculated due to insufficient data on metal concentrations in volatile plant exudates. As a result, the natural source emissions estimated herein are considered to be conservative (i.e., likely under-estimate actual total emissions). It is expected that this source could be significantly under-estimated in previous natural source inventories. Nriagu (1989) reported VOC emissions from terrestrial plants of between 2×10^{10} kg/yr and 2.5×10^{11} kg/yr. Since that publication, more detailed inventories of volatile compound emissions from plants have been developed. Guenther et al. (1995), based biogenic emissions data for numerous plant types and 43 different ecosystems, estimated that 1.145×10^{12} kg of non-methane hydrocarbons are emitted annually by terrestrial plants, nearly an order of magnitude higher than the maximum value considered by Nriagu (1989). Although hydrocarbons emitted from plants are known to be frequently complexed with metals (Beauford et al, 1975), the actual metal concentrations in the plant exudates are not well known. A study by Curtin et al. (1974) measured metal concentrations in exudates from conifers in the United States, but the trees studied were in locations with anomalously high metal concentrations in soils and/or plants, and are not considered to be representative of typical emissions. No other appropriate data of this type were located.

6.2   Uncertainties in Particle Flux Estimates

As noted by other authors, metal fluxes due to soil particle flux to the atmosphere is a significant natural source. As previously noted, we employed the soil flux values reported by Hagen and Woodruff (1975) for shrubland. Since those data were based dusty periods only, our analysis adjusted their data to obtain an annual average soil flux. The earlier report by Environment Canada (1981a) on particulate emissions to the atmosphere applied the data of Hagen and Woodruff (1975) data to all days. Therefore, it is believed that the soil fluxes calculated by Environment Canada (1981a) were 200 times too high.

Two factors not directly considered in our analysis with respect to metal emissions due to particulate fluxes were particle size and aerial suspension time. However, the data on particulate fluxes drawn from the literature for use herein generally related to particles of sufficiently small size to be aerially entrained. Ten percent or less of the total mass of soil raised by the wind actually remains in the air as suspended particulate matter (Hagen and Woodruff, 1975). Most particles in suspended soil range in size from 1-10 Fm (Eltayeb et al., 1993; Andronova et al., 1993). In the troposphere, particles of this size will remain suspended for approximately one week, however, they can remain suspended for much longer periods of time if they enter the stratosphere (Prospero et al., 1983). Gillette et al. (1978) suggest that particle size during dust storms is bimodal. Particles fall into one of two ranges: 1-30 Fm or 30-100 Fm. The smaller particles generally consist of clays, whereas the larger particles are usually quartz with clay coatings (Gillette and Walker, 1977). With sufficient data, our analysis could be refined to address particles of specific aerodynamic diameter (<10 µm, for example).

Dust storm days do not distinguish between dust raised locally and that transported from another area and gives no indication about the quantity of dust raised (Middleton, 1986a). A lot of variation in dust storm days is observed from year to year depending on precipitation and a variety of other factors (Middleton, 1985). Therefore, for this study, data collected over many years was preferable.

6.3   Uncertainties in Sea Salt Flux

As previously mentioned, sea salt flux is highly dependent on wind speed and other factors (Monahan, 1986). Due to a lack of adequate data, the estimates of sea salt flux used herein were global averages. Likewise, due to inadequate data, the spatial variability in the concentrations of metals in seawater, and in the enrichment of metals in sea salt, could not be more precisely quantified or assessed.

6.4   Potential Indirect Anthropogenic Contributions (Re-emission)

While the methods used to calculate fluxes of metals to the atmosphere ensured that direct anthropogenic emissions were excluded, the estimates still reflect some anthropogenic effects, since the concentrations of metals in the ocean, soils and vegetation may include anthropogenic deposits that lead to 're-emission'. Only volcanic emissions and meteoric dust will be free of potential re-emission of metals originating from anthropogenic sources. For all metals but Hg, these two latter sources represent less than 1% of total global emissions estimates derived herein, suggesting that re-emission could be having a significant influence on 'natural' emissions estimates, by us and other authors. Re-mission is a relatively lesser potential problem

with respect to Hg as volcanic emissions and meteoric dust constitute about 45% of total global 'natural' Hg emissions.

