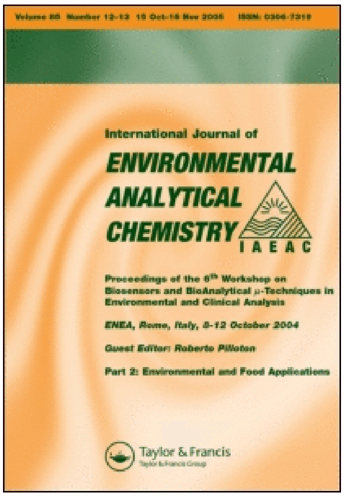

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Calcutta Pollutants: Part 1: Appraisal of Some Heavy Metals in Calcutta City Sewage and Sludge in Use for Fisheries and Agriculture

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Calcutta Pollutants: Part 1: Appraisal of Some Heavy Metals in Calcutta City Sewage and Sludge in Use for Fisheries and Agriculture

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A chelate extraction procedure followed by atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) is described for the determination of some heavy metals (Pb, Cu, Zn, Cd, Ni, Co, Mn, Fe and Cr) in sewage and sludge. The procedure is applied to the determination of Calcutta sewage and sludge. The concentration of the above-mentioned heavy metals in Calcutta sewage-sludge is lower in magnitude when compared with that of some cities in other countries.

KEY WORDS: Sewage, sludge, heavy metals, chelate extraction, AAS, ICP-AES.

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INTRODUCTION

It is well-known that sewage-sludge acts as a source of nutrients to the soil. In general, it is an useful source of nitrogen and phosphorus to the crops. Many workers made long-term experiments and showed that large improvements in yield can be achieved from the use of sewage-sludge, especially with nitrogen response crop. The problems of metals in sewage-sludge are evidently complex and there are differences in opinion as to the likely risks both to crops and animals following application of sewage-sludge to land. In many countries, probably the greatest concern regarding use of sewage waste on land is its heavy metal content. Sewage-sludges contain varying amounts of the so-called "heavy" or "true" metals such as Cd, Co, Mn, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn. They enter the sewage system primarily from industrial effluents. Nickel concentrations in sewage-sludges and its toxicity have been reported by many workers.[1–4] One of the main reasons for reduced crop growth that has been reported by the advisory work in England and Wales is due to presence of metals specially where sludges from industrial towns have been used.[5] Berrow and Webber[6] reported that zinc and copper with values more than 40 times the normal amount present in soils are the elements most likely to cause trouble in crops. They further mention that nickel can also cause serious hazard to crop growth. Chumbley[7] made the assumption that toxic effects of metals on plants are additive and from a survey of the available data, he concluded that while copper is twice, nickel is eight times as toxic as zinc. Webber[5] reported that zinc, copper and nickel will be toxic to plants when present over 200 ppm (in dry matter and 0.5 M acetic acid extract); 25 ppm (0.05 M EDTA extract) and 50 ppm (0.5 M acetic acid extract) respectively. The same three metals will be toxic to soil when present over 100–200 ppm (in case of zinc in 0.5 M acetic acid extract), 50–100 ppm (Cu, in 0.05 M EDTA extract) and 15–25 ppm (Ni in 0.5 M acetic acid extract) respectively. For the elements lead, cadmium, mercury and chromium the risks to animal and man eating the crops are likely to be greater than they are to the crop itself. Although heavy metals constitute only a small fraction of the sludge solids, usually $<1.0\%$ dry weight; nevertheless the heavy metal contents of soil may be significantly raised through long-term land applications of sludges.[8] Thus the build-up of heavy metals in the soil profile may constitute a hazard not only to plants, but also to consumers of the harvested crops.[9,10]

City of Calcutta (India) within a corporation area 104 sq km is supporting a population of 3.5 million. Fifty per cent of the city is supported with a combined system of sewers with facility for a total population of about 1.8 million. The estimated volume of waste water during dry season including modest contribution of industrial waste water is nearly 681,000 m^3/day. The waste water is carried through open canals over a distance around 30 km and is discharged in the Kulti estuary.

Although Calcutta is called a highly polluted city, the analytical data about pollutants of various kinds are still not available. Whether city sewage and sludge contains high concentration of heavy metals is not known, although 10–15 per cent of the total sewage is being used for fisheries and agriculture without any pretreatment.

