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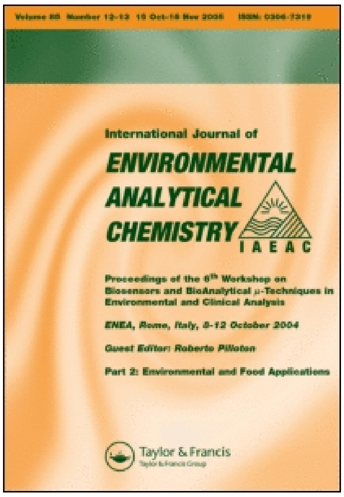

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A Study of the Determination and Distribution of Cadmium in Samples Collected in a Heavily Industrialized and Urbanized Region (Metropolitan Toronto)

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A Study of the Determination and Distribution of Cadmium in Samples Collected in a Heavily Industrialized and Urbanized Region (Metropolitan Toronto)

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KEYWORDS: Cadmium analysis; atomic absorption spectroscopy.

The atomic absorption spectroscopic analysis of cadmium in solid and liquid environmental samples is discussed in detail. Both flame and flameless atomization methods are evaluated. An assessment of the accuracy of the results is made using NBS standard orchard leaves sample SRM 1571. Results are given for a variety of urban environmental samples. These are compared with background values where possible.

Cadmium has long been recognized as an extremely toxic substance. Many researchers believe its toxicity to be greater than that of even mercury. Despite many recorded incidents of poisonings due to cadmium within industrial complexes, it is only recently that appreciable attention has been focused on cadmium contamination of outside environments. Perhaps the greatest stimulus for this attention resulted from the recognition in 1968 of the cadmium-induced Itai-Itai (Ouch-Ouch) disease in the Juntsu River area of Japan. The symptoms of this disease include, as the name suggests, extreme pain especially in the bones. In addition, the bones shrivel and become brittle. Although no specific treatment has been outlined, administration of vitamin D has been found to induce some improvement in the condition.[1] Probably as a result of this incident the Japanese government in 1969 initiated sponsorship of research in an attempt to outline the sources of cadmium pollution in Japan. The rather widespread contamination of environmental units in North America by cadmium is suggested by researchers such as Schroeder *et al.*[2] who feel that on this continent it is impossible to buy vegetables which are free from cadmium.

Apart from the chronic effects of cadmium poisoning, as documented through the victims of Itai-Itai disease, cadmium at lower exposure levels has been linked with recent upsurges in various respiratory, cardiovascular and tumor problems, especially in heavily populated urban environments. Carrol[3] in 1966 found that the average concentration of cadmium in air samples of 28 cities showed a striking correlation with deaths resulting from cardiovascular problems and hypertension. This was further emphasized by the fact that the death rate due to this problem did not correlate with general intensity of air pollution in cities. A review by Flick *et al.*[4] outlines work done on cadmium toxicity throughout the world. Studies cited by these authors outline possible links of cadmium to such problems as hypertension, arteriosclerosis, testicular tumors, cancer, and growth inhibition. The book "Cadmium in the Environment",[5] covers much the same subject matter as the above and includes some hitherto unpublished data on the Japanese Itai-Itai disease problems. Many other studies, beyond the scope of this work, have been done which clearly demonstrate the effects of cadmium exposure on human, plant and animal populations.

Some mainly qualitative studies outlining the extent of the cadmium contamination of diverse environmental units have been done. These often form a part of a study including several of the heavy metals, particularly lead and zinc with which cadmium is closely associated in natural sources. In most cases, few analytical data are given to allow an evaluation of the results.

Warren *et al.*[6] made an important advancement in our knowledge of environmental toxic metal distribution in a study of heavy metals in soils and vegetation of some widely scattered industrial and urban areas. These authors consider their work as an exploratory study only because too few samples were analysed to provide statistically valid conclusions. Of particular importance in this work are data which suggest that cadmium contamination of urban environments may be much more widespread than hitherto outlined by traditional studies. In the case of the latter, work has most often been concentrated around well-known source areas such as heavy metal mining, smelting and plating industry.

