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Cadmium in sediments

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Introduction

Compared to the analyses of hydrous phases, the investigations on solid substances has only recently become a major subject of interest in the research of aquatic systems. Even so, present activity in sediment analysis is so great that the overall effort is quite comparable to the study of water and biological sample material.

The sediment approach has a number of perspectives: First, sediments are an expression of the condition of a water system[40]. They can reflect the current quality of the system as well as the historical development of certain hydrologic and chemical parameters. Comparitive analysis of the total concentrations of longitudinal profiles and sediment cores is performed to determine metal anomalies in zones of mineralization as well as from pollution sources. The study of dated

sedimentary cores has proved to be especially useful as it provides a historical record of the various influences on the aquatic system by indicating both the natural background levels and the man-induced accumulation of elements over an extended period of time. Two examples are given in figure 1 from marginal seas of northern Germany; one from the German Bight, North Sea[12], the second from the Kieler Bucht, Baltic Sea[7]. In both examples the natural background in the deeper section of the cores for cadmium is approximately 0.25–0.30 mg/kg, that is, similar to the background values determined by other methods, e.g., average shale composition, fossil sediments from typical environments, and recent deposits from 'undeveloped' aquatic systems. From that 'background' the cadmium-concentrations increase about 7–8 times to reach their present levels in the upper layers of the core profiles.

Sediment analysis is used for selecting of critical sites for routine water sampling for contaminants that, upon being discharged to surface waters, do not remain soluble, since they are rapidly adsorbed by particulate matter and may thus escape detection by water analysis. Thus, sediment data play an increasing role within the framework of environmental forensic investigations[25], particularly in those cases, in which a short-term or past pollution event is not or only insufficiently traceable from water analysis. Here, however, the effects of different grain size must be considered[13,14].

In addition, sediments are increasingly recognized as a pollutant proper and as a carrier and possible source of contaminants in aquatic systems as well as with respect to the biological effects of polluted solid materials on agricultural land. Metals are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents, both within the sedimentary compartment and also back to the water column. This is especially true for 'dredged materials', which threaten not only organisms but also the quality of water. Human activities promote the accumulation of polluted sediments and the resulting increased maintenance dredging results in a high amount of contaminated sediments for which safe disposal sites on land or in the waters have to be found. An example of both the quantity and quality

problems arising from sediment accumulations is given in figure 2 from Rotterdam Harbor[29], where the increase in cadmium concentration in Rhine sediments (100-fold in 80 years; note logarithmic scale!) is due to increased industrial use and the increase in annual dredging rates is due to harbor extension and maintenance.

Sources and distribution of cadmium in river sediments

Towards the end of the 1960's, the possibilities of applying geochemical methods of exploration in water quality assessment was recognized both in North America as well as in Europe. Investigations on suspended matter and sediments by Turekian and Scott[37] in the Susquehanna River revealed signs of the characteristic pollution sources of industrial and communal emittants. In Europe, the studies of De Groot and coworkers[5,6] and Hellmann and coworkers[17,18] centred around metal investigations on the Rhine River and its tributaries, as well as on the behavior of trace sediment-associated metals in the mixing zone of fresh water and sea water[11]. Meanwhile hundreds of similar investigations have shown the usefulness of sediment analyses in monitoring and assessment of pollution sources[14].

Table 1 compiles characteristic examples of river sediment studies on cadmium, which were carried out during the last 10 years: Strong point-source emissions of cadmium from industrial plants have been recorded in sediments of the Hudson River and in a river of the Hitachi area, northeast of Tokyo. Maximum concentrations of 3000–50,000 mg Cd/kg sediment occurred near the effluent of a nickel-cadmium battery plant at Foundry Cove near Cold Springs, New York[2]; up to 368 mg Cd/kg was measured in the sediments of the irrigation ditch of a Braun tube factory in Japan[1]. Strong contamination by cadmium was detected in sediments from European rivers draining highly industrialized areas, for example, in the tributaries and reservoirs in the vicinity of Miasteczko Slaskie, the zinc and lead work on the upper reaches of Mala Panew River (Poland), in the Voglajna River near Celje in Slovenia (Yugoslavia), in the Ginsheimer Altrhein near Mainz (FR Germany) and in the Meuse and Vesdre Rivers at
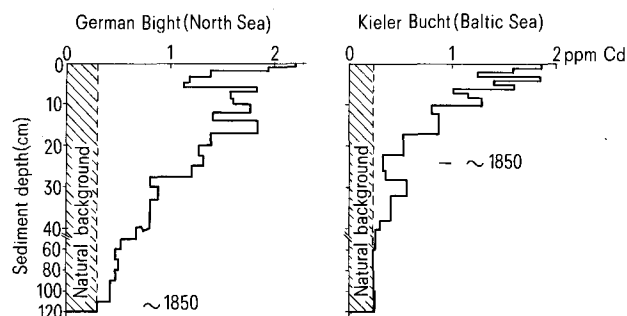