In this paper we will present the analytical data about heavy metals present in the sludge and water in the raw sewage, in use for fishery and agriculture. The analytical data of the samples have been checked by two instrumental techniques, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The sludge sample was digested by refluxing with aqua-regia.[11] The aquaregia digestion procedure was used by the Commission of European Communities[12] and results are comparable to certified values. Van Loon *et al.*[13] also reported that unashed sludge gives greater than 90% extraction efficiency for many elements except silver.

Matrix interference is a major problem for AAS method of determination, specially for graphite furnace.[14,15] Interference in the determination of chromium in sewage-sludge even by flame AAS has been observed.[16] Although various matrix modification techniques are successfully applied for direct determination, even then success could not be achieved for many metals especially when determination is to be made in a high salt matrix. To avoid matrix interference we have extracted the metal ions using a mixture of two chelating agents, diethyldithiocarbamate (Na-DDTC) and ammonium pyrrolidinedithiocarbamate (APDC) in carbontetrachloride. The procedure is close to the method applied by Lo *et al.*[17] for water analysis. In our procedure we have not used mercuric nitrate solution for back extraction of metal ions from organic phase to aqueous phase but have rotoevaporated the organic solvent and decomposed the metal complexes by adding small amount of pure nitric acid.

EXPERIMENTAL

Instruments

The Perkin–Elmer PE 3030 spectrophotometer equipped with a PE-HGA-500 graphite furnace atomizer, a model AS-40 autosampler and a deuterium background corrector was used for determination of Co, Pb, Mn, Ni and Cd. The same instrument with flame attachment was used for determination of Zn, Fe and Cu. The operating conditions are described by EPA instructions.[18]

A Bausch and Lomb-ARL simultaneous inductively coupled argon plasma vacuum emission spectrometer Model 34000 with 48 channels, served as the detector. The instrument is equipped with a Digital Equipment Corpn. (DEC) PDP 11/03 computer with dual RX 02 0.5 Mbytes floppy disks, a model 5520 spinwriter and a VT 100 function as input and output terminals. The spinwriter has 1/20 inch horizontal and 1/48 inch vertical resolution.

Reagents and solutions

Ammonium pyrrolidinedithiocarbamate (APDC) was obtained from Fisher Scientific Co and sodiumdiethyldithiocarbamate (Na-DDTC) from Merck product. Standard solutions of the elements were prepared from 1,000 ppm Titrisol solutions (Merck). All other chemicals were of analytical reagent grade. Suprapur grade acids were used to decompose the samples and for all other purposes. An acetate buffer was prepared by mixing equal volumes of acetic acid (0.2 M) and sodium acetate (0.2 M) and adding one of the components until the pH 4.5. The buffer (IL) was cleaned by 5 ml of extracting reagent and 20 ml of carbontetrachloride.

Extracting reagent

A mixture of APDC and Na-DDTC, one per cent each in 100 ml water was used. The solution was purified by shaking with carbontetrachloride.

Sample preparation

Sludge Sewage-sludges after collection from various points, were filtered through filter paper and the residues on the filter paper were dried at 80°C, thoroughly mixed, subsequently ground to fine homogeneous powder and passed through 2 mm sieve. The procedure adopted for aqua-regia digestion of sludge is the same as described by the commission of the European Communities.[12]

Liquid associated with sludge The liquid associated with sludge was collected from the surface when the sewage was running through the canal. It was usually not clear containing suspended material. It was filtered through qualitative filter-paper, added 1.0 ml of nitric acid to 250 ml of the filtered sewage and evaporated to dryness at medium heat on a hot plate. Further, 3.0 ml of HCl and 1.0 ml of HNO_3 were added to it and evaporated to dryness. Added few drops of HNO_3 and diluted to 50 ml mark in a volumetric flask. An aliquot was then taken for extraction followed by AAS and ICP-AES determination.

