EXPERIENTIA

Volume 40 Pages 117-234 15 February 1984

Cadmium – a complex environmental problem
Part II

Cadmium in sludges used as fertilizer

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Summary. In intensively populated countries efficient sewage treatment is essential to protect river quality. An inevitable by-product is sewage sludge which has to be disposed of safely and economically. Utilisation of sludge as a fertilizer of agricultural land is the most economic disposal route for inland sewage-treatment works and also benefits farmers by providing a cheap manure. Much of the cadmium in wastewater is concentrated into sludge which consequently contains higher concentrations of cadmium than soil does. It is impracticable to reduce cadmium concentrations in sludge below certain levels. When sludge is used on farmland rates of application must be controlled so that cadmium concentrations in soil never reach levels that could significantly contaminate food crops. Cadmium is a principal factor limiting the use of sludge on land. Nevertheless, it is a local problem since agricultural land in general receives more cadmium from aerial deposition and phosphatic fertilizers. The significance of accumulations of cadmium in soil depends mainly on its availability for crop uptake. Investigations are described which have attempted to identify and to determine the availability of forms of cadmium in soil. There is considerable research interest in cadmium in soil solution which is likely to be directly available for crop uptake. Another area of interest is the apparent disappearance of cadmium from sludge-treated soil. Soil analysis often cannot fully account for the cadmium added in sludge. Apart from the effect of soil conditions, especially pH value, crop uptake varies according to the particular crop examined. Highest concentrations of cadmium occur in tobacco, lettuce, spinach and other leafy vegetables. Using crop uptake data from field trials it is possible to relate potential human dietary intake of cadmium, on which hazard depends, to soil concentrations of cadmium, which can be controlled by regulating applications of sludge. This provides an objective basis for limits for cadmium concentrations in soils receiving sludge. Transfer of cadmium via farm animals to meat and dairy products for human consumption is thought to be minimal, even allowing for some direct ingestion of sludge-treated soil by the animals. Evidence from these and other investigations suggests that a loading rate limit of 5 kg Cd/ha (equivalent to a soil concentration of about 3.5 mg Cd/kg) affords adequate protection to the foodchain where sludge is used on agricultural land. More research work is needed to provide a basis for predicting the long-term availability of cadmium introduced to the soil in sludge.

Cadmium in sludge and sewage treatment

Water re-use and the protection of river quality depend on efficient sewage treatment. But in intensively populated countries this inevitably leads to the production of large quantities of sewage sludge requiring safe and economic disposal. Sludge treatment and disposal account for about half the total cost of sewage treatment. The size of the problem can be illustrated by some statistics for the UK. Here, over 95% of households and most undustrial premises are connected to the public sewer. There are 7800 sewage works serving 82% of the population and producing an estimated 40 million tonnes of sewage sludge (or 1.3 million t dry sludge solids) each year. The annual cost of sludge treatment and disposal, including capital charges and administration, approached £200 million – or approximately £4 per head – in 1981/82. In the EEC countries together, annual production of sludge probably exceeds 5×10^6 t dry sludge solids, and is increasing.

What does all this have to do with cadmium in sludges used as fertilizer? The answer is that utilization on agricultural land is the most economic sludge disposal option for inland sewage treatment works. In the UK agricultural land receives nearly 50% of the sewage sludge produced annually. From the conservation point of view, agricultural use is the only current means of disposal which has any benefits, namely that in soil the plant nutrients and organic matter in sludge improve conditions for plant growth. Utilization on land should therefore be of benefit to farmers and to the community at large since it is the least-cost disposal option. But the contaminants in sludge are a problem. Thus cadmium and other metals usually occur in sludge in higher concentrations than in soil, and metals added in sludge accumulate in top soil. When sludge is used on land, rates of application must be controlled so that concentrations of contaminants in soil never reach levels which could be harmful to crops or the animals which eat them. Cadmium is a principal factor limiting the use of sludge on land. The environmental and economic consequences of this observation are such that the agricultural effects of cadmium in sludges used as fertiliser have received considerable research interest over the last 10 years.

The purpose of sewage treatment is essentially to produce from raw sewage (wastewater) a final effluent conforming to standards of purity which allow its safe return to rivers. Treatment of municipal sewage involves separation of settleable solids (primary treatment) and conversion of dissolved and colloidal solids by a biological process (secondary treatment) to metabolites such as carbon dioxide, sulphate and water and also to microbial cells and residues in a flocculent form (humus or surplus activated sludge) which can be separated by a secondary stage of settlement. The end-products are a comparatively clean effluent, which can be returned to the river either directly or after some further (tertiary) treatment, and a sludge containing much of the polluting load of the original raw sewage. The volume of sludge produced will be approximately 1% of the volume of raw sewage treated. Sewage sludge is a putrescible, thin mud typically containing about 98% water. The solids content is 70-80% organic matter and the inorganic fraction will include appreciable concentrations of various contaminants reflecting the quality of the raw sewage from which it was derived. Sludges from the primary and secondary treatment processes are usually combined and thickened or treated before disposal, the ratio of primary sludge solids to secondary sludge solids often being about 2:1 by weight.