Figure 1. Chronological development of cadmium concentrations in the North Sea and Baltic Sea as derived from analyses of sediment cores from the German Bight[12] and Kieler Bucht[7] (from: Förstner[9]).
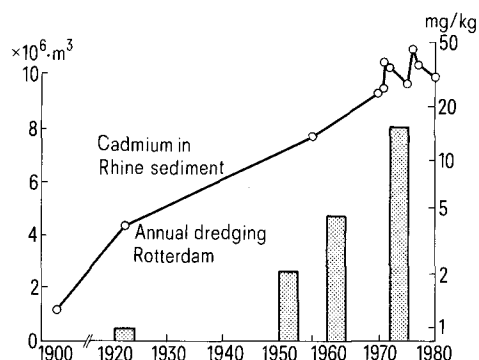

Figure 2. Increase of Cd concentrations in sediments and of dredging activities in Rotterdam Harbor[29].

Table 1. Cadmium in polluted river sediments (examples). For references see Förstner and Wittmann[14]

Sediment source	Cadmium (ppm)	Source	Reference
North America			
Susquehana River Harrisburg, PA	1.68		Malo (1977)
Grand River, MI	3.5	Domestic effluents	Fitchko and Hutchinson (1975)
Grand Calumet River, IN	9.7		Hess and Evans (1972)
	3.1–7.9	Domestic effluents	Romano (1976)
Murderkill River, DE	0.8–8.7		Bopp et al. (1973)
Illinois River	2.0 (0.2–12.1)		
Rideau River, Ont.	0.3–15	Mixed effluents	Agemian and Chau (1977)
Lake Cayuga tributaries	15.6		Kubota et al. (1974)
Saginaw River, MI	28		Hess and Evans (1972)
Coeur d'Alene River	Max. 80	Mine effluents	Maxfield et al. (1974)
Milwaukee River, WI	16.6	Industrial effluent	Fitchko and Hutchinson (1975)
Tennessee River	Max. 149 Max. 227	Mine effluents	Perhac (1972)
Los Angeles River, CA	860	Sewage effluent	Chen et al. (1974)
Hudson River estuary, NY	2.3	Ni-Cd-battery	Vaccaro et al. (1972)
Foundry Cove, NY	Max. 50,000	factory	Kneip et al. (1974)
South Africa, Australia, Japan			
Gold mine drainage, South Africa	0.21 (0.05–1.0)	Domestic and mine effluents	Wittmann and Förstner (1976a)
Jukskei River, South Africa	0.25–4.9		Wittmann and Förstner (1976b)
Molonglo River, Australia	0.8–3.3	Mining wastes	Australian Government Technical Commission (1974)
Tamar River, Tasmania	3.6 (< 0.1–6.0)	Mine effluents	Ayling (1974)
South Esk River, Tasmania	Max. 153	Mine effluents	Tyler and Buckney (1973)
Tama River, Tokyo	0.7–9.8		Suzuki et al. (1975)
Jintsu River, Toyama Pref.	3.27 (0.16–5.0)	Mine effluents	Goto (1973)
Takahara River (near Kamioka mine)	121 (4.1–238)	Mine effluents	Kiba et al. (1975)
Rivers around Himeji City (W of Osaka)	0.56–10.4 Max. 129		Azumi and Yoneda (1975)
Rivers in the Hitachi area, northeast Tokyo	Max. 368	Braun tube factory	Asami (1974)
Israel and Europe			
Gadura River (Bay of Haifa, Israel)	Max. 123	Battery factory	Kronfeld and Navrot (1975)
Lake Geneva tributaries, Switzerland	1.4 (0.09–12.4)	Industrial effluents	Vernet (1976) Viel et al (1978)
Upper Rhône, Switzerland	0.1–73		Ribordy (1978)
Elbe, FRG	2.9–19.9		Lichtfuss & Brümmer (1977)
Sajo River, Hungary	Max. 20		Literathy and Laszlo (1977)
Blies, Saar, FRG	0.5–24.0	Industrial effluents	Becker (1976)
Bavarian rivers, FRG	< 0.05–29.2	Industrial effluents	Bayerische Landesanstalt für Wasserforschung (1977)
Main River, FRG	17–151		Schleichert and Hellmann (1977)
Ginsheimer Altrhein, FRG	2–95	Industrial effluents	Laskowski et al. (1975)
Neckar River, FRG	Max. 320	Pigment factory	Förstner and Müller (1974)
River Conway, GB mineralized areas	21 (3–95)	Mine effluents	Thornton et al. (1975)
River Tawe, GB	Max. 355	Metal processing	Vivian and Massie (1977)
Sava basin, Yugoslavia Voglajna River	Max. 66	Industrial effluents	Štern and Förstner (1976)
Stola River, Poland	Max. 116	Mine effluents	Pasternak (1974)
Meuse River, Belgium	Max. 230	Industrial effluents	Bouquiaux (1974)
Vesdre River, Belgium (near Liège)	Max. 430		Bouquiaux (1974)