In recent times, sources of more widespread cadmium contamination have been outlined. For example, Lagerwerff and Specht[7] determined the cadmium content of soils near highways of differing vehicular traffic density. The data suggest a correlation between soil cadmium content and the amount of traffic.

The high volatility of cadmium at relatively low furnace temperatures is well known. Davis[8] studied cadmium emissions to the atmosphere for 1968 from a variety of sources in the United States in an attempt to obtain information on the magnitude and distribution of sources. Incinerator emissions from a 300-ton per day incinerator burning sewage sludge and mixed urban refuse were studied by Cross *et al.*[9] Appreciable cadmium emissions in the stack gas were noted (7×10^{-3} lb/hr). The cadmium content of aerosols[10] and particulates[11] was studied by Harrison *et al.* in the Ann Arbor and Chicago-N.W. Indiana areas respectively. In the case of the latter, cadmium contents varied with time, the source of metal appearing to be easterly winds from Detroit. In the Chicago area cadmium levels were not found to show much local variation.

The Metropolitan Toronto region provides an excellent study area for cadmium environmental contamination. There is a multitude of potential cadmium sources, including plating industry, battery works, incinerators, thermal hydro generating plants and high volumes of vehicular traffic. Many of these sources are concentrated on the southern perimeter, in a two- or three-mile corridor extending north from Lake Ontario.

The following report is a study of the atomic absorption determination of cadmium in a variety of sample types. Particular care is given to a comparison with known background levels where possible.

EXPERIMENTAL

Equipment and reagents

The results were obtained by atomic absorption spectroscopy. Both a Perkin-Elmer 303 and an Instrumentation Laboratories 153 instrument were used. The 303 was equipped with an HGA-70 heated graphite furnace. A Boiling burner (3–10 cm slots) for methylisobutyl ketone (MIBK) and a high solids burner (10 cm single slot) for acid extracts were used with the IL–153. Reagents and distilled water were checked for cadmium content and an extensive system of blanks was used to ensure freedom from contamination. All collecting bottles and other apparatus were acid-washed and rinsed with cadmium-"free" distilled water. The cadmium wavelength, 228.8 nm, was used.

Experimental procedures for solid samples

Soils, dusts, road sweepings, sewage sludges and fertilizers were analysed by an aqua regia acid extraction technique, used previously for sludges and fertilizers only.[12] This procedure is much more rapid than total decomposition which involves hydrofluoric acid and sulfuric acid fuming to decompose silicates.

Procedure Weigh 0.50 g of homogenized sample into a 100-ml acid-washed beaker. Add 9 ml of HCl and 3 ml of HNO_3. Cover the beaker with an acid-washed watch glass. Heat on a hotplate at medium heat for 30 min (or until bubbling ceases). During this time the volume of the acid decreases by about one-half. Dilute the sample with 5 ml of water and filter through a Whatman #42 or 44 paper into a 25-ml volumetric flask. Wash with several portions of distilled water and dilute to volume with water.

For some samples dilutions will be necessary. In this case the required aliquot can be diluted with water and sufficient nitric acid to ensure a final acid content of about 5% (v/v).

In many cases it is impossible to obtain 0.5 g of dusts. In these cases a smaller sample size and less acid may be used and the final dilution done in a 5 or 10-ml flask.

Cadmium standards were prepared from reagent-grade metal. The final acid content of standards was 5% (v/v) HNO_3.

Standards and samples are run on the Instrumentation Laboratories 153 atomic absorption spectrophotometer using the 228.8 nm Cd line, a slit of 80 mm and a burner height of 15 mm. Background absorbances measured at the 226.4 nm background line are subtracted from cadmium absorbances.

Table I gives typical data on the per cent extraction achieved by this procedure for sample types determined in this study. It is important to note that although aqua regia extraction results in 90% or over extraction for many samples, lower extraction efficiencies may be obtained. For purposes of most environmental studies acid-extractable metal is the substance of interest. In this study acid-extractable cadmium is reported.