Procedure

A suitable aliquot from the aqua regia digested sludge or water associated with sludge was taken in a separating funnel and final volume was made to 250 ml with water. To this was added 10 ml of buffer solution and 3.0 ml of extracting reagent. The mixture was shaken for a while, then 10 ml of carbon tetrachloride were added and the mixture shaken vigorously for about 5 minutes. The carbontetrachloride layer was transferred in a 50 ml Erlenmeyer flask. The aqueous phase was further extracted with 10 ml of carbontetrachloride and both the extracts were combined and rotoevaporated to dryness (at 30°C on water bath). Concentrated nitric acid was added to the flask (200 μl of nitric acid for 10 ml final volume) and just warmed on a hot plate until brown fumes appeared. The solution from the flask was quantitatively transferred in a volumetric flask for determination of metals by AAS or ICP-AES. The final volume to be made depends on concentration of the

Table I Metal content of sludges (in ppm)[a]

Sample nr.	1	2	3	4	5	6	7	8	9	10
Pb	246.5 (226.1)	198.6 (189.4)	120.6 (116.6)	130.6 (122.4)	101.4 (99.3)	83.6 (72.4)	69.7 (58.2)	57.6 (51.2)	47.6 (42.4)	48.16 (41.66)
Cu	190.6 (158.4)	181.5 (181.6)	147.4 (131.5)	155.4 (142.5)	122.6 (114.5)	90.4 (81.2)	72.6 (68.5)	61.4 (54.8)	41.3 (37.6)	29.2 (23.3)
Zn	748.1 (639.6)	546.4 (512.2)	395.6 (381.6)	440.4 (419.6)	349.7 (332.5)	339.6 (319.6)	323.5 (319.7)	310.8 (300.6)	267.5 (252.4)	277.4 (271.6)
Cd	2.39 (2.14)	1.40 (1.10)	2.01 (1.81)	2.21 (1.97)	2.01 (1.94)	1.80 (1.69)	1.07 (0.99)	0.97 (0.82)	0.34 (0.28)	0.39 (0.36)
Ni	67.4 (59.5)	58.4 (53.3)	40.2 (36.5)	51.6 (47.2)	44.6 (40.4)	42.2 (37.6)	41.5 (37.2)	39.6 (32.5)	28.7 (22.4)	26.2 (22.44)
Co	4.7 (4.3)	4.6 (4.7)	3.6 (3.8)	2.8 (2.2)	2.6 (2.5)	1.4 (1.0)	1.8 (1.6)	2.2 (2.6)	1.2 (1.5)	1.36 (1.12)
Cr	— (447.1)	— (229.3)	— (192.5)	— (187.6)	— (172.4)	— (175.3)	— (172.5)	— (101.6)	— (49.2)	— (53.4)
Mn	282.3 (268.6)	286.5 (279.6)	281.4 (259.6)	303.0 (289.6)	229.6 (209.4)	212.7 (202.6)	201.7 (192.5)	179.7 (165.5)	121.7 (99.6)	102.6 (98.3)
Fe	9227 (8528)	7321 (7123)	8925 (8162)	9027 (8848)	8127 (7795)	7725 (7016)	7252 (6828)	7325 (7028)	6642 (6138)	5348 (5127)

[a] The results in brackets are from ICP-AES and without brackets from graphite furnace and flame AAS. Results are the average of three determinations.

metal ions present. The blank was prepared under the identical conditions and was subtracted from the experimental value. Chromium was determined directly from the digested sludge by only ICP-AES. The chelate extraction procedure was not used for chromium.

RESULTS AND DISCUSSION

Table I shows the metal content of the sludges by AAS and ICP-AES. The sludge no. 1 was from the first point of collection close to Calcutta city at Bantala while no. 10 was collected at the Kulti estuary—the point of final discharge. Numbers 2 to 9 were in between Bantala and Kulti estuary. Three sewage water samples were analysed. Number 1 is the first point and collection of Bantala and no. 3 at Kulti estuary. Number 2 is between Bantala and Kulti estuary. These results are given in Table II.

Table II Total metal in sewage water (ppb)[a]

Sample nr.	Metals							
	Pb	Cu	Zn	Cd	Ni	Co	Mn	Fe
1	79.6 (71.4)	52.9 (48.4)	553.6 (520.4)	0.254 (0.244)	13.7 (11.4)	1.73 (1.68)	52.4 (47.5)	577 (523)
2	60.1 (52.4)	32.4 (30.2)	321.6 (301.3)	0.196 (0.191)	18.6 (16.5)	1.04 (1.12)	39.6 (36.8)	401 (412)
3	29.4 (26.1)	19.7 (17.8)	221.4 (211.1)	0.101 (0.104)	6.8 (5.4)	1.08 (1.00)	32.8 (30.2)	312 (293)

[a] Results in brackets by ICP. Results without brackets by GF-AAS. Average of three determinations.

