CONCENTRATIONS OF HEAVY METALS IN FORTY SEWAGE SLUDGES IN ENGLAND

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Abstract. Samples of forty sewage sludges taken in England during 1979 were analysed for ten heavy metals using a rapid flameless atomic absorption spectroscopic technique. For all metals the mean concentrations were influenced by a small number of sludges containing exceptionally high concentrations. Typically, the concentration ranges showed approximately a 100-fold spread. Calculations based on U.K. guidelines for limiting the addition of toxic metals in sludge to agricultural soils indicated that application rates would theoretically be limited for more than 75% of the sludges by the concentrations of Zn, Cu and Ni, expressed additively as the Zn equivalent. Calculations of the theoretical maximum quantities of sludges which could be applied to land on an annual basis suggested that a significant proportion of the sludges would be unsuitable for application to agricultural land at rates of more than 2 t ha^{-1} yr^{-1}.

1. Introduction

The application of sewage sludge, as a manure, to agricultural land has been practiced for many years. Although alternative modes of sludge disposal exist, such as dumping at sea and landfill, the economic and practical aspects of these alternatives compared with the potentially large areas of land available for sludge application suggest that there will probably be a growing interest in the agricultural use of sludge in the future. The dependence on this route of disposal in the U.K. was illustrated by data obtained in 1970 (Ministry of Housing and Local Government, 1970) and 1975 (Department of the Environment, 1978), showing that the proportion of sludge applied to agricultural land (about 40% of all sludge produced at inland sewage treatment works) did not change significantly during this period.

The use of sludge on agricultural land is most often limited by heavy metal contamination. Heavy metals are of concern because they may be accumulated by crops. Although phytotoxicity and gross reductions in crop yield are uncommon, these effects have been shown to occur in extreme cases (Cunningham *et al.*, 1975), especially where spiked sludges have been used to simulate high metal loadings (Bingham *et al.*, 1975). Concern regarding the toxicity of heavy metals has led to the formulation of guidelines limiting the application of sludge to land (Department of the Environment, 1977).

A survey of 42 sludges collected in England and Wales in 1964 was reported by Berrow and Webber (1972). Their results showed that the concentrations of heavy metals in sludges were very often much higher than their concentrations in soils,

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indicating that sludge application would almost inevitably result in increased metal concentrations in the soil. Furthermore, Berrow and Webber (1972) demonstrated a wide variation in the concentrations of heavy metals, and attributed this to various degrees of contamination from a number of industrial sources. In recent years some success in limiting the contamination of sludges from industrial sources has been documented (Department of the Environment, 1978).

The present survey was undertaken to obtain a range of values for the concentrations of selected heavy metals in sludges and to evaluate their suitability for disposal to land as defined in current U.K. guidelines (Department of the Environment, 1977).

2. Materials and Methods

2.1. Materials

Nitric acid (specific gravity 1.42) used throughout was 'Aristar' grade. Standard solutions were prepared using 'Analar' grade metal salts in 1% (v/v) nitric acid. Borosilicate glass or high density polyethylene or polypropylene containers were used for sample collection. All glassware used in the determination of heavy metals was decontaminated according to the method of Henriksen and Balmer (1977).

2.2. Sampling of sludges

Sludge samples of different types (i.e. primary, mixed primary and digested) were collected from 40 sewage treatment works in England during 1979. Although these could not be considered a representative sample of the total number of works in England, they were chosen to provide a cross section of urban and rural areas with various proportions of industrial flow.

Subsamples of each sludge were acidified to 1% (v/v) with nitric acid and transferred to borosilicate glass containers. Unacidified samples were retained for solids determination. Total solids were determined by drying at 105 °C according to the method recommended by the Department of the Environment (1972a).

2.3. Pretreatment of sludges and determination of heavy metals

Acidified sludges were diluted ten fold with 1% (v/v) nitric acid and homogenized using a model T45N Ultra Turrax disintegrator (Scientific Instrument Co., London) fitted with a titanium shaft. Primary sludges were homogenized at 8000 rev min^{-1} for 10 min and mixed primary sludges at 8000 rev min^{-1} for 8 min (Lester *et al.*, 1977).