About 90% (range 75-100) of the cadmium in raw sewage is separated into sludge. Usually, 70% of the metal is removed during primary sedimentation, and secondary treatment by the activated-sludge process removes approximately 60-70% of the remainder[31]. A survey of 183 UK sludges found that cadmium concentrations ranged from 0 to 180 mg/kg dry solids (ds) with a median value of 17 mg/kg ds and a mean of 29 mg/kg ds[16]. A survey of over 200 sludge samples from 8 states in the USA found cadmium concentrations of 3-3410 mg/kg ds with a median value of 16 mg/kg[38]. In the UK survey, the mean concentration of cadmium in sludges from sewage works receiving no industrial effluent was 7.5 mg/kg ds whilst sludge prepared at the Water Research Centre (WRC) using sewage derived from a residential area, contains about 2 mg Cd/kg ds. It is worth mentioning that anaerobic digestion of sludge can influence concentrations of cadmium and other contaminants. This is a popular treatment process which incubates the sludge anaerobically for about a month at 30-35 °C. During this time putrescible organic matter in the sludge is converted to carbon dioxide and methane by bacterial action, resulting in a loss of 30-50% of the original organic content of the sludge. This increases the ratio of inorganic:organic matter in the sludge and can effectively double the concentration of cadmium expressed as mg/kg dry solids. Even so, this would produce only about 4 mg Cd/kg ds in a digested sludge of residential origin or perhaps 8-10 mg Cd/kg ds in what is commonly called a 'domestic' sludge, being derived from a small sewage-treatment works with a predominantly residential catchment. Much of the camium in sludge therefore results from industrial discharges to sewers. Industry uses cadmium in a variety of ways including electroplating, electrical contacts, plastics stabilizers, ceramics, pigments, alloys, fluxes, glasses, lubricant-additives, nickel-cadmium batteries, solar cells and catalysts. In the UK, attempts to restrict industrial discharges of cadmium to sewers, and hence to control cadmium levels in sludge, have met with some success. Thus, a stricter policy on trade effluent control reduced cadmium concentrations at one large sewage-treatment works in the London conurbation from 145 mg/kg ds in 1972 to 18 mg/kg in 1977[51]. This example is indicative of a general trend towards declining cadmium concentrations in sludge. However, whilst attention to point sources of industrial discharge can result in substantial reductions where cadmium levels of sludge are high, it is not easy for large works to reduce the cadmium concentration of sludge below the range 20-40 mg Cd/kg ds. This is because as little as 0.008-0.01 mg Cd per liter of sewage will give rise to a concentration in sludge of 20 mg Cd/kg ds, assuming there is 85% removal of cadmium from sewage during treatment and that 350 mg of primary and secondary sludge solids are generated per l of sewage treated. It is difficult to isolate and control the many diffuse sources in the catchment of a large sewage treatment works which may be contributing to a cadmium load in sewage of < 0.01 mg/l. Poon's article in this review[39] deals with cadmium removal from effluents. Methods for the removal of cadmium from sludge itself are only at the developmental stage at the moment and their cost is likely to exceed the value of the separated cadmium and the decontaminated sludge. As to the forms of cadmium which may occur in sludge it appears that sludges contain a wide variety of sites at which metals may be held by mechanisms which include ion exchange, sorption, chelation, and precipitation. The form of the metal will be influenced by the type of treatment given to the sludge. Working with digested sludge, Stover et al.[45] used a sequential extraction technique to rank the forms of cadmium as follows: carbonate > sulphide > organically bound > adsorbed = exchangeable. The phosphate and hydroxide are also likely to occur. The organically bound fraction may be more prevalent in undigested sludge. It is well known that acidification of sludge will release metals including cadmium, a marked effect occurring as the pH value falls below 5.0. Whilst forms of cadmium in sludge are of interest and have some bearing on potential uptake by crops from sludge-treated soil, this will depend more directly on the fate of cadmium in sludge when it is mixed with soil. Stover et al.[45] reported that about 80% of the cadmium in sludge is present in forms which would require conversion to water-soluble, exchangeable or adsorbed forms in soil before uptake by plants could proceed. Of particular interest is microbial oxidation in soil which could result in the solubilization of carbonate, the conversion of sulphide to sulphate and the breakdown of sludge organic matter. Any of these processes could dramatically alter the availability of sludge-borne cadmium for uptake by plants.

Impact of sludge on soil levels of cadmium

Background soils normally contain 0.1–1.0 mg Cd/kg. A survey of 600 samples[1] of agricultural soil in the UK found that 50% of samples contained < 1.0 mg/kg although the range was 0.08–10 mg/kg and the mean < 1.23 mg/kg. High values occur rarely in soils derived from certain carboniferous shales or as a result of contamination by mining or smelting activities.