Although efforts were made herein to consider only those measurements likely to be unaffected by industrial sources, the long range atmospheric transport of metals ensures that even the most remote samples are affected to some extent by human inputs (Fitzgerald et al., 1998). The natural concentrations of metals in the ocean, soils, etc. cannot be considered wholly independent of anthropogenic sources, particularly since the accurate measurement of many metals in environmental media was not achieved until the mid-1970's or later. Also, the sources of Hg vapours can also act as sinks, causing estimates of natural Hg vapour emissions to include some re-emission of deposited anthropogenic Hg (Ebinghaus et al., 1999).

The 're-emission' of anthropogenic Hg has been a topic of considerable recent research, and estimates of relative contribution of re-emitted Hg to total global atmospheric loadings have been provided by some authors (Mason et al., 1994; Hudson et al., 1995; Jackson 1997, for examples). Re-emission estimates have ranged from negligible contributions (Mason et al., 1994) to as much as 20% of total global Hg emissions (Hudson et al., 1995; natural - 40%, anthropogenic - 40%, re-emitted anthropogenic - 20%). Assuming that as much as one third of all Hg emissions from non-(direct)-anthropogenic sources (20% ÷ (20%+40%)) are, in fact, re-emitted anthropogenic contributions, then the estimates presented herein, when adjusted to exclude potential re-emission, still exceed earlier calculations (Nriagu, 1989, and others) by a significant margin. This is also the case for the other metals under consideration, if one third of the natural emissions estimated herein are due to re-emission (see Table 5.10).

6.5 Spatial and Temporal Variability in Volcanic Activity

The estimates of metal emissions from volcanoes did not, and probably could not, adequately reflect the spatial heterogeneity of volcanic activity. Volcanic activity is extremely variable among different regions of the world. The vast majority (>94%) of known volcanic eruptions occur within the "volcanic belts", which encompass only 32 000 km in length and represent <0.1% of the earth's surface (McClelland et al., 1989). The continental United States (including those in Alaska and the Aleutian Islands) had 15 active volcanoes between 1975 and 1985, about 10% of the global total (McClelland et al., 1989). Canada has no active volcanoes, as is the case for Australia, and many parts of the continents of Europe, Africa and Asia (Simkin et al., 1981). Many more active volcanoes ring the Pacific Ocean, in Central America, South America and Asia. Active volcanoes also exist in continental Africa and in Italy (Simkin et al., 1981).

Likewise, the estimates of metal emissions from volcanoes did not, and probably could not, adequately reflect the temporal heterogeneity of volcanic activity. For the five year period from 1969 to 1973, for example, there were 109 reported volcanic events involving from 17 to 28 different volcanic events in any given year (Bullard, 1984). Between 1975 and 1985 there were 158 reported volcanic eruptions involving from 52 to 65 events in any given year (McClelland et al., 1989). Obviously, volcanic activity varies from year to year, decade to decade, etc. The type of activity also varied, and involved one or more of: ash and cinder emission, central crater formation, dome formation, normal explosion (due to steam build up), and sub-marine eruptions (Bullard, 1984).

6.6   Data Gaps

A variety of data gaps are apparent from the description of methods employed herein. Numerous assumptions and judgements were necessary to permit the derivation of natural metal fluxes to the atmosphere. These missing data included (but are not limited to) the following:

•   direct soil particle flux measurements for ecoregions other than shrubland;
•   size-fractioned aeolian particulate chemistry;
•   sea salt enrichment factors for Ni and Hg;
•   reliable global data on biomass burned during forest and brush fires;
•   direct quantification of the contribution of re-emitted anthropogenic metals deposition to natural emissions estimates.