Heavy metals were determined in the homogenized sludges by electrothermal atomic absorption spectroscopy. This was undertaken using Perkin-Elmer models 305 and 603 atomic absorption spectrophotometers fitted with heated graphite atomizers HGA-72 and HGA-76, respectively. Cadmium, Cr, Cu, Ni, Pb and Zn were determined using the procedure described by Carrondo *et al.* (1979a, b) and Stoveland *et al.* (1979). The method of Sterritt and Lester (1980) was used to determine

TABLE I

Operating conditions for flameless atomic absorption spectroscopy

Conditions	Metal									
	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sn	Zn
Wavelength (nm)	228.8	240.7	357.9	324.8	279.5	313.3	232.0	283.3	286.3	307.6
Slit width (nm)	0.7	0.2	0.2	0.7	0.2	0.7	0.2	0.7	0.2	0.7
Drying temperature (°C)	100	100	100	100	100	100	100	100	100	100
Drying time (s)	60	60	60	60	60	60	60	60	60	60
Ashing temperature (°C)	250	1100	1100	700	1000	1750*	800	350	900	450
Ashing time (s)	40	45	30	30	45	45	30	40	150	40
Atomizing temperature (°C)	2100	2700	2770	2770	2700	2770	2770	2300	2700	2500
Atomizing time (s)	5	4	5	4	5	8	5	5	5	5**
Linear working range for 50 μl sludge (mg l^{-1})	0.002–0.02	0.02–0.2	0.01–0.1	0.02–0.2	0.005–0.04	0.005–0.03	0.05–0.4	0.01–0.2	0.08–0.8	0.05–1

* A temperature ramp of approximately 10 °C s^{-1} used when increasing furnace temperature from 100 °C to 1750 °C.

** Purge gas flow interrupted during atomization.

Co, Mn, Mo and Sn. The analytical conditions used for the determination of these metals are shown in Table 1.

3. Results and Discussion

3.1. Distribution of Heavy Metal Concentrations in Sludges

The mean, median and range concentrations of ten heavy metals, expressed in terms of dry sludge solids, are shown in Table I. Although the scatter of heavy metal concentrations did not follow a statistically normal distribution, mean and median values were included to give an indication of the deviation of distributions from the normal. In all cases the means were higher than the median values. This trend was observed by Berrow and Webber (1972) and is indicative of a relatively small number of sludges containing exceptionally high metal concentrations. For example the highest concentrations of Co and Pb encountered were 13 and 20 times higher respectively than the next highest. The highest concentration of Pb encountered was equivalent to 4.5% (w/w) of the dry sludge solids and the highest Zn concentration was almost 1% (w/w). The highest Co, Cr, Cu, Mn and Ni concentrations were between 0.2% and 0.6% while Cd, Mo and Sn concentrations were an order of magnitude lower.

It should be noted that the sludges sampled by Berrow and Webber (1972) were not the same as those analysed in this study, and neither sample could be considered representative of the total number of sewage treatment works in England. A comparison of data obtained from surveys of this type is therefore of limited value. However, the results of this study compare well with those of Berrow and Webber (1972). Of the metals studied, Cd, Cr, Cu, Mo, Ni, Pb and Zn are included in U.K. guidelines and most of these metals have been of concern for several years. Cadmium, Ni and Zn concentrations were lower in the present survey than in the survey carried out by Berrow and Webber (1972) while Cr, Cu and Pb concentrations had not increased since then. In contrast, Co and Mo concentrations were possibly slightly higher in the present survey. This may be indicative of some success in limiting industrial effluent discharges of metals of current interest while the same may not have occurred for metals of lesser interest or not included in the guidelines.

In an attempt to quantify the extent to which exceptional contamination of sludges occurred, the mean: median ratios were calculated; these also are shown in Table II. Higher mean: median ratios were considered to be due to a higher incidence of excessive contamination compared to what may be considered a normal or background level. In addition to toxic metals from industrial sources, Berrow and Webber (1972) also determined elements not widely used in industry, such as Ga, La, Li, Sc and Yt. Although the mean concentrations of these elements varied from 8 mg kg^{-1} for Ga to 72 mg kg^{-1} for La the means were similar to the medians, possibly indicating a normal distribution unaffected by industrial sources of pollution. In this study, given the limitations imposed by the number of samples, the mean: median ratios indicated that the range of background concentrations of heavy metals in sludge

TABLE II

Ranges, mean and median concentrations of ten heavy metals in 40 sewage sludges in England

Metal	Dry weight concentration (mg kg^{-1})			Mean: median ratio
	Mean	Median	Range	
Cd	24.8	16.4	1.54–110	1.51
Co	105	36.5	11.3–2490	2.88
Cr	707	364	57.2–5190	1.94
Cu	721	565	170–2080	1.28
Mn	667	376	131–6120	1.77
Mo	16.2	4.43	0.102–214	3.66
Ni	290	110	16.2–2020	2.64
Pb	1550	299	27.5–45 400	5.18
Sn	57.5	14.7	2.64–329	3.91
Zn	1930	1140	93.5–9210	1.69

could be considerably altered by contamination with Mo, Sn and Ni and less so by Cu and Zn.