As described above, sludge often contains 20 mg Cd/kg or more and repeated, heavy applications could substantially increase soil concentrations as the added metal accumulates in top soil. In most countries where sludge is applied to land there are guidelines specifying maximum permissible levels of elements in soils. In the UK, the limit is 3.5 mg/kg[18] which is equivalent to an addition to the soil of 5 kg Cd/ha in sludge if it is assumed that the top soil is 20 cm deep with a density of 1 g/ml and that the background soil already contains 1 mg Cd/kg. Usually, guidelines suggest also that sludge should be applied to land in accordance with crop requirements for plant nutrients. Liquid digested sludge is widely utilized and is particularly rich in nitrogen. A dressing of 100 m^3/ha would probably be appropriate to meet the nutrient requirements of many crops. Typically, such sludge has a dry solids content of about 5% so 100 m^3 would contain 5 t ds and would add to the land 100 g Cd/ha if the cadmium concentration of the sludge was 20 mg/kg ds. This would increase the concentration of cadmium in the top soil by 0.05 mg/kg, an amount unlikely to be detected by routine soil analytical procedures. Over the years, 250 t ds/ha of this sludge could be applied to the same field to reach the maximum permissible soil concentration of cadmium. For fields receiving it, sludge represents the main input of cadmium. But in the UK only about 1.3% of the available agricultural land receives sludge each year and as shown above a normal annual application of sludge may be expected to increase the soil concentration of cadmium by about 0.05 mg/kg. The other main sources of cadmium for agricultural soils are aerial deposition and phosphatic fertilizer. Surveys in different parts of the world have shown that the latter contain 1–160 mg Cd/kg according to the origin of the rock phosphate from which they were prepared[13]. Whilst only a small percentage of agricultural land receives sludge, inputs from aerial deposition and from phosphatic fertilizers apply to all agricultural land. Hansen and Tjell[22] have assessed cadmium inputs to agricultural land in Denmark on a national and a local basis. Nationally, sludge contributed 5% of the cadmium; the remainder resulted from aerial deposition (70%) and inorganic fertilizers (25%). Locally, assuming that sludge containing 7 mg Cd/kg was applied at a rate of 5 t ds/ha yr, the contribution from sludge accounted for 90% of the total cadmium input, compared with 8% from aerial deposition and 2% from inorganic fertilizer. More recently, the input of cadmium to background soils in Denmark has been estimated at 5.1 g/ha yr[49]. The figure was composed of 3 g/ha yr from fertilizers, 2 g/ha yr from atmospheric deposition and just 0.1 g/ha yr from sewage sludge. Taking the EC countries together Hutton[28] has estimated the total cadmium input to arable soils in areas away from localized contamination to be 8 g/ha yr. Phosphatic fertilizer was thought to contribute 5 g/ha yr and atmospheric deposition 3 g/ha yr. The contribution from sewage sludge applications was considered to be too small on a national or regional basis to warrant inclusion. This helps to put concern about sludge into perspective.

The significance of cadmium accumulations in soils

The significance or hazard of cadmium accumulations in soils depends largely on how much of the cadmium is available for uptake by crops. The possibility of hazard resulting from leaching of cadmium through the soil profile into groundwater is likely to be minimal in agricultural soils treated with sludge, because these will normally be limed to a pH value of at least 5.5 and probably 6. Plant-available cadmium in soil can be assessed directly by means of plant analysis, indirectly by means of soil analysis or more desirably by a combination of the two. Novel suggestions for assessing the bioavailability of cadmium in soil include the use of earthworms which accumulate cadmium in sludge-treated soil[25].

Soil analysis

The 'total' amount of cadmium in soil is conventionally determined by strong acid extraction, often using nitric acid on its own or in admixture with hydrochloric or perchloric acid, before analysis of the digest by atomic absorption spectrophotometry (AAS). Instrumental methods such as neutron activation analysis and or X-ray fluorescence spectrophotometry (XRFS) can also be used. These methods involve minimal sample preparation and should in theory give a truer estimate of the total amount of cadmium present although they may be less accurate for measuring concentrations below 1 mg Cd/kg in soil. XRFS in particular has a higher limit of detection than AAS. Total concentrations are essential for assessing the extent of contamination by cadmium and guidelines for the use of sludge on land normally seek to control the total concentration of cadmium in soil. But however it is measured, the total concentration gives no insight into the significance of the observed contamination. This depends instead on the potential solubility of the cadmium which in turn determines its availability for crop uptake. Soil scientists have therefore used a variety of mild extractants as rapid chemical tests for assessing availability. Unfortunately, because conventional extractants tend to be insensitive to the soil properties which control the availability of metals to plant roots, for example pH value, it is often as difficult to relate extractable concentrations of metals in soil to probable plant uptake as it is total concentrations. Improved correlations between extractable Cd, and Cd in plant tissue, are obtained when results from different soils are grouped together on the basis of their chemical properties. Symeonides and McRae[46] have drawn attention to the frequent lack of theoretical justification in the selection of extractants and have emphasized the importance of testing extractants against plant performance before advocating their use. These authors recommend the use of ammonium nitrate (1 M) for assessing plant-available cadmium in soil. Other favored extractants include neutral ammonium acetate (1 M) and the chelating agent DTPA which was originally developed to identify soils where crops were likely to suffer from zinc deficiency[32]. Sauerbeck and Rietz[42] have recently evaluated 25 extracting solutions and concluded that the best results could be obtained by weakly acidic but well buffered extractants.

The most important development in this area has been the recognition that extractants are best used not to assess availability directly but to identify the major forms of cadmium in soil. Sequential extraction techniques are proving increasingly popular for this purpose. The original procedure of McClaren and Crawford[33] for identifying the main forms of copper in soil was modified by Stover et al.[45] to examine forms of various metals in sludge (see above). Following studies with model trace metal compounds, the procedure has now been further modified at the University of California, Riverside, to give data concerning the fractions of trace metals in exchangeable, sorbed, organic, carbonate, and sulphide forms. These solid-phase chemical forms are determined by sequential extraction with the following reagents respectively; potassium nitrate (0.5 M) 16 h, deionized water (extract 3 times and combine data), sodium hydroxide (0.5 M) 16 h, disodium salt of EDTA (0.05 M) 6 h, nitric acid (4 M) 16 h at 80 °C. Results so far obtained suggest that much of the cadmium in sludge occurs as carbonate and in neutral soils it persists in this form[44]. There is some evidence that cadmium introduced to the soil in sludge gradually reverts towards residual forms extracted by nitric acid but not by EDTA[19]. Sequential extraction studies on soils have usually found low levels of cadmium occurring in the exchangeable and adsorbed forms. For example, Emmerich et al.[19] found less than 3% and Sposito et al.[44] found 1.1–3.7%. This is of particular interest if, as seems likely, these forms represent the fraction which is most available for crop uptake.