Interferences Little problem was noted with other metallic elements interfering with cadmium absorbances under the conditions used. The acid content of samples and standards was kept roughly equal. Interference from other sample matrix constituents was mainly of the background absorption type.

A concerted attempt was made to check the homogeneity of samples taken to be representative of a given environment. Frequently multi-samples were taken from a given location at measured distances from one another. Table II shows typical variations due to sampling inhomogeneity and procedural reproducibility. Sample 1 was a dust which was divided into six fractions and analysed. Sample 2 was one sample solution of a dust repeated six times. Sample 3 represents four road-side soils taken two feet apart along the same road. Sample 3, a single soil sample, illustrates the reproducibility on a sample with a cadmium value near the detection limit.

TABLE I

Per cent extraction of cadmium obtained for acid extraction of typical samples

Sample	Decomposition	Cd (ppm)	Extraction (%)
Soil a	Total	2.0	90
	Acid	1.8	
b	Total	0.8	63
	Acid	0.5	
Dust	Total	42	
	Acid	40	95
Sludge	Total	44	
	Acid	45	102
Fertilizer	Total	67	
	Acid	65	96

TABLE II

Variation in cadmium results due to sampling and procedural repetition (ppm)

Sample	Mean (ppm)	S.D. (ppm)	Number of samples or Repeats
1	45	8	6
2	47	1	6
3	2.0	0.2	4
4	0.7	0.3	3

The repeatability of cadmium values for different fractions of the same sample, although considerably worse than for those obtained on a single sample solution, were relatively good considering the inhomogeneity of dust samples.

Detection limit The detection limit was controlled by the salt content of the sample solution. In particular, nonatomic absorption background absorption due to calcium proved to be the most restricting factor. Sample solutions high in calcium (e.g. from limey soils) showed detection limits of about Cd 0.5 mcg/g of solid. On the other hand, detection limits of Cd 0.05 mcg/g of solid could be achieved in solutions from organic materials and dusts.

Accuracy of results The only suitable standard sample available for an assessment of solid sample cadmium results appears to be the National Bureau of Standard's orchard leaves SRM 1571. Furnace-ashed (450°C for 6 hr) and wet-ashed samples of this standard were analysed for cadmium by the acid-extraction technique. Both samples gave a value of 0.1 ppm compared to the NBS provisional value of 0.11 ppm.

Experimental procedures for water samples

Procedure — Extraction/flame Cadmium in water was determined by the well-known extraction procedure, similar to that of Brooks *et al.*[13] using ammonium pyrrolidine dithiocarbamate (APDC) and MIBK and aspiration into a flame. Results were also obtained directly on aqueous samples using the HGA-70 heated graphite furnace.

Procedure — Heated graphite furnace Using an Eppendorf pipet, place a 10-mcl aqueous sample into the graphite furnace of the HGA 70. Use a drying temperature of 100°C for 30 sec, followed by an ashing temperature of 490°C (program 5) for 1 min. Atomization is accomplished at 2000°C.

Background correction is very important. Using the 226.4 nm background line, run 10-mcl samples as above, and subtract the background. If available, the deuterium lamp background corrector may be used in many cases. It was found that although this background compensation technique is simple and fast it may fail to give useful values for samples with very high background values.

Procedural evaluation It is essential to avoid loss of relatively volatile cadmium during the ashing step. Program 4 (330°C), as recommended by Perkin Elmer, avoids this problem. Results obtained in this study showed that program 5 (490°C) could be used without an appreciable cadmium loss from sample types tested. Use of this higher ashing temperature results in a more efficient destruction of matrix. Unfortunately, as noted above, background absorptions due to residual unashed matrix are still a large problem. At 750°C (program 6), the next highest programable ashing step, the loss of cadmium was greater than 10%.

Seven samples were analysed by extraction/flame and by the heated graphite furnace to allow for a comparison of results obtained (Table III). Although in some cases acceptable agreement is obtained, some values may vary by up to a factor of eight. The reason for this is not certain at this time, but data to date suggest that the higher graphite furnace values are due to the destruction of cadmium complexes and/or very fine cadmium particulates which do not extract into the MIBK.

