TRACE METALS AND CHLORINATED HYDROCARBONS IN SEWAGE SLUDGES OF KUWAIT

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Abstract. Levels of trace metals and chlorinated hydrocarbons were determined in sludge produced at the three main wastewater treatment plants in Kuwait (Ardhiya, Jahra, and Reqqa). Over the 6 mo study period (October 1984 to March 1985) levels at the three plants showed the following ranges ($\mu g\ g^{-1}$ dry weight); Cd, 0.5 to 5.0; Cu, 90 to 270; Zn, 1100 to 3000; Pb, 80 to 300; Ni, 25 to 60; Hg, 1.8 to 3.6; Ag, 1 to 35; PCBs, 0.1 to 3.6; lindane, 0.4 to 7.4; ΣDDT (i.e., DDT + DDD + DDE), 0.07 to 0.20; aldrin, below detection to 0.07; endrin, below detection to 0.27; dieldrin, 0.005 to 0.04). Mean levels were generally close or lower than mean concentrations reported in the United Kingdom and the United States. They were also lower than suggested concentration limits for application of sludge on agricultural land, which is one of the most cost-effective and attractive techniques for sludge disposal. For Kuwait to adopt this application, however, the characteristics of the local soil and prevailing environmental conditions, notably the frequent occurrence of severe dust storms, should be considered.

1. Introduction

Selection of an appropriate technique for sludge disposal depends, to a large extent, on the characteristics of the sludge. The application of liquid or dewatered sludge on land is one of the most effective and attractive methods (Webber *et al.*, 1984) because it has a relatively high content of nutritive elements such as Ca, Mg, P, N, and organic C. However, there is a risk that toxic constituents in sludge, such as trace metals and chlorinated hydrocarbons, may accumulate in soil and contaminate ground water or crops and enter the food chains (Dacre, 1980).

Of the metals that may occur in sludge, Cr, Pb, Zn, Cu, and N are toxic to most plants and Co and B are two other potential plant toxins (Vesilind, 1979). Some other metals in sludge particularly Cd may have minor effects on the plant but may accumulate in its edible parts and affect their consumers (Davis, 1984; Hansen and Tjell, 1983).

Sewage sludges may also contain appreciable amounts of chlorinated hydrocarbons such as PCBs, DDT (+ DDE + DDD), aldrin, dieldrin, chlordanes, lindane, endrin, kepone, mirex and heptachlor (Dacre, 1980). These hydrocarbons are hazardous to the health of animals and man because they have low water solubility, long half-lives in the environment, high affinity to lipids (leading to their bioaccumulation and biomagnification in terrestrial and aquatic food chains), and are all highly toxic to mammals (Dacre, 1980).

This study was undertaken to determine levels of toxic trace metals and chlorinated hydrocarbons in sludges produced at the main wastewater treatment plants in Kuwait (Ardhiya, Jahra, and Reqqa) and to preliminarily evaluate the amenability of these

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sludges for disposal on land or at sea. The Ardhiya plant deals with about 150000 $m^3 d^{-1}$ sewage flow and employs a two-stage activated sludge system for sewage treatment. Sludge is digested anaerobically and then subjected to further gravity thickening before it is dewatered. The Jahra and Reqqa plants employ identical treatment systems, extended aeration activated sludge, and are designed to cope with 70000 and 100000 $m^3 d^{-1}$, respectively. At present, however, these two plants receive only 20 to 30% of their hydraulic design capacity. Sludge is not subjected to any treatment, except gravity thickening before it is dewatered on drying beds.

2. Materials and Methods

2.1. SAMPLING

Two grab samples of sludge, 250 mL each, were collected monthly from each of the three plants over a period of 6 mo starting October 1984. They were frozen immediately after collection and were kept at −20 °C until they were analyzed, one for trace metals and the other for chlorinated hydrocarbons.