It is now widely accepted that in order for uptake into roots to occur, soluble forms of cadmium must exist adjacent to the root membrane for some finite period[5]. This observation has led to greater efforts to understand the soil properties which influence concentrations of cadmium in soil solution. These properties are pH value, redox potential, texture, mineral composition (content of clays and oxides of iron and manganese) and profile characteristics, cation-exchange capacity, amount and type of organic compounds in the soil and soil solution, presence of other heavy metals (which may compete for adsorption sites, etc.), soil temperature and moisture content, and other factors which affect microbial activity[23]. These soil properties function interactively to control the solubility of cadmium in soil so the system is inevitably complex. The one generalization that can be made with some confidence is that a decrease in soil pH value will increase the solubility of cadmium which in turn increases crop uptake of the element. Guidelines for sludge utiliziation on land normally recommend that the soil pH value should be maintained at ≥ 6. A detailed discussion of this area was presented by Davis and Coker[13].

Advances in analytical techniques have permitted more detailed examination of the forms of cadmium in soil solution and their relationship with the solid phase. Using High Performance Liquid Chromatography (HPLC), Tills and Alloway[48] investigated the main cadmium containing species present in soil solution. They found that all the cadmium occurred in a peak associated with low molecular weight organic molecules which would also contain inorganic compounds and Cd^{2+} ions. They concluded that most of the cadmium in the soil solution of sludged soils is cationic, confirming the observations of Bingham[3] and Bolt and Bruggenwert[4]. Apart from directly measuring the species of cadmium present in soil solution these can be predicted with computer models which make use of known chemical equilibria and properties of the soils concerned. Using the GEOCHEM programme, Emmerich et al.[20] calculated that 50–60% of the total cadmium in soil solution occurred in the free ionic form. A similar model was developed at the Water Research Centre to predict the speciation and solubility of lead in drinking water[29].

A practical problem which has so far defied a convincing theoretical explanation concerns the apparent disappearance of some of the cadmium added to soil in sewage sludge. Many researchers have been unable to account fully for the cadmium introduced to soil in field and even laboratory trials. For instance, Chang et al.[8] recently reported investigations into the cadmium content of soil from a field trial 4 years after sludge applications ceased. They could account for only 43–60% of the cadmium originally added although there was no apparent movement beyond the depth of the soil profile examined (0–60 cm). Figure 1

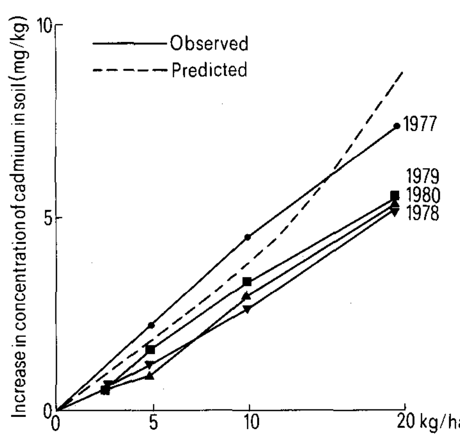

Figure 1. Observed and predicted concentrations of cadmium in soil in relation to cadmium applied in sludge (Coker et al.[9]).

shows another example from a field trial reported by Coker et al.[9]. More than a year after application of the sludge the soil concentrations of cadmium were lower than predicted although all the sludge was confined to the sampled area, worms were absent from the soil and leaching is unlikely to account for the loss since the soil in question was a calcareous boulder clay. Furthermore, crop uptake removed less than 1% of the cadmium added to the soil in sludge. Since the effect is always negative, random errors in sampling seem unlikely to explain the loss and in the example above changes in soil bulk density were taken into account. It is conceivable that the cadmium introduced to the soil reverts to forms which are not solubilized during the nitric acid digestion often used to determine total cadmium concentrations in soil but this explanation seems unlikely. This is an interesting problem with important implications which requires thorough investigation.

Crop uptake of cadmium

Apart from the influence of soil conditions described above, crop uptake varies according to the particular crop concerned. There are wide differences between species and also between cultivars of the same species. Figure 2 illustrates concentrations of cadmium found in the leaves and edible parts of a range of different crops grown to maturity in a pot trial with a soil containing 69 mg Cd/kg. Data of this type permitted Davis and Carlton-Smith[12] to develop a league table of crop sensitivity based on cadmium concentrations

