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An inventory of heavy metals inputs to agricultural soils in England and Wales

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Abstract

An inventory of heavy metal inputs (Zn, Cu, Ni, Pb, Cd, Cr, As and Hg) to agricultural soils in England and Wales in 2000 is presented, accounting for major sources including atmospheric deposition, sewage sludge, livestock manures, inorganic fertilisers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts. Across the whole agricultural land area, atmospheric deposition was the main source of most metals, ranging from 25 to 85% of total inputs. Livestock manures and sewage sludge were also important sources, responsible for an estimated 37–40 and 8–17% of total Zn and Cu inputs, respectively. However, at the individual field scale sewage sludge, livestock manures and industrial wastes could be the major source of many metals where these materials are applied. This work will assist in developing strategies for reducing heavy metal inputs to agricultural land and effectively targeting policies to protect soils from long-term heavy metal accumulation.

Keywords: Heavy metals; Sources; Inventory; Soil; Agriculture

1. Introduction

The soil is a long-term sink for the group of potentially toxic elements often referred to as heavy metals, including zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), chromium (Cr) and cadmium (Cd). Whilst these elements display a range of properties in soils including difference in mobility and bioavailability, leaching losses and plant uptake are usually relatively small compared to the total quantities entering the soil from different diffuse and agricultural sources. As a consequence, these potentially toxic elements slowly accumulate in the soil profile over long periods of time. This could have long-term implications for the quality of agricultural soils, including phytotoxicity at high concentrations, the maintenance of soil microbial processes, and the transfer of zootoxic elements to the human diet from increased crop uptake or soil ingestion by grazing livestock. Therefore, reducing

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heavy metal inputs to soil is a strategic aim of developing soil protection policies in the UK and EU (DETR, 2001; EC, 2001). However, information on the significance and extent of soil contamination with heavy metals from different sources is required so that appropriate actions can be effectively targeted to reduce inputs to soil.

A quantitative inventory of heavy metal inputs to agricultural soils is necessary to determine the scale and relative importance of different sources of metals, either deposited from the atmosphere or applied to farmland. Information on heavy metal input rates is also useful for estimating accumulation in soils (e.g. Harmsen, 1992). However, the quality of any inventory depends on the availability of the appropriate data and its robustness. Over time, new research can improve the quality of data available, and changes in farming practices or in the regulatory environment can have a significant impact on input estimates. Hence, it is important that such work is updated periodically so that confidence can be placed in the results.

Heavy metal inputs to agricultural land in the UK estimated by Critchley (1983) identified atmospheric deposition as the principal source of metals entering soil when viewed at a national level, whereas inorganic fertilisers and pesticides were responsible for relatively small rates of addition. Sewage sludge and livestock manures were also identified as significant sources of metals, albeit to a more limited land area. However, a number of important changes have taken place since 1983 which are likely to have affected the inputs of heavy metals to soils. These include, for example, the introduction of limits on metal supplementation of pig feeds (Anon, 2000a), reduced concentrations of metals in sewage sludge due to tighter trade effluent standards (Gendebien et al., 1999), the banning of pesticides containing mercury and arsenic, the sourcing of rock phosphates by the UK fertiliser industry that are low in Cd and reductions in atmospheric emissions of metals from industry as a result of improved emissions control.

The agricultural use of sewage sludge is a well established practice in the UK and is managed, regulated and monitored (UK SI, 1989; DoE, 1996) to minimise environmental problems. In particular, the controls specify precautionary maximum permissible heavy metals concentrations in soil and maximum annual rates of addition (Table 1) to protect soil fertility, crop yields and quality, and human and animal health (Smith, 1996). These values can also provide a benchmark to assess and compare heavy metal accumulation rates from diffuse sources such as atmospheric deposition and as contaminants in livestock manures, inorganic fertilisers and other materials applied purposefully to agricultural land for crop production. The regulations on agricultural use of sewage sludge currently represent the only statutory based mechanism for controlling heavy metal inputs to soils in the UK. However, a voluntary certification scheme was recently introduced for composted 'wastes' specifying limits on heavy metal concentrations in material that is ready for sale or distribution (Composting Association, 2000). New mandatory limits on heavy metals in livestock manures are currently being considered in Germany to protect soils from heavy metal accumulation from this important source (Environment Daily, 2002).

In this study, we present an inventory of heavy metal inputs to agricultural land in England and Wales from atmospheric deposition, sewage sludge, livestock manures, inorganic fertilisers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts, based on recent published data on heavy metal contents and estimated quantities of materials applied to soil for crop production. The relative importance of the different sources of metals at a national and individual field scale was estimated from the total quantities of metals deposited on agricultural land, as well as the annual rates of metal inputs per hectare of farmland. We have also assessed the implications of these input rates in terms of the time required to reach the statutory soil metal limits that are the basis of the controls to protect agricultural soil quality where sewage sludge is applied (UK SI, 1989; DoE, 1996).