2.2. DETERMINATION OF TRACE METALS

After they were thawed, samples of wet sludge were oven-dried at 60 °C, a procedure which, according to EPA (1979), causes no loss of Hg. Two 0.5 g aliquots of each dried sample were digested by a strong HNO_3–H_2O_2 proceedure (Jenniss *et al.*, 1980). Digestates were filtered and filtrates were analyzed for Hg by cold vapor AAS (EPA, 1979) and for Al, Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn on a Jarrell Ash Model 800 inductively-coupled plasma atomic emission spectrometer precalibrated with external

TABLE I

Measured and certified concentrations of trace metals in EPA reference sample ($\mu g\ g^{-1}$ dry weight)

Metal	Measured concentrations			Mean certified value
	Range	Average	C.V.[a]	
Al	4660–5440	5070	6.9	4558
Cd	16–18	17	6.4	20.7
Cr	180–200	195	4.4	204
Cu	950–990	970	1.9	1095
Hg	6.7–8.7	7.5	12.7	16.3
Fe	16170–17980	17150	4.3	16155
Mn	193–220	204	5.1	204
Ni	154–184	167	7.1	198
Pb	455–540	510	7.1	519
V	11–17	13	23	13
Zn	1150–1310	1240	4.8	1323
Ag	3–30	17	13	80.8

[a] Coefficient of variation = (standard deviation/average) × 100.

standard mixtures. Analyses were carried out at the Central Analytical Laboratory of the Kuwait Institute for Scientific Research. All glassware and laboratory equipment coming in contact with the samples, reagents or digest solutions were cleaned with hot soapy water, then rinsed thoroughly with distilled water, 10% HNO_3, distilled water and, finally, deionized water prior to use. A procedural blank was run for each patch of 6 digestions.

Replicate digestion of a dry EPA reference sample (U.S. EPA Municipal Digested Sludge, Sample No. 3641) showed a high degree of precision and accuracy in the determination of all metals except Ag, Hg, V, and Cr (Table I). The lower precision and accuracy of Cr determination are due to interference from relatively high and variable blank readings in the final digest solutions, as shown by the procedural blanks. The lower precision and accuracy of Hg and V determinations are probably due to their lower concentrations in the sludge samples and, therefore, to the proximity of their concentrations in the final digest solutions to the instrumental detection limits (0.06 and 0.005 ppm for V and Hg, respectively). Further analysis by the more sensitive flameless AAS was not considered because of the preliminary nature of this study.

2.3. DETERMINATION OF CHLORINATED HYDROCARBONS

Aliquots (10 to 15 g) of wet sludge were dried by grinding with at least 1.25 times their weight of anhydrous magnesium sulphate. Grinding was continued until a free-flowing powder was formed. Dried aliquots were soxhlet-extracted with dichloromethane (CH_2Cl_2) for 16 hr at a rate of 6 to 8 cycles hr^{-1}. Procedural blanks of 10 to 12 g of anhydrous magnesium sulphate were similarly extracted. Extracts were cleaned and fractionated by florisil column chromatography as described by De Lappe *et al.* (1983) for polyurethane foam pads. Three fractions were produced per sample, eluting with hexane (F1), 30% CH_2Cl_2 in hexane (F2) and 50% CH_2Cl_2 in hexane (F3). Volumes were adjusted so the DDE eluted completely in F1, DDT in F2, and dieldrin in F3. Under these conditions, PCBs and aldrin eluted in F1, DDD and lindane in F2, and endrin in F3. Sulfur was removed from Fls by adding copper granules activated by successive rinses of concentrated HCl, methanol, dichloromethane and hexane. All glassware coming in contact with the samples, extracts or fractions were washed with hot soapy water, rinsed with distilled-deionized water, kilned in furnace at 450 °C for 8 hr, then rinsed thoroughly with purified solvents prior to use.

Compounds in each fraction were determined by splitless injection on a Perkin–Elmer Sigma 115 gas chromatograph equipped with a fused silica column (DB-1 from J&W Scientific, U.S.A.; 30 m long × 0.32 mm internal diameter; 0.25 μm film thickness). Carrier flow (H_2) was adjusted to 1.5 $cm^3 min^{-1}$ and make-up flow (95 : 5, Ar : CH_4) was adjusted to 60 $cm^3 min^{-1}$. Oven temperature was held at 40 °C for 1 min after injection, then was programmed at a rate of 40 °C min^{-1} to 135 °C and 3 °C min^{-1} to 220 °C. The injector was kept at 270 °C and the ^{63}Ni electron-capture detector was kept at 300 °C. Compounds in each fraction were identified and quantified by comparison to external standards injected on the same day. Conversion factors based on concentrations of sludge dry solids (Ghobrial *et al.*, 1986) were used to report concentrations on a dry weight basis. Correction for impurities in procedural blanks was not necessary as the latter showed no traces of the compounds of interest.