Liège (Belgium). There is particularly strong cadmium pollution in the catchment area of River Tawe in the lower Swansea Valley, Wales, where coal has been mined since the 14th century, providing the basis for smelting and other industries[39]. The major source of strong accumulations of cadmium in the lower Neckar River, a tributary of the Rhine, was a pigment dye production plant that released (until February 1973) an annual total of approximately 10–20 tons of cadmium in dissolved and particulate form into the river; because of the numerous lock reservoirs in sections of the river, where highly polluted sediments settle, regeneration necessarily proceeds at a very slow rate[35].

In mineralized areas, particularly in regions of sulfidic lead-zinc mineralizations, significant accumulation of cadmium takes place in the river sediments. The area around Coeur d'Alène River in Idaho, the Tennessee River near Knoxville, many rivers in Wales, southeast England, and especially the Takahara River/Jintsu

River region in Japan, in which the catastrophic Itai-Itai disease occurred are examples of the lead-zinc mining effect. The discharge of effluents from tin and tungsten mines has caused severe pollution of the South Esk River in northeastern Tasmania.

Cadmium enrichments between 5 and ca. 10 mg/kg in river sediments are often caused by communal wastewater effluents, sometimes with an industrial component, for instance from the electroplating industry. In the Milwaukee River, Wisconsin, this effect for the most part is dominant over domestic sources: effluents from brewing, tanning, incineration, the chemical industry, foundries, metal works and manufacturing are common sources of cadmium[8]. Particularly high concentrations of cadmium have been analyzed by Chen et al.[3] in suspended silts in the dry weather flows from the urbanized Los Angeles area. By analyzing sediments collected since 1922 and from polders reclaimed in the 15th and 18th centuries Salomons and De Groot[30] were able to show that pollution of the lower Rhine is still increasing for cadmium (fig. 2), whereas mercury, arsenic and lead pollution is decreasing.

It is a general experience, that as a result of increasing efforts to reduce the wastewater input the metal discharges in highly polluted rivers are now decreasing after a maximum in the early 1970's. From a review of data from the Rhine River at the German-Dutch border it is shown by Malle and Müller[24] that the suspended solid contents did hardly change since

1973, while the contents of Cr, Cu, Zn, Cd, Hg and Pb are retrograde; the decrease in the Cr and Hg contents mainly occurred in the suspended solids, Zn and Cd concentrations were found to be reduced in the liquid phase. It should be noted, however, that of the total amount of metals transported by the rivers Rhine and Meuse, about $^2\!/_3$ accumulates in the Netherlands, which in fact acts as an effective 'treatment plant' for these river discharges[34]. This situation may be regarded as beneficial for the North Sea, but poses problems for the management of inland waters and the land-fill areas in the Netherlands (fig. 2).

