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**GEOCHEMICAL AVAILABILITY OF Cd, Pb AND Zn
IN WET AND DRY DEPOSITION**

K.R. Lum¹, E.A. Kokotich¹ and W.H. Schroeder²

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¹ Environmental Contaminants Division
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6

² Air Quality and Inter-Environmental Research Branch
Atmospheric Environment Service
Downsview, Ontario M3H 5T4

• Environment Canada

MANAGEMENT PERSPECTIVE

This article follows on the DOE ~~Cadmium Action Plan~~ which, among other recommendations, called for the use of analytical methodology acceptable to all components of DOE for the purpose of establishing baseline concentrations, without which trend analysis is a colossal waste of time and money, and investigating pathways and effects. The work reported in this article was aided by a grant of \$10K from AGRB-AES, as part of their program on the effects of acid deposition on geochemical cycling and biological availability of trace elements.

The analysis of precipitation samples from rural sites in both Canada and the United States are presented. Comparison with published data shows that our results are very likely the only reliable measurements of cadmium and thus constitute the first baseline data for North America. Although the results for lead may be influenced by a container wall effect, they are realistic when compared with the limited data in the literature and hence these data also represent new baseline information. Deposition of cadmium at rural sites in the U.S. is 20 times that for Canada. The fact that this ratio is similar to the population ratio is perhaps adventitious as the ratio for lead is about 5.5.

The results on the biogeochemical availability of cadmium, lead and zinc on atmospheric particulate matter substantiates our earlier suggestion (Lum et al, 1982) that toxic metals (and phosphorus) are likely to have a significant environmental impact on aquatic systems because of their ease of solubility. We now suggest that the possible sites of greatest impact will likely be at interfaces e.g., forest canopies and at the air-water interface in lakes and rivers.

PERSPECTIVE-GESTION

Cet article s'inscrit dans le cadre du plan d'action sur le cadmium du MDE. Ce plan recommandait entre autres d'utiliser une méthodologie analytique acceptée par tous les services du MDE pour la détermination des concentrations de base, valeurs sans lesquelles l'analyse des tendances n'est qu'un énorme gaspillage de temps et d'argent, et pour l'étude des voies d'assimilation et des effets. Les travaux décrits dans cet article ont été financés grâce à une subvention de 10 000 \$ que la DRQA (SEA) a accordée dans le cadre de son programme destiné à étudier les effets des dépôts acides sur le cycle géochimique des éléments traces et sur l'abondance des formes biologiquement assimilables.

Nous avons analysé des échantillons de précipitations prélevés dans des emplacements ruraux du Canada et des États-Unis. En comparant les résultats de cette analyse avec les données publiées sur la question, nous avons constaté que nos valeurs sur le cadmium sont fort probablement les seules qui soient valables et qu'elles constituent de ce fait les premières données de base applicables à l'Amérique du Nord. Bien que l'effet de paroi des contenants ait pu influencer sur le dosage du plomb, nos résultats sont plausibles lorsqu'on les compare avec les quelques données fournies à ce sujet dans

la littérature; depuis, elles constituent aussi de nouvelles données de base. Le dépôt de cadmium mesuré dans les emplacements ruraux était 20 fois plus élevé aux États-Unis qu'au Canada. Le fait que le rapport entre les populations des deux pays soit le même qu'entre les concentrations mesurées n'est peut-être qu'une coïncidence, car le rapport calculé pour le plomb vaut environ 5.5.

Ce que nous avons appris sur le cadmium, le plomb et le zinc biogéochimiquement assilable dans les particules atmosphériques vient étayer l'hypothèse que nous avions auparavant avancée à ce sujet (Lum et coll., 1982), soit que les métaux toxiques (et le phosphore) ont probablement des effets significatifs dans les milieux aquatiques parce qu'ils sont solubles. Nous pensons maintenant que c'est aux interfaces que ces effets se font surtout sentir, c'est-à-dire dans le couvert forestier et à la surface des eaux.

ABSTRACT

Cadmium and lead have been determined in precipitation samples from nine rural sites in Canada and five in the United States. Samples from two precipitation events were analysed from three of these sites. The average concentrations of cadmium and lead for the Canadian sites were 27.7 ng/L and 2.07 ug/l and for the U.S. sites, 48.8 ng/L and 2.08 ug/l respectively. The average amount of cadmium deposited in the precipitation events sampled at the U.S. sites was ten times the amount deposited at the Canadian sites. For lead, the U.S. to Canada ratio was 5.5.