To test the accuracy of our procedure, standard sludge and water associated with sludge should be analysed. Since the reference standards of these kinds were not available to us, we have tested our procedure with other standards (Bovine liver, NBS, SRM no. 1577a; River Sediment SRM no. 1645, Standard trace metal in water samples no. 1643b).

The results of these samples will give an indication of the accuracy of our procedure. Table III shows the results.

Table IV compares the results of the heavy metals found in

Table III NBS standards[a]

St.		Pb	Cu	Zn	Cd	Ni	Co	Mn	Cr	Fe
1645	NBS	714±28	109±19	1720±169	10.2±1.5	45.8±2.9	N.A.	785±97	2.96±0.28	11.3±1.2
sediment	ours	701±19	82.4±14	1753±144	12.7±1.2	53.6±3	13.7±0.6	713±32		9.9±0.8
		(729±24)	(107±22)	(1760±120)	(10.6±2)	(49.3±2.4)	(11.6±0.4)	(772±39)	(2.84±0.30)	(10.6±0.6)
1577(a)	NBS	0.135	158	123	0.44	N.A.	0.21	9.9	—	194
Bovine-	ours	0.149±0.03	146±13	120±9	0.41±0.03	0.94±0.09	0.19±0.02	9.2±0.9	—	187±9
liver										
1643(b)	NBS	23.7±0.7	21.9±0.4	66±2	20±1	49±3	26±1	28±2	—	99±8
NBS	ours	21.6±0.4	20.7±0.7	64±5	19±0.9	48±2	25±0.9	27±1		89±6
water										

[a] Or μg/gm for sediment & Bovine liver and ng/gm for water. For sediment Cr and Fe are in % by wt. Results in brackets are by ICP-AES and without brackets by AAS. NA = not available.

Table IV Comparison of metal contents of sludges between Calcutta, Toronto (Canada) and New Jersey (USA). Results in $\mu g/gm$.[a]

	Pb	Cu	Zn	Cd	Ni	Co	Cr	Mn	Fe
Calcutta	236.3	174.5	693.8	2.26	63.4	4.5	447.1	275.4	8877.5
Toronto Canada	1600	1300	7700	50	350	N.A.	4300	300	17000
New Jersey	3410	3400	8370	76.7	67.0	N.A.	19300	N.A.	15100

[a] Average results. NA = not available.

Calcutta sludge and the sludge from Toronto, Canada[13] and Pennsauken, N.J., USA.[19]

It is evident from Table IV that the studied heavy metals of Calcutta sewage-sludge are in a lower magnitude compared to that of some results of Canada and USA. The liquid associated with the Calcutta city sludge contains heavy metals and their concentration seems higher in context to few metals when compared to the only result[13] obtained from Toronto [Zn-235 ppb, Fe-57 ppb, Pb < 2ppb, Ni-125 ppb, Cu-530 ppb, Cd-1.0 ppb]. However, they filtered the liquid associated with the sludge by 60 μ filter. The reason of our higher results for few elements may be due to our filtration through qualitative filter paper. This water of the running sewage is directly used for agriculture and by fish cultivating lands. Since metals are cumulatively deposited, even this low concentration in the long-run can significantly increase metal concentration of the soil and land used for cultivation of fish. We are also studying the heavy metals of the soil, water and land using this sewage water. The results will be reported later. Regarding the sewage sludge of Calcutta, it seems that the over-all heavy metal contamination is not a problem at present, but the soil may get enriched after long use, hence, it should be studied from time to time. Although from the analytical results of sewage-sludge, it appears that heavy metal pollution problem in sewage is not at danger-level nevertheless due to relaxed pollution rules local pollution may be a problem. For example the factory preparing battery may contaminate its area by metals like lead, antimony, proper care should be taken before they are discharged. The overall result of heavy metals in Calcutta sewage indicates that not too many factories are using and producing heavy metals.

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