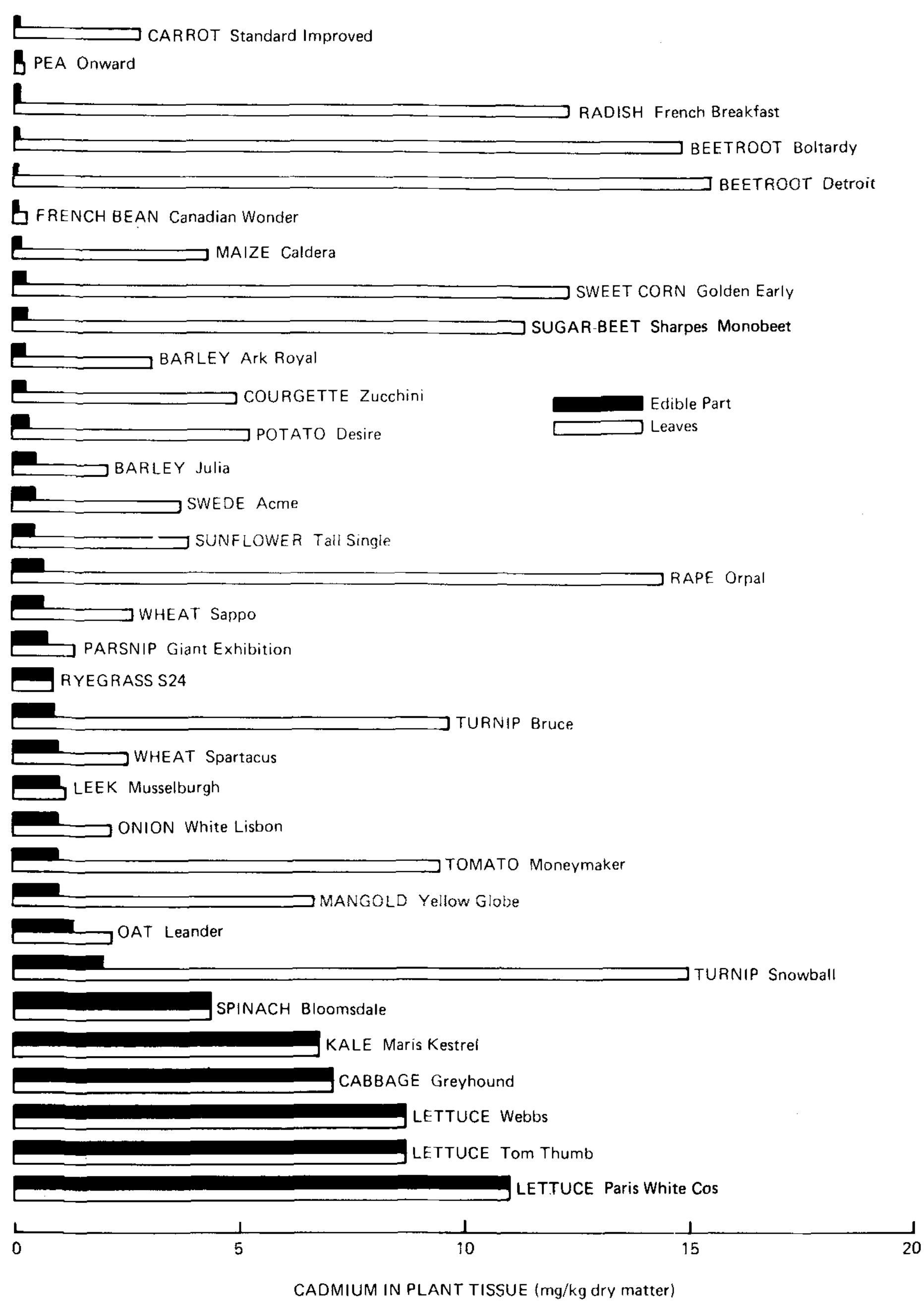

Figure 2. Cadmium concentrations in different crops all grown in the same soil (Davis and Carlton-Smith[12]).

found in the edible parts. The most efficient assimilators of cadmium from soil were 3 cultivars of lettuce which scored 73–100 on the comparative scale used, followed by spinach (58), celery (47) and cabbage and kale (38–40). All the other crops tested were in the range (1–15) with 2 legumes (French bean and pea) at the bottom of the scale. An ornamental cultivar of tobacco was included in these uptake tests and it is of interest that this plant achieved a comparative rating of 310 based on the cadmium content of its leaves. Tobacco is an important source of human intake of cadmium; smoking a pack of 20 cigarettes is equivalent to 25 µg of cadmium in the diet[37]. Amongst crop plants, highest concentrations of cadmium may be expected to occur in the leaves of vegetables such as lettuce, spinach and other beets, and cabbages. Spinach is a member of the beet family (Chenopodiaceae) and this group are also able to assimilate other sludge-borne metals (nickel, copper and zinc) from soil with comparative ease. These plants tend to be rich in oxalate which has an affinity for metals and might explain the uptake ability of the beet family. This is speculation by Chaney[6] has recently reviewed plant physiological aspects of metal uptake. He observes that more research needs doing on the next step, this being the absorption by man of cadmium in ingested food. Jarvis et al.[30] examined the distribution of cadmium between the roots and shoots of 23 plant species after exposure to a nutrient solution containing 0.01 Cd/l. In all except 3 species (lettuce, kale and watercress) more than 50 per cent of the cadmium taken up was retained in the roots. The concentration in the roots was always greater than in the shoots, and in the fibrous roots of fodder beet, parsnip, carrot and radish it was greater than in the swollen storage roots. In the case of ryegrass approximately 88% of cadmium was retained in the roots. These authors concluded that although the roots of several species can take up large quantities of cadmium from solution, there are mechanisms (possibly associated with the solubility of cadmium phosphate) which may restrict the movement of cadmium through plants, and thus to animals. Although Chaney[6] cites exceptions, it appears in general that cadmium concentrations in plant parts decrease in the order fibrous roots > leaves > seeds = storage organs. Field sampled plants usuallly contain < 0.02–1.0 mg Cd/kg dry matter with a mean concentration of about 0.30 mg/kg; leafy crops will tend to contain cadmium concentrations towards the higher end of the range[13].