Atmospheric particulate filters from high-volume samplers located in south-central Ontario, were subjected to a three-part sequential chemical extraction procedure to simulate environmental conditions during and after precipitation events to determine the biogeochemical availability of cadmium, lead and zinc.. Water-soluble forms dominated the "particulate-speciation" of the three metals. The average percent water-soluble forms for the three metals six collection periods were Cd, 85% > Pb, 43% > Zn, 26%. The ease of solubility of the three metals on atmospheric particulate matter suggests that the greatest impact in terrestrial and aquatic systems will likely occur at interfaces, e.g., at forest canopies and at the air-water interface.

Cd, Pb et Zn biogéochimiquement assimilable dans les dépôts humides ou secs

RÉSUMÉ

On a dosé le cadmium et le plomb présents dans des échantillons de précipitations prélevés dans neuf emplacements ruraux du Canada et dans cinq autres emplacements aux États-Unis. On a analysé les échantillons de deux précipitations provenant de trois de ces emplacements. Au Canada, les concentrations moyennes de cadmium et de plomb étaient respectivement de 27,7 ng/L et 2,07 µg/L; aux États-Unis, elles s'élevaient à 48,8 ng/L et 2,08 µg/L. La quantité moyenne de cadmium apportée dans les précipitations était 10 fois plus élevée aux États-Unis qu'au Canada. Dans le cas du plomb, le rapport était de 5,5.

On a soumis à une extraction séquentielle en trois étapes les filtres à particules atmosphériques d'échantillonneurs à grand volume installés dans le centre-sud de l'Ontario; il s'agissait de reproduire les conditions du milieu avant et après les précipitations afin de mesurer la quantité de cadmium, plomb et de zinc géochimiquement assimilable. Les formes hydrosolubles dominaient le profil de caractérisation des particules des trois métaux. Les valeurs des formes hydrosolubles mesurées durant les six périodes d'échantillonnage se répartissent comme suit : Cd, 85 %; Pb, 43 %; Zn, 26 %. Etant donné la grande solubilité des trois métaux dans les particules atmosphériques, leur effet sur les milieux terrestres et aquatiques devrait surtout se faire sentir aux interfaces, c'est-à-dire dans le couvert forestier et à la surface des eaux.

INTRODUCTION

There is now general acceptance that the atmosphere is a major source of several trace elements eg., cadmium, lead, zinc, mercury, selenium, arsenic, to terrestrial and aquatic ecosystems (e.g., Lantzy and Mackenzie, 1979; Nriagu, 1979; Schaule and Patterson, 1981; Nriagu, 1984). In particular, for cadmium and lead, the atmosphere is regarded as the principal pathway of contamination of land and surface waters. The increased biogeochemical availability of trace metals, as a result of their co-occurrence with acidic constituents in atmospheric deposition, has become an important concern in research on the environmental impact of these pollutants (e.g., Wallace et al., 1977; Hodge et al., 1978; Ochs and Gatz, 1980; Galloway et al., 1982; Lum et al, 1982; Lindberg and Harris, 1983; Tri-Academy Committee on Acid Deposition, 1985; Gatz and Chu, 1986). Thus, although many studies have shown that most trace metal emissions are efficiently removed from the atmosphere by wet and dry deposition, data on trace metals in precipitation and their attendant biogeochemical availability are few in number. In this article, we present information on the amount and spatial distribution of cadmium and lead in wet deposition collected from rural sites in Canada and the United States as well as the results of a sequential chemical extraction procedure to determine the biogeochemical availability of cadmium, lead and zinc in atmospheric particulate matter collected at a rural site in South-Central Ontario, Canada.

SAMPLE COLLECTION AND TREATMENT

Precipitation samples obtained from the CAPMoN (Canadian Air and Precipitation Monitoring Network) program and from the U.S. Geological Survey were part of an inter-laboratory data quality project.

Air particulate filters from high-volume samplers located at Dorset in the Muskoka Region of South-Central Ontario were kindly provided by Dr. Len Barrie of the Atmospheric Environment Service.

ANALYTICAL METHODS

Precipitation samples were analyzed for cadmium by direct injection graphite furnace AAS using a Hitachi 180-80 Zeeman Effect system (Lum and Callaghan, 1986), which gave a detection limit of 3 ng/L. Lead was similarly analyzed on a subset of samples to evaluate the sensitivity of this instrumental system (detection limit was 25 ng/L for a 50 uL sample).

High-volume ("Hi-vol") sampler filters with and without particulate material were subjected to a three-stage sequential chemical extraction procedure (Figure 1). The extracts were analyzed by graphite furnace AAS for cadmium and lead and flame AAS for zinc.

RESULTS AND DISCUSSION

Cadmium in precipitation.