Mobilisation of cadmium from sediments

Trace metals temporarily immobilized in the suspended matter and in bottom sediments of aquatic systems may be released as a result of physicochemical changes, such as a) increased salinity, b) an alteration in the redox conditions, c) lowering of pH, and d) increased input of organic chelators. In figure 3 examples are given for these parameters from laboratory experiments.

a) Increased salinity at the river/sea interface

Experiments performed by Van der Weijden et al.[38] with artificial seawater indicate partial desorption of cadmium from particulate matter, presumably by inorganic complex formation; preferential remobilization is probably due to the high stability of the cadmium-chloro-complex. Similar developments have been described by Rohatgi and Chen[27] from experiments with sewage sludge in seawater solutions; 93% of the original cadmium content of sewage particles was released after 4 weeks' treatment. The simultaneous influence of chlorinity and pH on the adsorption was studied by Salomons[28]; figure 3A shows that with an increase in chlorinity the amount of added metal (5 µg Cd/l) which adsorbs onto the suspended sediment (100 mg/l) decreases; with an increase in the pH the adsorption increases. It has been demonstrated by Salomons et al.[34] that already at chloride levels of 200 mg/l – which are 'normal' for the lower Rhine River – the adsorption of cadmium on the suspended matter is affected. In figure 3B the combined influence of chlorinity and suspended matter on the adsorption of cadmium is shown; already a small increase in the chlorinity causes a large decrease in the amount of metals removed from solution.

These sorption effects obviously are not fully reversible, as has been demonstrated by Salomons[28] from desorption experiments (table 2).
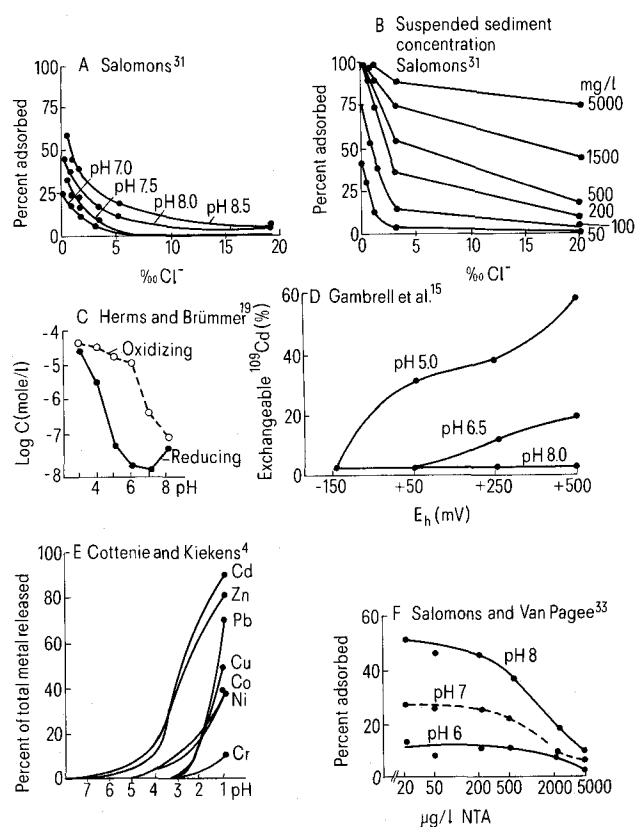

Figure 3. Factors affecting the remobilization of cadmium from solid matter (explanations see text).

Table 2. Percentage of cadmium not released from suspended matter in river water after treatment with NaCl or ammonium acetate

Adsorption period	1 day	3 days	8 days	24 days	60 days
NaCl (35‰)	24%	30%	33%	37%	40%
1 N ammonium acetate	31%	36%	38%	45%	52%

Apparently, the adsorbed cadmium becomes more strongly bound to the sediment with increase in time.

b) Redox changes

A change in redox conditions is usually caused by an increased input of nutrients (reducing effects) or by the land disposal of strongly polluted sediments (oxidizing effects). Oxygen deficiency in sediments leads to an initial dissolution of manganese oxides, followed by that of hydrous iron oxides. Since these metals are readily soluble in their divalent states, any coprecipitates with metallic coatings become partially remobilized. On the other hand, it was found from dredge experiments that larger concentrations of cadmium were released to the water column under oxygen-rich than under oxygen-deficient conditions; under oxidized conditions larger releases of cadmium were measured as salinity increased. The first effect is attributed to the release, upon oxidation, of trace metals bound to sulfide phases; the second observation can be explained by the enhanced formation of soluble inorganic complexes (see section a)). In figure 3C the effects are described of the redox conditions on the cadmium concentrations in equilibrium solutions from marine mud samples under different pH-values[18]. In the range between pH 4 and pH 7 the solubility of Cd in the oxidizing, sulfide-free milieu is strongly increased (at pH 6 approximately 1000-fold compared to the reducing, sulfidic conditions). Isotope studies performed by Gambrell et al.[15] with Mississippi River sediments indicated that exchangeable ^{109}Cd levels are significantly increased as cadmium-contaminated sediment is transported from a near-neutral pH, reducing environment to a moderately acid, oxidizing environment (fig.3D). Under these conditions, Cd levels of subsurface drainage water from upland disposal of dredged materials may be increased, and cadmium availability to plants growing on the material enhanced[15].