Concern about enhanced concentrations of cadmium in crop plants relates mainly to implications for the human foodchain. This is because cadmium is principally a zootoxic element; concentrations of cadmium in crops which are potentially harmful to man precede the concentrations that damage the crop itself. The foodchain could therefore be significantly contaminated by apparently healthy crops. For the principally phytotoxic elements (for instance copper, nickel and zinc) the opposite is true and the crops will display symptoms of toxicity before they contain concentrations which could damage human or animal health. In the case of cadmium, crop growth is unlikely to be affected until tissue concentrations exceed 10 mg Cd/kg dry matter, but concentrations of much less than this could lead to potentially harmful human dietary intake of the element.

Implications for the human foodchain of cadmium in sludge applied to land

Cadmium is a cumulative poison so subtle increases in the diet sustained over long periods could conceivably lead to toxicity problems in man. Proper assessment of the problem requires that soil concentrations of cadmium can be related to potential increases in dietary intake of the element. In this way applications of sludge to agricultural land can be adjusted to keep soil concentrations of cadmium below levels likely to generate potentially a toxic dietary intake. For assessing potential dietary intake, reliable crop uptake data obtained in field conditions are needed from trials using sewage sludge. Much useful information can be obtained from agricultural investigations at sites dedicated for sludge disposal where cadmium levels have been built up gradually following a long history of sludge deposition (see Rundle et al.[40] for example). Whilst data from pot trials or even from experiments using inorganic cadmium salts are useful for some investigations these data must be eschewed for dietary modelling purposes. The drawbacks associated with such data were described recently by Chaney[6].

Data from a field trial with sludge are shown in figure 3. The details of this experiment were described

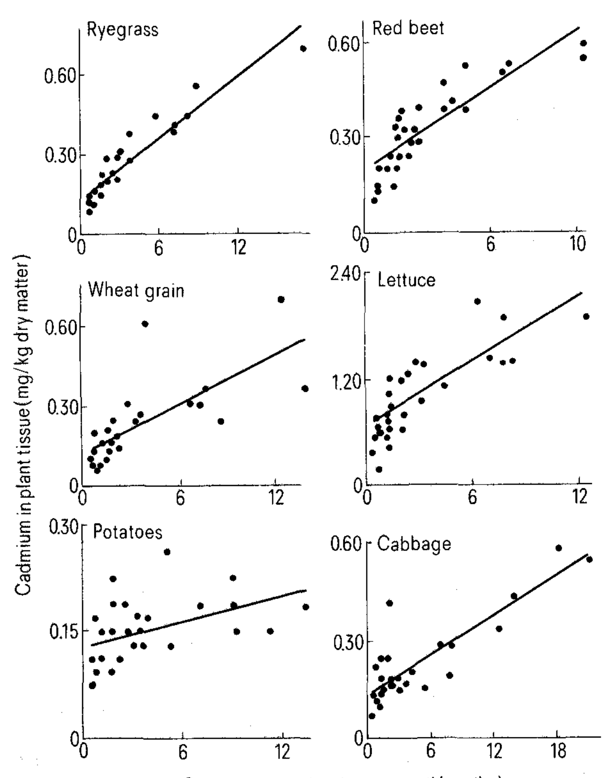

Figure 3. Results of a field trial showing the relationship between cadmium concentrations in soil and in six principal crops (Davis, Stark and Carlton-Smith[15]).

by Davis and Stark[14] and Davis et al.[15]. There is an approximately linear and statistically significant relationship between the cadmium concentrations in the soil and cadmium concentrations in all 6 crops tested. As expected, highest concentrations of cadmium occurred in lettuce but significant increases occurred in all the other crops tested which included wheat grain and potato tubers. These latter two crops are the major plant components of the human diet, together supplying 74% of the plant part of the food intake of the average UK consumer[34]. Using charts of standard dietary intake in conjunction with the crop uptake data of figure 3, it has been possible to produce a preliminary model (fig. 4) relating concentrations of cadmium in sludge-treated soil to potential dietary intake of cadmium for an average consumer taking all his crops from sludge-treated soil. On this basis it is clear that small increases in the cadmium content of staple food such as potatoes and particularly wheat have a substantially more profound effect on potential dietary intake of cadmium than larger increases in concentration of the element in crops like lettuce. This would apply even to those who eat several times the normal amount of lettuce. In view of the importance of wheat (cereal products supply 40% of the plant part of the diet for the average UK consumer) it is of interest to take account of milling. In this case it was found that the flour contained only 57% of the cadmium in the whole wheat grain from which it was made. Thus potential dietary intake is reduced if an individual takes his wheat as flour instead of whole grains. No account is taken in the model of the influence of enhanced soil concentrations of cadmium on meat and dairy products for human consumption. It was felt that these are insensitive to increases in the cadmium content of soil except perhaps for offal (liver and kidney) which composes only about 0.5% of the diet on a fresh weight basis[34].

Figure 4 shows that there is a linear relationship between cadmium in soil and potential dietary intake of cadmium. The gradient of the slope is greater if cereals are eaten as whole grain rather than flour.