Although it is established that there is a time/volume dependence of the concentration for a given trace metal in wet deposition samples collected at various stages during precipitation events (e.g., Nurnberg et al, 1982), comparing metal concentrations in samples derived from one or more events nevertheless provides useful information. Indeed, such data are a pre-requisite for calculating mass loadings of metals deposited at receptor sites.

Samples of precipitation from nine rural sites in Canada, collected in the summer of 1985, show a range of cadmium concentrations from 10 to 79 ng/L (Table 1). Although the July 12-13 sample from Bay d'Espoir, Newfoundland, has the highest concentration, the amount of cadmium deposited during this precipitation event is similar to that deposited several days later. On this basis, the event at Sutton, Quebec, had by far the largest wet deposition of cadmium.

By comparison, the results for samples from five sites in the continental United States show a wider range of cadmium concentrations, viz. ~10 to 130 ng/L. The scatter in the results for the samples from Arkansas and Texas is very likely caused by contamination during sample processing. The data for three replicate samples from the South Carolina and Georgia sites are very reproducible (relative standard deviation 5 - 7

%) and the results from the Oswego location are within 10 % of the mean value. As already seen for the site in Newfoundland, Canada, there can be a considerable variation in cadmium concentrations in precipitation events (even in successive events). This phenomenon is also evident from the data for the South Carolina site.

Wet deposition of cadmium at rural U.S. sites is appreciably higher than at Canadian rural sites: about 10 times larger. This ratio is not changed greatly by omitting the Oswego site which is close to a moderately large city. This result is not perhaps unexpected given the greater abundance of source emissions in the U.S. compared to Canada and is reminiscent of the population ratio of the two countries.

In general, background concentrations of cadmium in precipitation from the U.S. and Canada are less than 50 ng/L. The arithmetic mean for all the measurements is 42 (s.d. = 39) ng/L. Note that cadmium concentrations in precipitation at both the Georgia and Texas locations are considerably lower and, from the data in Tables 1 and 2, fall into the lower end of the background range near 10 ng/L. The arithmetic mean for the Canadian sites is about two-thirds (67 %) of the overall mean and concentrations at most sites in this country are between 10 and 30 ng/L.

Our data on cadmium in wet deposition fall within the range of concentrations representative of remote locations according to the review of Galloway et al. (1982). Recent measurements in a residential area of Illinois (Gatz and Chu, 1986) show a median value of 150 ng/L for soluble

cadmium in wet deposition. Insoluble (non-filterable) cadmium for the 31 samples collected by Gatz and Chu had a median concentration of 7 ng/L. This means that the determination of soluble cadmium very nearly represents the total concentration of cadmium in wet deposition. The annual average concentration of cadmium for 42 precipitation-weighted means for samples collected at thirty six sites and over 13 sampling periods in Ontario in 1982 was 113 ng/L, standard deviation = 46 ng/L, (Chan et al., 1986). Thus, these results as well are significantly lower than the median concentration given by Galloway et al. for rural locations (viz., 500 ng/L). An average monthly concentration of 180 ng/L at Lewes, Delaware has been reported by Tramontano et al. (1986). These authors also made measurements of precipitation at High Point, Bermuda which may be regarded as a rural location and obtained a monthly average of 62 ng/L. Comparison with our data raises the question of possible adsorptive losses on the polyethylene bags used in the Canadian and U.S. precipitation network collectors which could conceivably result in measured concentrations in the 10 - 20 ng/L range. Good and Schroder (1984) investigated the adsorption characteristics of three types of sample bags (viz. polypropylene, polyethylene and polyester/polyolefin) for precipitation sampling and concluded that such containers are suitable collection vessels for cadmium. In the case of collection with conventional polyethylene bottles, cadmium concentrations can apparently increase by about a factor of 2-4 (Ross, 1986).

Lead in wet deposition

As can be seen by inspection of Table 3, the range of lead concentrations for all sites (Canadian and U.S.) is <0.05 to 6.82 ug/L. This greater degree of scatter relative to cadmium can be attributed mainly to sample processing as can be seen from the replicate measurements on the U.S. samples. Reproducibility is best for the triplicate samples from Oswego and Summerton (June 4-11). The role of sorption and desorption on plastic surfaces and their relationship to the measurement of lead in wet deposition is quite controversial. Good and Schroder (1984) found that the same three plastic bag formulations discussed in the preceding section were unsuitable for storing samples to be analyzed for lead. However, for a contact time of 24 hours or less, negligible adsorption was observed for polyethylene bags (Chan et al., 1983). In contrast, for conventional polyethylene plastic bottles, Ross (1986) suggests that the "container wall effect" would cause a change in lead concentration of the collected precipitation by a factor of 0.25 to 2. Thus, in the case of lead, the container material does appear to have an effect on the final measured concentration, but the direction and magnitude of change are not predictable with the present state of knowledge. In spite of this, we believe that some valuable information on lead in precipitation can be derived from comparisons with other published data.