The most significant data gap identified related to the lack of information necessary to quantify biogenic emissions of metals other than Hg. Particularly, data are required on the emission of non-volatile metals from vegetation, or at least data on concentrations of non-volatile metals associated with the volatile organic substances emitted by terrestrial and marine vegetation. Recent data (Benjamin et al., 1996, 1997; Kempf et al., 1996; Drewitt et al., 1998; Helmig et al., 1999; Isebrands et al., 1999; among others) suggest that emission rates for volatile organic compounds (VOC) from vegetation may be greater than was assumed by Nriagu (1989). Additionally, improved models are now available (Geron et al., 1994; among others) to better quantify biogenic VOC emissions. However, the absence of reliable data on the co-emission of non-volatile metals relative to biogenic VOC emissions precludes the reliable quantification of metal emissions from biogenic sources and, therefore, we omitted this source of natural emissions from the analysis presented herein. The omission of this natural metal source may have resulted in a significant underestimation of total natural metal fluxes to the atmosphere.

Entrainment of soil particulate matter into the atmosphere was identified as the major natural source for most of the non-volatile metals considered herein. However, estimates were conducted without consideration of particle size-specific metals concentrations (due to lack of data). It is smaller soil particles that will be suspended through wind erosion and that will remain aloft for longer periods of time. Therefore, additional data on the chemistry of size-fractionated aeolian particulate matter should be collected, since evidence suggests that metals are concentrated in the smaller soil particle size fractions.

7.0   CONCLUSIONS

7.1   General

Presented herein are quantitative estimates of natural emissions to the atmosphere of Cd, Cu, Pb, Hg, Ni and Zn. The omission of biogenic emissions from terrestrial vegetation for all but Hg may have resulted in a significant underestimation of total natural metal fluxes to the atmosphere for those non-volatile metals. Natural emissions estimates for Canada and continental North America are believed to be the first reliable analyses of their kind. Also presented for the first time are statistically rigorous estimates of the 90%

confidence limits on estimated mean and median emission values. These confidence limits were derived through the application of probabilistic analysis, incorporating known variability in the numerous factors required to quantify metal emissions to the atmosphere from natural sources.

With respect to global emission estimates, the estimates presented herein are between 1 and 2 orders of magnitude greater than those of Nriagu (1989). Given gains in the volume of available data and literature from which to derive such estimates, the improvements in data collection and analytical methods, and the quantification of fluxes from previously unmeasured or unrecognized sources, it is believed that the estimates presented herein, and their 90% confidence limits, are the most reliable estimates of natural source emissions to date.

For Cd, Cu, Pb, Ni and Zn, the entrainment of soil dust particles into the air is a predominant source of natural emissions to the atmosphere. For mercury, volcanic emissions of Hg vapour predominate. Various uncertainties that hamper precise quantification of atmospheric emissions have been recognized throughout, but statistical methods have been employed to provide 90% confidence limits (spanning from the 5th percentile to the 95th percentile probabilities surrounding the mean) in order to provide some measure of the uncertainty surrounding expected average emissions. This is the first published inventory of natural source emissions of metals to provide such quantitative confidence limits.

The on-going regulatory concern for metals in the environment is generally at odds with the goal of sustainable and/or environmentally sound exploitation of natural resources. Despite a general recognition that natural sources contribute to the environmental load of metals, there has been no rigorous attempt to update natural emission estimates in more than a decade. However, for the sustainable use of metals, an integral and important component of western economies, it is essential that the contributions of natural releases to the atmosphere be quantified as accurately as possible. Only then can regulations designed to control or curtail metal pollution achieve the desired goal. Also, by recognizing the uncertainty in such estimates of natural emissions, and by quantifying that uncertainty, regulatory agencies can better predict the environmental consequences of their planned legislation.