One basis for an objective soil concentration limit for cadmium would be that concentration which produces

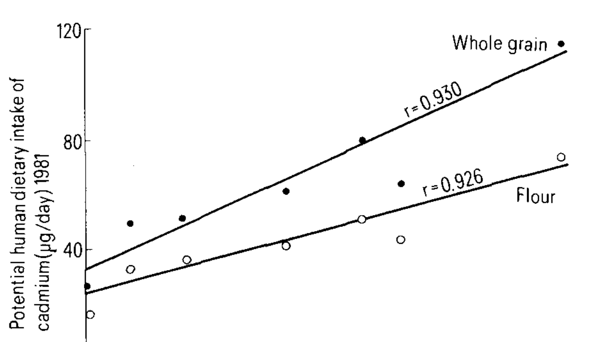

Figure 4. The relationship between cadmium concentrations in soil and potential dietary intake of cadmium for an average consumer taking all his/her crops from sludge-treated soil (Davis, Stark and Carlton-Smith[15]).

a potential dietary intake of 70 µg/day, the value calculated independently by both the World Health Organisation[51] and the United States Environmental Protection Agency[21] as being the maximum acceptable daily intake of cadmium. For the whole grain diet this value is generated by a soil concentration of 6.24 mg Cd/kg and for the flour diet the soil concentration is 12.90 mg Cd/kg. Tolerable accuracy of the model is suggested by the finding that unsludged soil could generate a dietary intake of about 20 µg/day, close to the estimated value for UK citizens[17]. On this basis, it is suggested that a soil concentration in the range 6.0–12.0 mg Cd/kg (equivalent to a loading rate of 10–22 kg Cd/ha) is acceptable for calcareous soils (pH value 7–8) receiving sludge. It is intended to improve and consolidate the model used to arrive at this value and to include data from acidic soils, but it has the following built-in safety factors:

a) Only 1.27% of agricultural land in the UK receives sludge each year. The average dressing increases the soil concentration of cadmium by about 0.05 mg/kg/yr. It is almost inconceivable that any individual would live on crops taken wholly from sludge-treated soil.

b) Whilst the model is based on an average consumer (who, in reality, does not exist), an unusual diet consisting for instance of 5 times the normal intake of lettuce would have little effect on dietary intake of cadmium. Wheat is much more important but few people grow their own supplies. This crop is usually collected and stored centrally so any contaminated sample would be diluted out. The diet of most individuals would include at least some refined grain (flour) of lower cadmium content.

c) The WHO/EPA maximum acceptable daily intake of cadmium of 70 µg/day is not a toxic threshold but has its own safety factor. It is estimated that 200 µg/day of cadmium sustained over a 50-year period would be needed to produce kidney damage (of doubtful clinical significance) in the most sensitive individual. (See Davis and Coker[13], and Naylor and Loehr[35]).

The other possible pathway for the transfer of cadmium into the human foodchain is in meat and dairy products from animals fed with fodder crops grown on sludge-treated soil. Farm animals probably absorb $< 5\%$ of the cadmium they ingest. Ryan et al.[41] have summed up the findings of numerous investigations into the effects of elevated cadmium intake on the cadmium concentration of the muscle tissue of experimental animals. They reported almost unanimous agreement that cadmium does not seek muscle tissue and no significant differences are found between experimental animals and control animals. This finding was independent of whether the animals graze on grass grown on sludge-amended soil or are given an inorganic cadmium source in their food. Exceptions to this rule are associated with very high levels of cadmium in the animals diet which would be most unlikely to occur in practice.

In addition to muscle tissue, it has also been found that cadmium does not accumulate in other important animal products. Thus Crossmann and Seifert[11] report that recommended limits (in Germany) for cadmium in milk (0.0025 ppm of cadmium) and eggs (0.05 ppm cadmium) will only be exceeded if animal feed exceeds 50 ppm and 13 ppm of cadmium respectively. Sharma et al.[43] concluded that cadmium concentrations in animal feed of up to 10 mg/kg would cause no appreciable increase in the cadmium content of meat, milk or eggs. Constraints on sludge utilization on land are such that cadmium originating from sludge could never approach these levels in animal feed. Since cereal grains are poor assimilators of cadmium from soil (fig. 2) and farm animals do not accumulate cadmium in their muscle tissue, problems due to cadmium in sludge used on land can be minimized if the land is used to grow grain for animal feed. According to Ryan et al.[41] there would in these circumstances be no need for a cadmium soil limit to protect public health. Land use of this kind may therefore be the best option if farming is to take place on soils highly contaminated with cadmium. The average human diet includes only small amounts (see above) of offal (liver and kidney) which may accumulate cadmium and will only pose a problem for unusual consumers eating large quantities of it. Normally, dilution through the marketing process would reduce the risk considerably. Also farm animals for human consumption are short-lived so the question of long-term accumulation in the visceral organs does not arise.

One further aspect of animal nutrition must be mentioned and this relates to the inadvertent ingestion of soil and sludge by animals grazing sludgetreated grassland. Grass grazed by cattle during the months November-March may contain 3–6% soil on a dry matter basis[47], for sheep this may well be doubled[24]. Also, sludge adheres to grass and can be ingested as the grass is grazed[6]. However, a 'no-grazing period' is usually recommended between applications of sludge to pasture land and grazing by cattle. The principal purpose of this recommendation is to avoid problems of pathogen transmission but it also serves to minimize direct ingestion of sludge. The latter can also be reduced by keeping animals off sludge-treated pasture in the winter months when grass growth is slow and the soil is soft. Baxter et al.[2] have demonstrated the potential importance of direct ingestion in an animal experiment in which cattle were fed a diet containing 12% sludge (cadmium content 88 mg/kg ds) for a 9-month period. In these experimental conditions increases in the cadmium content of kidney, liver and even muscle tissues occurred.

In practice, problems due to cadmium in sludge applied to grassland seem minimal. Nelmes et al.[36] investigated a farm with a long history of sludge deposition carried out on a sacrificial basis where soil concentrations of cadmium ranged up to 29 mg/kg and the cadmium content of herbage was 5–10 mg/kg dry matter in autumn and winter and 4–5 mg/kg in summer. These levels are much higher than is usually permitted for agricultural land receiving sludge. Nevertheless, Nelmes et al.[36] found that the health of grazing animals on this farm was unaffected by cadmium and that the transfer of cadmium to man in foodstuffs from dairy or beef cattle on the farm was minimal. Direct ingestion is avoided if the sludge is injected below the surface of grassland.