Examination of the 17 determinations of six samples from the U.S. shows lead concentrations range from 0.2 to 5.0 ug/L with an arithmetic mean of 2.08 ug/L (s.d. = 1.67). The ten Canadian samples show a similar mean, 2.07 ug/L (s.d. = 1.91). For Ontario in 1982, the average

Concentration of lead for the same 42 precipitation-weighted means described above for cadmium, was 5.2 ug/L with a standard deviation of 2.6 ug/L (Chan et al., 1986). The higher Ontario average likely results from the inclusion of several stations in or near urban centers and the fact that this province has the largest population in Canada and hence a larger number of automobiles compared to the rest of the country. As well, Southern Ontario, where most of the samples were obtained, is literally sandwiched between states in the U.S. which also have large populations and urban centres.

The amount of lead deposited (during the sampling periods covered in this study) is greatest for the Sutton, Quebec site. This is similar to the situation for cadmium. Comparison with the U.S. sites shows that about five times more lead is deposited by precipitation in the U.S. This result is significantly different from that found for cadmium.

Our average lead concentration falls in the range of median values given by Galloway et al. (1982) for remote and rural areas and is in reasonable agreement with the monthly average at Lewes, Delaware, 3.02 ug/L (Tramantano et al., 1986). Five Canadian sites and one U.S. site (Bellville, Georgia) have similar concentrations to the monthly average measured by Tramontano et al. (1986) at Bermuda, 0.722 ug/L. Considerably higher concentrations have recently been reported for rainwater in France (Servant, 1986). However, these data are from 1972-1973 and the high average concentrations for rural and mountainous regions, 16 and 9 ug/L respectively, are likely caused by the relative insensitivity of the

methods used (colorimetry and flame atomic absorption) and contamination introduced during pre-concentration by evaporation of 1 L of sample. This conclusion is supported by the measurements of Batz and Chu (1986), who reported a median value of 9.54 ug/L for soluble lead in 51 samples from a residential area in Illinois. Furthermore, concentrations of lead in wet deposition in the Sudbury, Ontario basin average 11.5 ug/L (Chan and Lysis, 1986). Interior regions of Greenland can be regarded as truly representative of remote sites, and there is general agreement that present-day lead concentrations in Greenland snows are about 0.2 ug/L (Boutron and Patterson, 1983; Boutron, 1986). Thus, it is reasonable to conclude on the basis of our measurements at Canadian and U.S. locations, that background concentrations of lead in wet deposition in rural areas of North America are <1 ug/L.

SEQUENTIAL CHEMICAL EXTRACTION OF ATMOSPHERIC PARTICULATE MATTER ON FILTERS

Investigation of filter blanks.

Although the filter medium of choice when using the Hi-vol sampler to collect trace elements in ambient air, is widely considered to be Whatman 41 paper (Barri  et al., 1981), we decided to examine glass fiber filters as well because we envisaged that, in an extraction procedure for trace metals involving mineral acids and heat, the Whatman paper may be difficult

to decompose completely. Severe drawbacks in the use of this sampling medium for particles in air have been recognized and this has led to the very recent conclusion that its inefficiency precludes the possibility of obtaining reproducible data on atmospheric aerosols (Lodge, 1986).

The procedural blanks resulting from the extraction of six filters of each type (4.25 cm diameter GF/C and 9.0 cm diameter Whatman 41) with 6N HCl are summarized in Table 4. Although the reproducibility of the lead blanks is not as good as for cadmium, it is clear that the Whatman filter paper contributes less cadmium and lead compared to the GF/C. Soaking the filters in 2N HCl for 1 hour, rinsing with deionized distilled water, followed by drying in a laminar hood, does lower the blank, but interestingly the effect is less impressive for the Whatman 41 paper. The availability of glass fiber filters that do not contain a binder and are comparatively low in trace metals (e.g., Gelman Type A/E), combined with more rigorous acid-cleaning would be needed if glass fiber filters were to be used for sample collection. Their advantage lies in the fact that, unlike paper, they are readily soluble in hydrofluoric acid, do not char, and hence can be readily decomposed to determine total elemental content.