Detection limit The detection limit for cadmium in waters done by MIKB extraction is 0.2 ppb. A similar detection limit is found for aqueous water samples run directly by the HGA-70 furnace technique.

TABLE III

Results (ppb) for MIBK flame and heated graphite furnace

Sample	Cd (flame)	Cd (furnace)
1	0.9	1.0
2	3.8	4.0
3	4.5	3.8
4	1.0	1.0
5	0.8	2.7
6	0.2	0.6
7	0.2	1.5

Background non-atomic absorption interferences

Interferences from sample matrix constituents were mainly of the background non-atomic absorption type (light scattering and/or molecular absorption). This problem is most marked in the atomic absorption determination of elements whose resonance lines occur in the u.v. spectral region, particularly at wavelengths lower than 250 nm. Throughout all of this work significant background absorptions were encountered of varying magnitudes at the 228.8 nm resonance line of cadmium.

In the case of flame work the largest problems were associated with the presence of high concentrations of calcium salts. With flameless methods unavoidable smokes during atomization, associated with the presence of high acid concentrations and almost any abundant matrix salt, gave high background values. In both cases a background correction could be made by subtracting the background absorption measured at the 226.4 nm line.

Test of HGA-70 graphite furnace for high matrix content solutions

Because of the large background absorption problems associated with heavy matrix content of acid extract solutions and the adverse effect of this on the detection limit of cadmium it was felt that little would be gained by using the HGA 70 for sample solutions of this type. However, as a test of the suitability of this equipment, 10-mcl aliquots of acid extract solutions of soils, sludges and orchard leaves were placed into the graphite furnace and the samples were run by the procedure given above for water samples. Table IV compares cadmium values obtained by flame and flameless techniques. Despite large background corrections which were necessary with the flameless technique, surprisingly good agreement is obtained between flame and flameless results.

TABLE IV

Comparison of flame and flameless results for acid extracts (ppm)

Sample	Flame	Flameless
Sludge a	6	6
Sludge b	147	155
Sludge c	2	1
Sludge d	6	7
Orchard leaves	0.1 (0.11)[a]	0.07 (0.11)[a]
Soil a	6	6
Soil b	1	0.6
Soil c	1	0.8

[a] Provisional value of NBS orchard leaves.

RESULTS AND DISCUSSION

Cadmium in soils and dusts

It is important to establish background values against which contaminated samples can be compared. Values which have been found in connection with this study, together with a representative sampling of literature values, are given in Table V.

Soil samples were collected with a plastic scoop and placed in plastic bags. They were air-dried and then heated in an oven at 110°C for 6 hr. Samples were sieved and homogenized at the 80-mesh grain size. Blanks (quartz sand)

TABLE V

Cadmium background abundances in soils and rocks (ppm)

Material	Cd	Reference
Soils	0.4–0.6	This study—England
	<0.1–0.5	This study—Canada
	0.3	6
	0.1–0.7	14
Crust	0.2	15
Shale	1.5	16
Igneous Rock	0.15	17

TABLE VI

Average cadmium in soils (ppm)

Zone[a]	Sample description	Cd
1a	2′ from road	8
1a	20–50′ from road	3
1a	Street sweepings	9
1b	2′ from road	2
1b	20–50′ from road	<0.5
1c	2′ from road	4
1c	20–50′ from road	1
2	2′ from road	1
2	20–50′ from road	<0.5
London 1a	2′ from road	10
1a	20–50′ from road	4
1a	Street sweepings	22

[a] See Figure 1.

were also sieved to check contamination. No appreciable contamination was found.

Table VI shows cadmium values for soils in various locations over the Metropolitan Toronto Area (see Fig. 1). Samples obtained by the authors in England are included for comparison.