This procedure was tested by analyzing three samples that had been spiked (on a wet weight basis) with known concentrations of authentic standards just prior to drying them with magnesium sulphate. On average, spike recovery was better than 90% for DDE, 80% for dieldrin, 70% for DDD, and 60% for aldrin and endrin; the lowest recoveries were observed for DDT (37%). Results of duplicate analysis of three sludge samples for PCBs and lindane were almost identical. However, there were no recovery studies for these compounds.

3. Results and Discussion

3.1. TRACE METALS

Sludge samples collected from Ardhiya, Jahra and Reqqa wastewater treatment plants in October 1984 were analyzed for Al, Ag, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, and Zn. In this screening step all metals were detected at concentrations ranging from 2 $\mu g\, g^{-1}$ dry weight (Cd) to about 24 $mg\, g^{-1}$ (Al). However, only Ag, Cd, Cu, Hg, Ni, Pb, and Zn were determined in subsequent months, based on the following:

- Zn, Cu, and Ni are toxic to terrestrial plants (Williams, 1983; Davis, 1984).
- Cd tends to accumulate in edible parts of terrestrial plants with subsequent adverse effects on plant-consuming animals or humans (Hansen and Tjell, 1983; Davis, 1984).
- Ag, Cd, Cu, Hg, Pb, and Zn may have adverse effects on the marine ecosystem if sludge is disposed of in the sea (Forstner and Wittmann, 1981, pp. 43–44) or if sludge applied on land reaches the marine environment indirectly.

Temporal variations in sludge metal levels may be affected by temporal variations in the levels of trace metals in the influent wastewater or in the efficiency of the treatment process involved (Reimers, 1983). Given the limitations of our sampling program, a detailed consideration of temporal variations in sludge metal levels in the studied plants is not possible. Based on the average levels of metals in local sludges (Table II), two groups can be identified. The first group contains Ag, Cd, Pb, Zn, and Hg, and the second group contains Ni, Mn, V, Al, Cr, and Fe. Levels of the first group of metals are highest, on average, in Ardhiya sludge whereas levels of the second group are highest in Reqqa sludge. These differences in metal abundance among the three sludges may result from contributions of specific sources in the catchment areas. Outstanding possibilities include urban/domestic contributions of Pb, Cd, Zn, Cu, and Ag to Ardhiya sludge, industrial contributions of Hg to Ardhiya and Jahra sludges (e.g., from Salt and Chlorine Plant effluents), and industrial contributions of V, Al, Fe, and Cr to Reqqa sludge (e.g., from Shuaiba Industrial Area).

Levels of most metals in local sludges are lower than their levels in sludge from the United States and England but are comparable to levels in sludges from Sweden (Table II), results that reflect the lower level of industrialization in Kuwait.

Except for Ag in Ardhiya sludge, levels of trace metals in local sludges are lower than

TABLE II

Levels of trace metals in local sludges compared with suggested limit values for using sludge on agricultural land, to average levels in sludge from other countries, and to average levels in the continental crust

Metal	Level in Kuwait sludge[a]			Suggested limit for use on agricultural land					Level in other sludges[h]			Average level in the continental crust[i]
				Other Western countries[c]			CEC directive[d]		Sweden[e] (n = 114)	U.S. activated AWI sludges[f]	Britain[g] (n = 40)	
	Ardhiya	Jahra	Reqqa	Austria[b]	Range	Median	Recommended	Mandatory				
Al	6600	7500	23700	NA	NA	NA	NA	NA	NA	10000	NA	NA
Ag	20	5	9	10	NA	NA	NA	NA	NA	150	NA	0.07
Cd	4	2	3	10	8–30	7	20	40	2–3	35	24.8	0.02
Cr	22	32	105	500	200–1200	1000	750	NA	63–110	4300	707	100
Cu	240	120	170	500	500–3000	1100	1000	1500	300–360	1100	721	55
Fe	14800	13900	18300	NA	NA	NA	NA	NA	NA	40500	NA	56300
Hg	3.3	2.9	2.3	NA	5–25	10	16	NA	2–4	20	NA	0.08[j]
Mn	180	180	240	NA	500–3000	500	NA	NA	NA	310	667	950
Ni	40	34	42	200	30–500	200	300	400	13–24	380	290	75
Pb	240	110	190	500	300–1200	NA	750	1000	65–120	1500	1550	12.05
V	24	23	29	NA	NA	NA	NA	NA	NA	700	NA	135
Zn	2600	1300	2300	2000	1000–10000	3000	2500	3000	640–900	3300	1930	70