Choice of a sequential chemical extraction procedure

Chemical extraction procedures are widely used by geochemists and soil scientists to obtain operationally defined trace elemental associations with specific binding substrates in particulate material

(Salomons and Forstner, 1984). Because of the small amount of sample generally collected on atmospheric aerosol filters, especially outside of urban areas, we chose not to use the six step procedure previously applied to urban particulate matter (Lum et al., 1982). Our current procedure (Figure 1.) is based on the recognition of the relatively high degree of solubility of many trace metals in atmospheric particles (Wallace et al., 1977; Hodge et al., 1978; Lindberg and Harris, 1983; Gatz and Chu, 1986). Thus, the sample is contacted first with deionized-distilled water for ten minutes, then by a mixture of nitric and sulphuric acids at a pH of 4.0 for 24 hours and finally digested with aqua regia and hydrofluoric acid. The extraction at pH 4.0 is intended to simulate a common environmental occurrence in precipitation events.

The procedural blanks with acid-washed 9.0 cm Whatman papers are summarized in Table 5. The highest blanks for cadmium are found in the deionized-distilled water extract. This is obviously not from the water but likely arises from residual cadmium not washed from the filter. For lead and zinc, the highest blanks are found in the last extract. This is not surprising, as the largest amount of reagents and manipulation in a standard fume-hood are involved in this step. The significance of these procedural blanks depends on the range of concentrations of the metals in atmospheric particulate matter and the magnitude of the field blanks. These considerations are addressed in the following section where the extraction procedure is applied to samples from a rural area of South-Central Ontario.

Biogeochemical availability of Cd, Pb and Zn in
atmospheric particulates from a rural area of South-Central Ontario

Six samples and one field blank were subjected to the above extraction procedure. Subsamples of the Hi-vol filters collected were prepared by cutting them into quarters with a new pair of stainless steel scissors which had been washed with detergent and wiped with 2N nitric acid and finally washed with distilled-deionized water. The dimensions of the pieces for analysis were recorded and duplicates were extracted. An average concentration for each pair was calculated and the results (Table 6) have been corrected for the average field blank contribution. The volume of air (at 1 atmosphere pressure and a temperature of 20 degrees C) filtered through the strip of filter available for analysis was 424 m³ (L.Barrie, personal communication). Using this information, the results were converted to a weight per volume basis.

The total concentration for each of the three metals for each sampling period has been summarized in Table 7 and compared with reported values for non-urban sites. The Dorset site in south-central Ontario is about mid-way between Toronto and the Sudbury Basin and hence it seems reasonable to draw comparisons with other sites at which deposition from industrial and urban activities is important. Our average concentrations are in good agreement with the mean background concentrations given for

cadmium, lead and zinc outside the plume of the INCO smelter at Sudbury, although the range of Pb concentrations in our data indicate other sources of this metal deposited at the Dorset site. These sources are likely to be from Toronto and the urban areas of southwestern Ontario as it has been shown that lead deposition decreases north and east of the Dorset area (Evans and Rigler, 1985). Comparison with the compilation of airborne concentrations of inorganic elements by Wiersma and Davidson (1986), shows that our data are in the range of reported values for remote areas. Our data are also in good agreement with the concentration given by Cawse (1981) for the English Lake District. Comparison with the data of Dams and De Jonge (1976) suggests that their location in the Swiss Alps (Jungfrauoch) is not as affected by industrial and urban emissions of lead and zinc as the Dorset site. The high average concentration of lead reported by Lindberg and Harris (1983) does not seem to be consistent with the relatively low average concentration measured for cadmium. The presence of 22 coal-fired power plants located in a 350 km radius of their site might have been expected to cause some elevation in both the cadmium and lead values. The latter metal's concentration appears to be related to automobile emissions in the study area (Lindberg and Harris, 1983).

Examination of the results in Tables 6 and 7 shows that the biogeochemical availability of cadmium is dominated by water-soluble forms. Water-soluble forms of lead and zinc are also quantitatively important and the degree of solubility follows the order cadmium >> lead > zinc. For cadmium, water-soluble forms account for 32 to 100 % of the total particulate concentration, with the majority of samples