It is difficult to establish a background value for cadmium in soils. It is not possible to tell from the literature whether in some cases samples used to

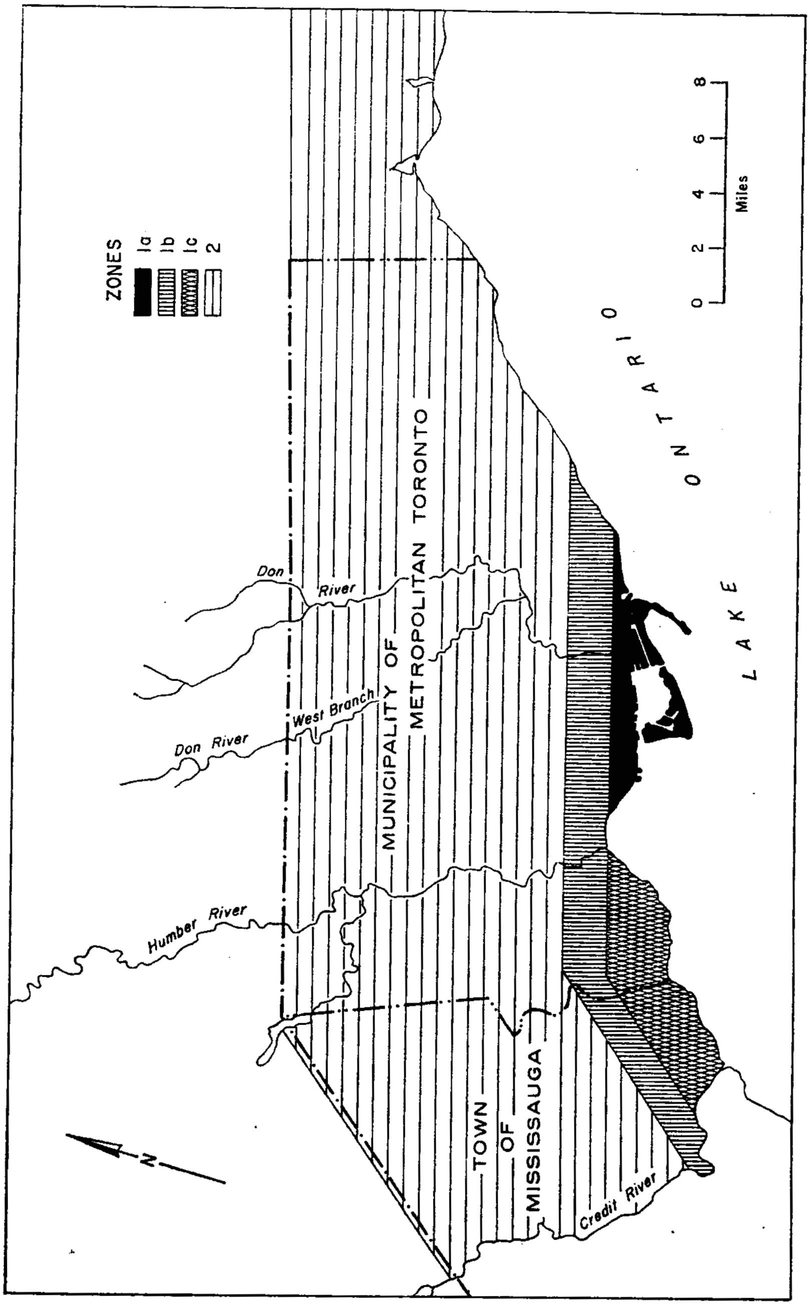

FIGURE 1 Map of Metropolitan Toronto and vicinity. Industrial and traffic density (density is greatest in South Central area).

establish cadmium abundances might have been contaminated with cadmium. The authors believe background soil values to be less than 0.5 ppm, but because literature values cluster in this region we will accept 0.5 ppm as background.

TABLE VII

Average cadmium in dust (ppm)

Zone	Cd
1a	33
1b	28
1c	45
2	23
London 1a	35

TABLE VIII

Cadmium in waters (ppb)

Water type	Sample description	Cd
Don River (urban)	year av.[a]	3
	max.	10
	winter-early spring av.	5
	summer av.	1
Lake Ontario	Toronto Harbour av.	0.6
	Open Lake av.	<0.2
	Near submerged sewage pipe av.	1
Rain and snow	Zone 1 av.	2
	Zone 2 av.	2
	Rural (North of Metro) av.	<0.2

[a] Don River average applies to average found for the section of the river found to be highest in cadmium.