Control of contamination problems due to cadmium in sludge used as fertilizer

In most countries where sludge is used in agriculture there are guidelines which restrict soil concentrations of cadmium to a level judged to be safe. In the UK, the maximum recommended soil concentration of cadmium where sludge is used on land is 3.5 mg/kg to be approached gradually over a 30-year period[18]. It is shown above that the average annual application of sludge designed to meet crop requirements for nutrients would increase the soil concentration of cadmium by perhaps 0.05 mg/kg so about 250 t ds/ha of a sludge containing 20 mg Cd/kg ds could be added over the 30-year period before the permissible maximum was reached. The limit of 3.5 mg/kg in soil therefore allows enough sludge to be applied to the land for the operation to be beneficial to farmers and to permit economic sludge disposal. First and foremost, it is essential that the limit is environmentally acceptable in providing adequate protection to the human foodchain. The model described above which relates potential dietary intake of cadmium to soil concentrations of cadmium suggests that the 3.5 mg Cd/kg limit in soil is acceptable. The Commission of the European Communities[10] has proposed a limit of 3.0 mg Cd/kg. Webber and Monks[50] have suggested an international loading rate limit of 5 kg Cd/ha which is equivalent to a soil concentration limit of about 3.5 mg Cd/kg. They consider that such a loading rate represents little if any hazard to the foodchain. In the USA the Environmental Protection Agency[21] has recommended a maximum loading rate of 5 kg Cd/ha for soils of low cation exchange capacity (< 5 meq/100 g). There is increasing agreement that a limit of about 3.5 mg Cd/kg is environmentally acceptable for soils receiving sludge. Provided that rates of application of sludge to land can be controlled and a soil limit observed, there is no need for a concentration limit for cadmium in sludge itself. Such a limit is needed, however, if sludge is to be supplied to small farmers or gardeners in circumstances where the rate of application of sludge will not be supervised. UK guidelines[18] recommend a limit of 20 mg Cd/kg ds in sludges supplied to the general public but no limit is considered necessary in sludges for agricultural use.

A better understanding of the chemistry and bioavailability of cadmium in soils should lead to a position where soil concentration limits can be modified according to soil conditions. In developing this approach the EPA[21] has devised a system in which limits for cadmium vary according to the pH value and cation exchange capacity of the receiving soil. Certainly there would appear to be a case for a less stringent limit for calcareous soils (pH value > 7 and containing more than 5% calcium carbonate), where the soil pH value is likely to remain permanently near neutral. Also, there is a need to continue the development

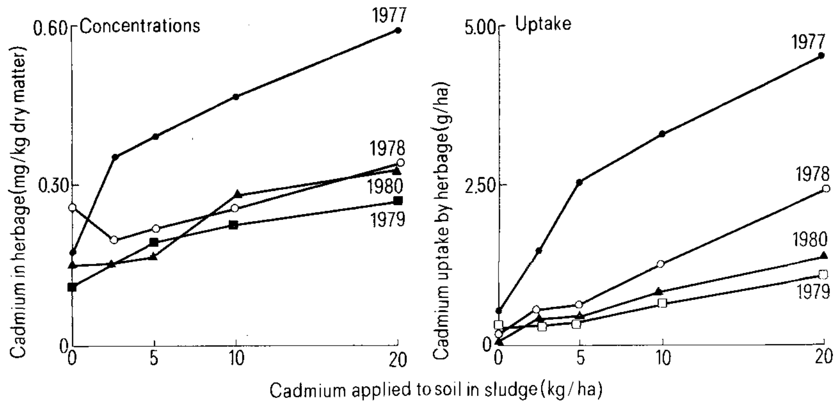

Figure 5. The effect of time on the availability to herbage (mainly ryegrass *Lolium perenne* cv. S23) of cadmium in sludge-treated soil. Sludge was applied to soil in 1976 (Coker et al.[9]).

of management practices, such as growing grain for animal feed only, which minimise cadmium contamination of the foodchain and permit farming to continue on historically contaminated land.

A challenging problem from the research point of view is to predict the availability in the long-term of cadmium introduced to the soil in sludge. This question has important environmental implications. There would be less concern about cadmium in sludge if it could be confirmed that uptake of cadmium from sludge-treated soil decreases with time after sludge is added to the soil even after sludge applications stop, and that cadmium accumulations in soil cannot suddenly be released for plant uptake following a change in management practice, bearing in mind that future land use cannot be predicted. In near-neutral soils it appears that cadmium originating from sludge does gradually revert to less available forms. Figure 5 presents some data to support this observation from Coker et al.[9]. Hinesly et al.[26,27] have produced similar data for maize which led them to conclude that plant uptake depended principally on the amount of cadmium applied immediately before planting rather than the total amount applied in previous years. It is quite possible that once equilibrated with soils of near neutral pH value, cadmium accumulations remain immobilized in forms permanently unavailable for plant uptake. Experimental evidence is still awaited to support the widely held view that organic matter in sludge keeps cadmium in forms unavailable for plant uptake, and that this cadmium may be released when sludge organic matter decays in soil (the 'time-bomb' effect). Nevertheless, current knowledge about the long-term availability of cadmium is incomplete, especially with respect to non-calcareous soils (see Chaney et al.[7]).

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