containing 90 % or more of these forms. The range of percent water-soluble forms of lead is <1 to 72 %, and for zinc the range is 12 to 48 % with a mean value of 26 % (s.d. = 13). Although, the solubilizing action of the pH 4 extractant releases significant amounts of the three metals, this effect is not as large as for the initial leach with distilled water. Table 6 shows that most (average of the 18 determinations = 61 %) of the metal content of the atmospheric particulate sample can be solubilized by these two extractants. As can be seen from Table 7, there is a considerable variation in the degree of solubility of the three metals in atmospheric particulate matter collected from different areas. The variation in these results from study to study appears to be partly the result of the dependence of degree of water-solubility to the concentration of insoluble particulate matter. The NBS sample (Lum et al., 1982) was collected in the St. Louis, Missouri area and is believed to be typical of an industrialized urban area. Such an area would generally have a higher particulate matter loading than a residential area which in turn would have a higher loading than a wooded area such as the Dorset site. Furthermore, the relationship between insoluble particulate matter and trace element solubility is not a perfectly linear one. For example in atmospheric deposition, lead was likely to be soluble to > 80 % at total insoluble matter concentrations <3 mg/L, and at >30 mg/L, solubility was likely to be <20 % (Gatz and Chu, 1986). In addition to solubility, bioavailability of trace elements in atmospheric particulate matter also depends on the size of the particles (Lindberg and Harris, 1983) and their surface chemical characteristics (Keyser et al., 1978). Thus, it would not be profitable to dwell too much on the variation in percent solubility in any given data

set. Overall, though, our data and those of other workers show that in general, the order of ease of solubility is cadmium>lead>zinc.

Our results support the hypothesis that release of cadmium, lead and zinc would occur following deposition on wet surfaces such as leaves and in surface waters (Salomons, 1986 and references therein). The magnitude of the impact on micro and macro terrestrial and aquatic systems from this trace metal release depends on many factors, one of which is the "instantaneous" solution concentration. This in turn depends on the relative amount of dilution of the metal(s) solubilized from the particulate matter, the presence of complexing agents e.g., those exuded by plant leaves, and the total available concentration of the metal(s) on the particulate matter. Thus, percent water-soluble content cannot be viewed in isolation. For example, although the percent water-soluble content of cadmium and lead are low for the NBS sample, the very high particulate concentrations suggest that probable impact of this material would be high in and around urban/industrial areas. Impact at rural sites would depend on proximity to urban centers and the dispersion and deposition patterns in the area. In terms of probable impact, it may be more useful to examine the dissolved (bioavailable) toxic metal concentrations at interfaces e.g., at forest canopies, where neutralization of acidic constituents would be less than at ground level and desorption of trace metals from particulate matter would be expected to be rapid.

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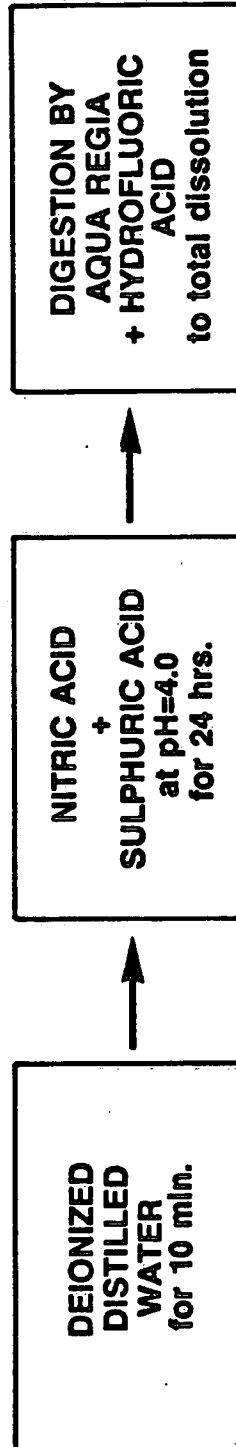


TABLE 1. CADMIUM IN PRECIPITATION FROM RURAL SITES IN CANADA.

SAMPLE SITE	COLLECTION DATE(S)	SAMPLE VOLUME (mL)	CONCENTRATION ng/L	AMOUNT DEPOSITED (ng Cd)
BAY D'ESPOIR, NFLD.	85/7/12-13	106	79	8.4
BAY D'ESPOIR, NFLD.	85/7/16-17	426	22	9.4
KEJIMKUJIK, N.S.	85/8/1-2	2402	10	24.0
HARCOURT, N.B.	85/7/15-16	275	29	8.0
HARCOURT, N.B.	85/7/28-29	Field Blank	5	--
SUTTON, QUE.	85/7/6	2137	34	72.6
MONTMORENCY, QUE.	85/7/7-8	950	10	9.5
PICKLE LAKE, ONT.	85/7/18-19	1365	18	24.6
BONNER LAKE, ONT.	85/7/23	278	18	5.0
ISLAND LAKE, MAN.	85/6/8-9	2411	12	28.9
ISLAND LAKE, MAN.	85/8/1-2	325	19	6.2
CREE LAKE, SASK.	85/7/26	No record	54	--

STATISTICAL SUMMARY OF TABULATED DATA

Cd CONCENTRATION IN CANADIAN PRECIPITATION = 27.7 (s.d. = 21.3) ng/L.