c) Acidic waters

A lowering of pH leads to the dissolution of carbonate and hydroxide minerals and (as a result of hydrogen ion competition) to an increased desorption of metal cations. Long-term changes in pH conditions have been observed in waters poor in bicarbonate ions, which are affected by atmospheric SO_2 emissions. From a compilation of Haines[16] it is suggested that lakes with a pH of 4.1–5.3 exhibit 5- to 10-fold higher Cd concentrations in the water phase than lakes with a pH of 6.0–7.8. Cadmium enrichment in acidic mine effluents is significant, but less than metals such as Fe, Mn, Ni and Co. On the other hand the experimental data for step-wise acidification of soil samples (fig.3E) indicate a higher mobility of Cd and Zn compared to Pb, Cu, and Cr in the pH-range of 3.5–1.5[4].

d) Organic complexing

Interaction with organic substances plays an increasingly important role in the transport of heavy metals in both surface water and groundwater, since the amount of organic complexing material increases further because of secondary sewage treatment effluents. An even more serious impact on heavy metal remobilization from polluted sediments may result (a matter of considerable controvercy during the last few years) from the growing use of synthetic complexing agents (e.g., nitrilotriacetic acid, NTA) in detergents to replace polyphosphates. The data in figure 3F (from Salomons and Van Pagee[33]) indicate that the effect of reduced adsorption of cadmium is even more problematic than the possible (active) remobilization of cadmium, since already at NTA-concentrations of 200 μg/l and at higher pH-values (see pH 8 curve) the normal elimination of dissolved cadmium by fixation upon solid phases is significantly lowered. This could imply a potential danger for drinking water obtained from bank filtration or artificial recharge[36].

Estimation of environmental impact of Cd-polluted sediments

Of the various processes, products, and substrates of metal enrichment in aquatic solids, three major types should be distinguished for the interpretation and assessment of their sources, distribution and environmental effects:

- A rise in pH and oxygen content promotes the formation of metal hydroxides, carbonates and other metal precipitates. Hydrous Fe and Mn oxides constitute significant 'sinks' for heavy metals through the effects of sorption/coprecipitation;
- in waters rich in organic matter, minerals may be solubilized by the combined processes of complexation and reduction; reincorporation of metals into the sediment involves the mechanisms of adsorption, flocculation, polymerization, and precipitation[21];
- metals are transported and deposited as major, minor, or trace constituents in the detrital minerals derived from rocks and soils, in organic residues, and in solid waste material.

Only part of the metals present – mainly the former types – may take part in short-term geochemical processes and/or are bioavailable. For the differentiation of the relative bonding strength of metals in different phases, sequential extraction procedures have been developed; while the determination of the relative binding strength seems to pose basically operational problems, the correlation with the biological uptake mechanisms is as yet not satisfactory. A promising approach to bridge the gap between the chemical speciation data of the solid matter and of the biological uptake values is the application of pore water analyses[32].

Examples for the solid phase partition of Cd have been given in table 3, according to an extraction sequence developed by Förstner and Calmano[10]. Compared to other metals, such as Pb and Cu, cadmium is characteristically enriched in the more mobile fractions 'cation exchange' and 'easily reducible phases', and is, therefore, more mobile than most of the other heavy metals. The data from table 3 also suggest a general decrease in the residual bonding form, that is, the predominantly inertly fixed cadmium content, as the anthropogenic metal enrichment increases. Such species differentiations can be used for the estimations on the remobilization of metals

Table 3. Chemical forms of cadmium in aquatic solids

Sediment fraction[a–e]	Weser (1)	Estuary (2)	Rhine River (3)	Rotterdam Harbor (4)	Neckar River (5)
Cation exchangeable[a]	8%	18%	27%	12%	13%
Easily reducible[b]	32%	49%	42%	61%	64%
Moderately reducible[c]	45%	14%	2%	13%	10%
Organic/sulfidic[d]	12%	17%	17%	12%	12%
Residual fraction[e]	3%	2%	12%	2%	1%
Total Cd (mg/kg)	3.0	4.3	9.0	18.1	33.6