[a] This study: average of six determinations except for Al, Cr, Fe, Mn, and V (one determination).
[b] Brantner (1981).
[c] Belgium, Canada, Denmark, Finland, France, Germany, Netherlands, Norway, Switzerland, Sweden (Webber *et al.*, 1984).
[d] Commonwealth of European Countries Directive (Webber *et al.*, 1984).
[e] Sjoqvist (1984).
[f] Reimers (1983).
[g] Sterritt and Lester (1981).
[h] n = number of observations.
[i] Taylor (1964).
[j] Level in granitic rocks (Forstner and Wittmann, 1981).
NA Not available.
All concentrations are given in $\mu g\, g^{-1}$ dry weight.

suggested limit values for application on agricultural land (Table II). Before adopting such an application locally, however, the characteristics of the local soil and prevailing environmental conditions should be taken into consideration. For example, evidence presented by Davis (1984) suggested that uptake of Cd by crops depends on the total Cd content of the soil and not only on the level of Cd in the sludge applied. Another factor that probably needs to be considered locally is the occurrence and frequency of dust storms. Application of sludge to land under dust-storm conditions may create a health problem due to resuspended, metal-rich sludge particles that may be inhaled. Dust storms may also cause long distance atmospheric transport of sludge particles from land to sea areas, thus leading to potential impact on the marine environment. A preliminary assessment of these impacts can be obtained by comparing levels of trace metals in sewage sludge to their levels in the continantal crust (Table II). This comparison shows that levels of Cr, Fe, Mn, Ni, and V in local sludge are lower than in the continental crust, whereas levels of Ag, Cd, Cu, Hg, Pb, and Zn are significantly higher. Therefore, metals of only the latter group are likely to cause an environmental health problem, and they should be studied in more detail in the future.

3.2. CHLORINATED HYDROCARBONS

The limitations of our sampling program does not allow for a detailed consideration of temporal changes in organochlorine concentrations. However, differences in average concentrations between sludges from the three treatment plants and the relatively high levels of PCBs and lindane (Table III) may reflect organochlorine use patterns in the respective cathment areas. Organochlorine pesticides in sewerage systems may be derived, in general, from human excretion, home use, or industrial use; PCBs may be derived, in addition, from transformer and capacitor manufacturing and waste paper recycling.

TABLE III

Mean chlorinated hydrocarbon concentrations in sludge from Ardhiya, Jahra, and Reqqa treatment plants, compared with reported typical values

Chlorinated hydrocarbons	Levels of local sludges ($\mu g\ g^{-1}$)			Typical values[a] ($\mu g\ g^{-1}$)
	Ardhiya	Jahra	Reqqa	
PCBs	0.27	0.15	2.9	0.34 (0.01–21.5)
Lindane	3.6	1.5	2.3	0.41 (0.01–70)
ΣDDT (= DDT + DDD + DDE)	0.13	0.13	0.09	NA
Aldrin	[b]	N.D.	0.05	0.34 (0.01–0.21)
Dieldrin	0.03	0.02	0.01	0.5 (0.01–53)
Endrin	0.06	0.02	0.02	0.11 (0.01–0.71)

[a] Means and ranges reported by McIntyre and Lester (1984) for 40 sludges from the United Kingdom.
[b] One sample showed a concentration of 0.06 $\mu g\ g^{-1}$.
N.D. = not detected.
N.A. = not available.

Levels of chlorinated hydrocarbons in local sludges are generally close to or lower than the mean concentrations reported for 40 sludges in the United Kingdom (McIntyre and Lester, 1984), except for PCBs in Reqqa sludge and lindane in sludge from the three treatment plants (Table III). Aldrin was not detected in Ardhiya or Jahra sludges except for one sample from the former, which showed a concentration of 0.06 $\mu g\ g^{-1}$.

Enforcing a water quality standard of one part per trillion for PCBs in seawater (0.000001 ppm; EPA, 1976) would effectively eliminate all sea disposal of contaminated sludge, particularly in areas with low dispersion potential. On the other hand, levels of PCBs in local sludges were all below 10 $\mu g\ g^{-1}$, which has been established in the United States as a limit for PCBs in sewage sludge applied to lands producing food-chain crops (McIntyre and Lester, 1984). This does not indicate, however, that local sludges are amenable to such an application. As with trace metals, local conditions should be taken into consideration while enforcing this or similar limits in Kuwait.

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