Samples in Zone 1 taken near roads are subjected to similar traffic densities. However, industry, thermo-hydrogeneration, etc. is more concentrated in Zone 1a and decreases in the order 1a > 1b = 1c > 2.

There appears to be a clear correlation of high cadmium values and proximity to the roadways. The fact that soils in Zone 1b were taken from locations with equal traffic densities as 1a but have lower cadmium values suggests other inputs. This is further borne out when lead values are shown. The average lead content in samples from 1a and 1b is about the same (Zone 1a lead 480 ppm, Zone 1b lead 500 ppm, with both samples 2′ from the road).

Dust samples were collected in plastic beakers on sites throughout the test region (see Table VII). Although the dust cadmium values are similar for most zones, the dust volume decreases in the order 1a > 1b = 1c > 2.

It is difficult to establish a background value for cadmium in waters. Mullin and Riley[18] give a value of 0.11 ppb for ocean waters. In lakes, which the present authors expect to be uncontaminated, values of less than 0.2 ppb are found. Table VIII lists values for cadmium in various water samples collected in the Metropolitan Toronto urban area.

Water samples were collected in bottles and beakers that had been washed with acid and rinsed with distilled water. Samples were acidified to pH 2 after filtration.

It is interesting to note the difference in winter-early spring and summer averages for Don River waters.

Cadmium content of run-off from salted winter streets into the Don River is 3 ppb compared to 2 ppb or less during summer rain storms. The Don River is the receptor of effluent from at least five sewage treatment facilities. The average cadmium content found in effluents from these five plants is 3 ppb.

Cadmium in sewage sludge and processed sewage fertilizer

Plating and other metal processing industry discharges metal wastes into municipal sewages.

Van Loon and Lichwa[12] reported the presence of highly toxic metal contents in sewage sludge and processed sewage fertilizer. Table IX lists cadmium values for representative samples. Sewage samples were filtered and the sludge was dried at 100°C. Fertilizer was analyzed on homogenized samples.

The Ashbridges Bay and Humber Bay sewage treatment plants are the major Metropolitan Toronto treatment facilities. These plants receive a complex mixture of industrial and municipal effluent. The Aurora and Thornhill plants receive effluents from some small specialized heavy metal industry. The Newmarket plant, the only one of the above which employs nutrient removal (lime), has little heavy metal input.

Sludge is commonly disposed of on agricultural land as a fertilizer. Some sewage sludge is dried and formed into commercial fertilizer. Milorganite is a processed sewage fertilizer manufactured from Milwaukee sewage sludge. Sogreen Turf Builder consists of 80% Milorganite and 20% inorganic fertilizer. These are only two randomly chosen fertilizers of a growing list using processed sewage sludge as a base. Urban parks, golf courses, lawns, and even vegetable crops are fertilized with processed sewage-based fertilizer.

TABLE IX

Average cadmium in sewage sludge and processed sewage fertilizer (ppm)

Sample description	Cd
Ashbridges Bay S.T.P.[a]	45
Humber Bay S.T.P.	147
Aurora S.T.P.	10
Thornhill S.T.P.	5
Newmarket S.T.P.	2
Milorganite	66
SoGreen Turf Builder	47

[a] S.T.P. = Sewage Treatment Plant.

CONCLUSIONS

Results obtained on the analysis of the standard NBS orchard leaves sample give good credibility to the cadmium values reported for solid samples. Since no aqueous standard sample is available for comparison purposes with water samples an assessment of the accuracy of these results is not so clear.

The above study indicates a widespread build-up of cadmium concentrations in the sample types tested. Background cadmium values available suggest that environment units tested have cadmium contents of from near background to 200 times this value. As expected, cadmium contamination is greatest in areas with heavy industry and high density vehicular traffic.

At present, work is being done in this laboratory to assess the bio-availability of cadmium in these sample types.

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