(1) Dredged sediment; (2) suspended matter; (3) station Wesel (Dutch/German border); (4) Broekpolder; (5) lock reservoir Lauffen.
[a] 1 M ammonium acetate, 1:20 solid/solution ratio, 2 h shaking time; [b] 0.1 M hydroxylamine hydrochloride +0.01 M nitric acid, 1:100, 24 h; [c] 0.2 M ammonium oxalate +0.2 M oxalic acid, pH 3, 1:100, 24 h; [d] 30% hydrogen peroxide +1 M ammonium acetate, pH 2.5; 1:100, 24 h; [e] hydrofluoric/perchloric acid digestion.

under changing environmental conditions and on the potential uptake by biota:
In the estuarine environment the 'exchangeable fraction' might be affected in particular; however, changes of pH and redox potential could also influence other easily extractable phases, e.g., carbonates and manganese oxides. Lowering of pH will affect, according to its strength, the 'exchangeable', then the 'easily reducible' and in case parts the 'moderately reducible fraction', the latter consisting of Fe-oxyhydroxides in less crystallized forms. Redox changes concern under 'postoxic' conditions, during reduction of, for example, nitrate and manganese oxide, the 'easily reducible fraction', i.e., metals associated with manganese oxides and partly amorpous Fe-oxyhydrates; in strongly reducing environments, e.g., in highly polluted sediments, the 'moderately reducible fraction' is affected too, especially the iron compounds present as coatings[20]. The effects on organically bound metals are more complicated; however, it has been argued that this fraction is highly susceptible to environmental changes, especially during early diagenetic reaction, where recycling of mineralized organic matter and pore-fluid transfer processes are controlling the dynamics of pollutants and nutrients in sediments.
The still somethwat unsatisfactory situation with respect to the assessment of the quantitative extent of bioavailable element concentrations from solid speciation data has been explained by Luoma and Bryan[22,23] as being due mainly to the effect of competition between more or less strong adsorption sites in the solid substrate and selective mechanisms of the metal uptake by the different organisms which cannot simply be drived from the chemical extraction data. On the other hand, the usefulness of a differentiated approach on the interactive processes between water/biota and – even if only operationally – defined solid phases has been clearly evidenced. The possible environmental implications, e.g., during dredging operations, after land disposal of waste material, from acid precipitation, for redox changes in the subsoil, and organic complexing near sewage outfalls, which may lead to a partial remobilization of the particle-bound cadmium and other metals, can be qualitatively estimated, particularly when the hydrochemical conditions are known. With respect to the more important environmental parameters, such as pH and redox

potential[26] a weak acid-reducing extractant offers a relatively good indication of the mobile and potentially bioavailable fraction of transition metals, equivalent to the non-apatite inorganic phosphorous fraction of the solid P-compounds[31]. The results of these extractions as well as the methods used in soil science, e.g. treatment with dilute EDTA or DTPA solutions, show a good correlation with the data from pot experiments, i.e., that cadmium is more readily accessible for plant uptake than most of the other potentially toxic trace metals.

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Cadmium in the atmosphere

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Summary. Cadmium is present naturally in the air mainly as a result of volcanic emissions and release by vegetation. Anthropogenic sources, which overall give rise to emissions one order of magnitude greater than natural sources, are largely primary non-ferrous metals production and waste incineration. Measured concentrations of airborne cadmium are typically < 1 ng m^{-3} at remote sites, 0.1-10 ng m^{-3} at rural sites and 1-100 ng m^{-3} at urban and industrial sites, dependent upon the nature and proximity of local sources. Particle sizes are generally < 2 µm, and often considerably smaller, consistent with an anthropogenic source and a long atmospheric lifetime. Cadmium deposition to the land occurs with fluxes varying from 0.05 ng cm^{-2} month^{-1} in Greenland to circa 1000 ng cm^{-2} month^{-1} in the vicinity of major industrial sources. The possible significance of a motor vehicular source of airborne cadmium is also reviewed.

Introduction

The atmosphere plays an important role in the dispersal of cadmium within the environment. Despite the fact that the largest natural source of cadmium in air (volcanic emissions) as well as the major anthropogenic sources are very localized, their influence may be seen at remote sites throughout the Northern Hemisphere. Thus within this article, the major sources will be reviewed, as well as the reported levels of cadmium measured in ambient air.

Sink processes for atmospheric cadmium are wet and dry deposition, which lead to cadmium enrichment of soil, vegetation and surface waters. The atmospheric