3.2. Metals limiting sludge use in agriculture

The metal concentrations in each sludge were compared with maximum permissible additions of metals in sludge to agricultural land in the U.K. in order to ascertain which metals would theoretically limit such an operation. Limitations on the quantities of dry sludge solids which may be applied to land over 30 yr were calculated according to the equation (Department of the Environment, 1977):

$$\text{Application limit (t ha}^{-1}) = \frac{\text{recommended maximum addition of metal (kg ha}^{-1}) \times 1000}{\text{concentration of metal in sludge (mg kg}^{-1})}.$$

These values were calculated for Cd, Mo, Cr, Pb and the Zn equivalent. No data were obtained for As, B, Hg and Se. The Zn equivalent concept supposes Cu to be twice and Ni eight times as toxic to crop plants, on a weight basis and the toxicities of these three elements are assumed to be additive (Chumbley, 1971). Therefore, the degree of contamination of a sludge is given by:

$$\text{Zn equivalent} = [\text{Zn}] + 2[\text{Cu}] + 8[\text{Ni}] \qquad (\text{mg kg}^{-1})$$

A summary of the results obtained is shown in Table III. Over 75% of the sludges sampled would be limited by their Zn equivalent concentrations, while few incidences of limitation by Cd, Mo and Pb and none by Cr were encountered.

Based on the limitations imposed by heavy metal concentrations, the theoretical average quantities of dry sludge solids which could be applied to agricultural land per annum in the U.K. were calculated. There were 14 sludges which could be applied

TABLE III

Distribution of the heavy metal concentrations limiting the application of sewage sludge to agricultural land

Limiting metal	Limit of addition to land ($kg\ ha^{-1}$)*	Number sludges limited
Zinc equivalent	560	33
Cd	5	4
Mo	5	2
Pb	1000	1
Cr	1000	0
	Total:	40

* The period over which additions may be made is defined as '30 yr or more'.

at limits of 2 to 5 t ha^{-1} yr^{-1} and 11 at rates of 6 to 10 t ha^{-1} yr^{-1}. Nine sludges had calculated maximum rates of addition of less than 2 t ha^{-1} yr^{-1}. The maximum permissible rate of application observed was 24 t ha^{-1} yr^{-1}.

A wide range of sludge application rates have been reported in the literature. In an experiment at a market garden site in the U.K. (Johnston, 1974; Johnston and Wedderburn, 1974) sludge dressings were applied every 2 yr for 19 yr. The two application rates used were approximately equivalent to 38 and 62 t ha^{-1} yr^{-1}. Applications ceased when it became apparent that high concentrations of Zn were accumulating in the soil. Application rates approaching 450 t ha^{-1} have been used in experiments to determine the uptake of heavy metals by crops and their phytotoxic effects (Dowdy and Larson, 1975). Bunting (1963) in an 8 yr study, applied sewage sludge at rates of 12.5 t ha^{-1} and 25 t ha^{-1} in a comparative experiment to determine its value as a fertilizer. Additions of sludge based on available N and P concentrations (Department of the Environment, 1972b) would be approximately equivalent to 3 to 4 t ha^{-1}.

Almost 25% of the sludges analyzed in this study had theoretical maximum annual limits of application which were less than what may be considered the lowest practicable application rate of about 2 t ha^{-1}. Even if these sludges were not applied every year for up to 30 yr the maximum addition in any one year could only be six times the average annual limit (Department of the Environment, 1977), i.e. less than 12 t ha^{-1}. This may be an indication that a considerable proportion of sludges in England is unsuitable for disposal to agricultural land and that there is a dependence on other modes of disposal.

The quantities of sludge which may be applied to land under the limitations of heavy metal concentrations have been calculated on the basis of the metal content of the sludge only. In case where soils have been previously contaminated with heavy metals, or which are naturally high in some elements, the quantities of sludge applied would have to be reduced accordingly. Furthermore, if sludges were applied regularly, at rates approaching the limit, according to U.K. guidelines sites would no longer be suitable for disposal after a history of sludge application of 30 yr or less.

4. Conclusions

The concentrations of heavy metals in sludges may vary widely according to industrial contamination of influent sewage. In over 75% of the sludges sampled the Zn equivalent would theoretically limit the rate of application of these sludges to agricultural land. Thus, Zn, Cu and Ni appear to be elements which, according to current criteria, would most frequently present the greatest hazard to agriculture. Several sludges containing high concentrations of Sn and Co were encountered indicating that these elements are also potentially of concern and that they should not be ignored in imposing limits on sludge use in agriculture.

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