AMOUNT OF Cd DEPOSITED = 19.7 (s.d. = 20.5) ng.

TABLE 2. CADMIUM IN PRECIPITATION FROM RURAL SITES IN
THE UNITED STATES.

SAMPLE SITE	COLLECTION DATE(S)	SAMPLE VOLUME (mL)	CONCENTRATION ¹ (ng/L)	AMOUNT DEPOSITED ng Cd
NEAR ARKADELPHIA, ARK.	85/6/11-18	5590	17(8-26)	~95
NEAR SUMMERTON, S.C.	85/6/4-11	4716	43(41-45)	~201
NEAR SUMMERTON, S.C.	85/6/11-18	3587	130(124-137)	~466
NEAR BELLVILLE, HAGEN, GA.	85/6/11-18	7156	9.5(9-10)	~71
BENNETT BRIDGE, OSWEGO, N.Y.	85/6/11-18	3915	77(70-85)	~301
NEAR EAGLE LAKE, TX.	85/6/18-25	7575	16(8-31)	~75

¹

- Mean value and range; results from replicate analyses.

STATISTICAL SUMMARY OF TABULATED DATA

Cd CONCENTRATION IN U.S. PRECIPITATION = 48.8 (s.d. = 47.1)ng/L.

N = 6, SITE AVERAGES.

AMOUNT OF Cd DEPOSITED = 201.5 (s.d. = 158) ng

TABLE 3. LEAD IN PRECIPITATION FROM RURAL SITES IN
CANADA AND THE UNITED STATES .

SAMPLE SITE ²	CONCENTRATION ug/L	AMOUNT DEPOSITED ug Pb
BAY D'ESPOIR, NFLD., 7/12-13	6.82	0.72
BAY D'ESPOIR, NFLD., 7/16-17	2.28	0.97
KEJIMKUJIK, N.S.	0.82	1.97
HARCOURT, N.B.	2.36	0.65
SUTTON, QUE.	3.18	6.80
MONTMORENCY, QUE.	2.36	2.24
PICKLE LAKE, ONT.	0.64	0.87
BONNER LAKE, ONT.	0.91	0.25
ISLAND LAKE, MAN. 6/8-9	0.55	1.33
CREE LAKE, SASK.	0.80	--

AVERAGE CONCENTRATION IN CANADA = 2.07(s.d. = 1.91)ug/L
AVERAGE AMOUNT DEPOSITED IN CANADA = 1.75 ug(s.d. = 1.99)

ARKADELPHIA, ARK.	1.80(1.45-2.45)	~8.0
SUMMERTON, S.C., 6/4-11	2.79(2.40-3.10)	~13.2
SUMMERTON, S.C., 6/11-18	1.20(0.86-1.72)	~4.3
BELLVILLE, GA.	0.21(0.025-0.46)	~1.5
OSWEGO, N.Y.	5.02(4.71-5.17)	~19.6
EAGLE LAKE, TX.	1.44(0.92-1.96)	~10.9

AVERAGE CONCENTRATION IN THE U.S. = 2.08(s.d. = 1.67)ug/L
AVERAGE AMOUNT DEPOSITED IN THE U.S. = 9.58(s.d. = 6.49ug)

1

- Concentration for U.S. sites are shown as a mean and range.

2

- Collection dates are only shown for sites where two samples were obtained, otherwise refer to Tables 1 and 2.

TABLE 4. COMPARISON OF CADMIUM AND LEAD CONTENT IN GLASS
FIBRE (GF/C) AND WHATMAN (NO. 41) FILTER MEDIA.

FILTER MEDIUM	TRACE METAL CONTENT	
	Cd, ng/cm ²	Pb, ng/cm ²
A. NON-ACID WASHED FILTERS. N = 6.		
GLASS FIBRE		
RANGE	0.05 - 0.54	7.1 - 22.6
MEAN VALUE	0.26	13.5
STANDARD DEVIATION	0.17	7.6
WHATMAN NO. 41		
RANGE	0.03 - 0.22	0.13 - 0.98
MEAN VALUE	0.07	0.61
STANDARD DEVIATION	0.07	0.35
B. ACID-WASHED FILTERS. N = 6.		
GLASS FIBRE		
RANGE	0.025 - 0.048	0.35 - 1.70
MEAN	0.035	1.04
STANDARD DEVIATION	0.008	0.48
WHATMAN NO. 41		
RANGE	0.002 - 0.061	0.04 - 0.53
MEAN	0.013	0.25
STANDARD DEVIATION	0.024	0.18

TABLE 5. PROCEDURAL BLANKS FOR SEQUENTIAL CHEMICAL
EXTRACTION OF ACID-WASHED WHATMAN NO. 41 FILTER PAPERS.