7.2   Cadmium

Natural emissions of cadmium to the atmosphere occur mainly via soil particle flux and fires; minor amounts are also emitted with sea salt spray or from volcanic eruptions. The predicted contribution of meteoritic dust to natural cadmium emissions is not significant. Mean estimates of the total natural cadmium flux are 5.3×10^4 kg/y for Canada, 7.1×10^5 kg/y for North America, and 4.1×10^7 kg/y globally (Table 5.10).

7.3   Copper

Soil particle flux is the dominant natural source of copper in the atmosphere, with much smaller contributions from sea salt spray, volcanoes and fires. Meteoritic dust does not appear to be a significant source of copper in the atmosphere. The mean natural emission rates for copper are 2.6×10^6 kg/y for Canada, 5.0×10^7 kg/y for North America, and 2.0×10^9 kg/y globally (Table 5.10).

7.4 Lead

Natural emissions of lead to the atmosphere are predominantly from soil particle flux; fires, sea salt spray and volcanoes also emit some lead to the atmosphere. Predicted emissions due to meteoritic dust are insignificant. The mean predicted natural emissions of lead to the atmosphere are $9.7x10^5$ kg/y for Canada, $4.5x10^7$ kg/y for North America, and $1.8x10^9$ kg/y globally (Table 5.10).

7.5 Mercury

The analyses indicate that the largest natural source of mercury in the atmosphere is volcanic emissions. Evasion of mercury vapours from soil is also a relatively large source, though there is considerable uncertainty in this estimate (the 5th and 95th percentiles differ by almost 2 orders of magnitude). Soil particle flux and evasion of mercury vapours from sea water and plants are relatively minor natural sources of mercury in the atmosphere; emissions from fires, sea salt spray and meteoritic dust are relatively insignificant. All sources of mercury vapour evasion are subject to uncertainty, since these are bi-directional processes whereby both anthropogenic and natural mercury can be deposited and re-emitted; these processes are also dependent on factors such as temperature, solar radiation, wind, turbulence and vegetation cover.

The mean natural emission rates predicted for mercury are $1.1x10^6$ kg/y for Canada, $5.6x10^6$ kg/y for North America, and $5.8x10^7$ kg/y globally (Table 5.10).

7.6 Nickel

Much like copper and lead, natural emissions of nickel to the atmosphere are mainly due to soil particle flux, with much smaller contributions from volcanoes, fires, and sea salt. Due to the lack of published sea water to sea salt enrichment factors for nickel, the emission rate due to sea salt spray is likely conservative. Meteoritic dust emissions are much smaller than the other sources examined. Mean natural emissions of nickel to the atmosphere are predicted to be $1.0x10^6$ kg/y for Canada, $2.5x10^7$ kg/y for North America, and $1.8x10^9$ kg/y globally (Table 5.10).

7.7 Zinc

Globally, the largest source of natural emissions of zinc to the atmosphere is sea salt, closely followed by soil particle flux. However, the emissions due to sea salt are subject to a high degree of uncertainty, with the 5th and 5th percentile estimates differing by more than 2 orders of magnitude. This uncertainty results from large differences in estimates of zinc enrichment on emitted sea salt particles. Fires and volcanoes are minor sources of zinc in the atmosphere, and contributions from meteoritic dust are insignificant. Mean predicted natural emission rates are $4.6x10^6$ kg/y for Canada, $3.8x10^7$ kg/y for North America, and $5.9x10^9$ kg/y globally (Table 5.10).

7.8   Data Gaps

The most significant gap identified related to the lack of data to quantify biogenic emissions of metals other than Hg. Data are required on the concentrations of non-volatile metals associated with volatile organic substances emitted by terrestrial and marine vegetation to enable the quantification of metal emissions form this natural source. Also, data are required to establish reliable enrichment factors for both nickel and zinc in sea salt spray, and also on the chemistry of aeolian particulate matter.

8.0   REFERENCES

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