EXTRACT	METAL	CONCENTRATION	
	²	²	²
	Cd, ng/cm	Pb, ng/cm	Zn, ng/cm

¹
DD WATER

RANGE	0.002 - 0.027	0.002 - 0.009	<0.1-2.0
MEAN	0.015	0.004	0.50
STANDARD DEVIATION	0.011	0.003	0.80

H 4.0

RANGE	0.002 - 0.004	0.0006 - 0.0022	<0.1-2.0
MEAN	0.003	0.0013	0.50
STANDARD DEVIATION	0.001	0.0008	0.80

RESIDUAL

RANGE	0.003 - 0.012	0.128 - 0.196	3-7
MEAN	0.007	0.157	5
STANDARD DEVIATION	0.005	0.031	2

¹
= deionized-distilled

TABLE 6. BIOGEOCHEMICAL AVAILABILITY OF Cd, Pb AND Zn IN
ATMOSPHERIC PARTICULATE MATTER.

SAMPLE, DATE	WATER SOLUBLE		pH 4.0 SOLUBLE		RESIDUAL FORMS	
	² ng/cm	³ ng/m	² ng/cm	³ ng/m	² ng/cm	³ ng/m
CADMIUM						
1/NOV. 19, 1984	0.07	0.02	N.S.	N.S.	N.S.	N.S.
4/NOV. 19, 1984	0.21	0.05	N.S.	N.S.	N.S.	N.S.
5/NOV. 19, 1984	0.13	0.03	0.06	0.02	0.21	0.05
1/NOV. 26, 1984	3.1	0.76	0.20	0.05	0.25	0.06
4/NOV. 26, 1984	2.8	0.67	0.08	0.02	0.05	0.01
5/NOV. 26, 1984	2.3	0.55	0.05	0.01	0.07	0.02
LEAD						
1/NOV. 19, 1984	4.8	1.3	2.0	0.53	1.4	0.39
4/NOV. 19, 1984	4.3	1.1	1.9	0.47	11	2.7
5/NOV. 19, 1984	3.9	0.98	0.98	0.25	6.1	1.5
1/NOV. 26, 1984	0.20	0.05	9.1	2.2	61	15
4/NOV. 26, 1984	200	47	8.7	2.1	68	16
5/NOV. 26, 1984	140	34	5.7	1.4	62	15
ZINC						
1/NOV. 19, 1984	3	0.8	1	0.3	22	5.9
4/NOV. 19, 1984	4	1.0	1	0.3	3	0.8
5/NOV. 19, 1984	17	4.3	40	10	59	15
1/NOV. 26, 1984	15	3.6	6	1.4	32	7.8
4/NOV. 26, 1984	14	3.4	4	1.0	28	6.7
5/NOV. 26, 1984	11	2.7	3	0.7	37	9.0

**TABLE 7. TOTAL ELEMENTAL CONCENTRATIONS AND PERCENT
WATER-SOLUBLE FORMS IN ATMOSPHERIC PARTICULATE MATTER FROM
DORSET, ONTARIO, AND OTHER SITES.**

SAMPLE, DATE	Cd T	% SOL. Cd	Pb T	% SOL. Pb	Zn T	% SOL. Zn
	³ ng/m		³ ng/m		³ ng/m	
1/NOV. 19, 1984	0.018	100	2.2	58	7.0	12
4/NOV. 19, 1984	0.052	100	4.3	26	2.1	48
5/NOV. 19, 1984	0.102	32	2.8	35	29	15
1/NOV. 26, 1984	0.865	88	17	<1	13	28
4/NOV. 26, 1984	0.699	96	65	72	11	31
5/NOV. 26, 1984	0.580	95	50	67	12	22
AVERAGE VALUE	0.386	85	24	43	23	26
CHAN ET AL., 1986	1		34		24	
WIERSMA & DAVIDSON, 1986	0.022-2.2		0.027-72		0.035-110	
DAMS & DE JONGE, 1976	0.326		2.9		6.6	
CAWSE, 1981	<0.8		31		15	
LINDBERG & HARRIS, 1983	0.17	31-78	110	2.3-63	32	0-62
HODGE ET AL., 1978						
CALIFORNIA COAST		69-94		17-54		44-82
MEXICO COAST		63-90		6-29		18-60
GATZ AND CHU, 1986		66		5		67
LUM ET AL., 1982		10		0.7		37