2. Methodology

2.1. Atmospheric deposition

Extensive data were available on the total deposition (wet plus dry) of heavy metals to soil for

Table 1
Maximum permissible concentrations of potentially toxic elements in soils after application of sewage sludge and maximum annual rates of addition (DoE, 1996)

PTE	Maximum permissible concentration in soil (mg/kg dry soil)				Maximum permissible average annual rate of addition over a 10 year period (kg/ha)
	Soil pH value				
	5.0–5.5	5.5–6.0	6.0–7.0	>7.0	
Zn	200	200	200	300	15
Cu	80	100	135	200	7.5
Ni	50	60	75	110	3
	For pH 5.0 and above				
Cd	3				0.15
Pb[a]	300				15
Hg	1				0.1
Cr	400				15
Mo	4				0.2
Se	3				0.15
As	50				0.7
F	500				20

[a] The limit value for Pb will be reduced to 200 mg/kg dry soil in a future revision of The Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996) and the Sludge (Use in Agriculture) Regulations (UK SI, 1989).

a period of 42 months (1995–1998) from a network of monitoring stations at 34 rural sites in England and Wales (Alloway et al., 2000). Each monitoring station comprised duplicate inverted polystyrene 'frisbees' (22 cm diameter) mounted on posts 1.8 m above ground connected to polyethylene collecting bottles. The sites of the monitoring stations were selected to be remote from major roads and nearby industrial sources of pollution, with many located at agricultural research stations or working farms. Collecting bottles were changed monthly and the contents filtered through 0.45 μm membrane filters to separate the 'soluble' and 'insoluble' fractions. The soluble fractions following filtration were analysed in duplicate directly by ICP-OES for Zn, Cu, Ni, Pb, Cr and Cd, whilst the filter residues were dried and subsequently digested with concentrated nitric and hydrochloric acids followed by dilution, filtration and duplicate analysis by ICP-OES. Arsenic and Hg in the soluble fractions and digested filter residues were analysed by vapour generation atomic absorption spectrometry. Analytical quality control was assured by the use of reference solutions and the inclusion of an in-house solution of simulated rainfall with each batch. The analytical methods used were found to be sufficiently sensitive for all the heavy metals in both filtrate and filter residues (data not shown), except for Hg where the results should be viewed with caution.

Total metal deposition was estimated for the inventory from the average deposition rate for each metal and the total area of land on agricultural holdings in England and Wales as specified in the June Agricultural Census for 2000 (DEFRA, 2000).

2.2. Sewage sludge

Detailed statistics on the quantities of sewage sludge applied to agricultural land are collected by UK water service providers as required by EU and UK legislation (CEC, 1986; UK SI, 1989). The most recent survey of sludge production, quality, reuse and disposal was for the period 1996/1997 (Gendebien et al., 1999). During 1996/1997 approximately 50% of sludge production (480 000 t of dry solids-ds) was applied to 73 000 ha of agricultural land in England and Wales. Total metal inputs to land from this source were calculated from the weighted average metal concentrations for sludge used in agriculture (i.e. weighted on the basis of the quantity of sludge applied of different concentrations) and the total quantity of sludge dry solids applied. The loading rate from this source was also determined for comparison with livestock manures at a rate of application equivalent to 250 kg total N/ha (MAFF, 1998) using a weighted average total N concentration in sludge of 4.4% ds.

2.3. Livestock manures

Total heavy metal inputs to agricultural land from livestock manures were estimated from the livestock numbers reported in the June 2000 Agricultural Census (DEFRA, 2000), excreta production quantities (Anon, 2000b) and mean manure heavy metal concentrations for each livestock class (cattle, pigs, poultry) and manure type (slurry, farmyard manure, broiler litter, layer manure), based on data reported by Nicholson et al. (1999). Heavy metal loading rates were calculated assuming a manure application rate equivalent to 250 kg/ha total N as recommended in 'The MAFF Water Code' (MAFF, 1998) and the typical N content of livestock manures (Anon, 2000b).

2.4. Fertilisers and lime

Detailed statistics on fertiliser use on farms in the UK are provided in the Survey of Fertiliser Practice (Chalmers et al., 2001). Heavy metal contents in phosphate and other fertilisers used in the UK were recently surveyed (Marks, 1996). However, there was only limited and historical information on metal concentrations in liming materials (Chater and Williams, 1974).

2.5. Agrochemicals

The amounts of Zn and Cu applied to land in England and Wales were derived from published data on pesticide usage (Garthwaite and Thomas, 1999; Thomas and Wardman, 1999) and information on the heavy metal contents of the active ingredients (Whitehead, 2001).

2.6. Irrigation water

The amount of irrigation water used in England and Wales is reported every 2–3 years and varies greatly depending on the season (Anon, 1997). In this study, average values (from 1984, 1987, 1990, 1992 and 1995) for the area irrigated and the volumes of water applied were used, together with the Zn and Cu analyses of 23 borehole supplies and 7 stream/river samples to estimate metal inputs to soil from this source.

2.7. Industrial 'wastes'

The quantities and typical composition of industrial 'waste' materials applied to agricultural land in England and Wales were recently published in a European survey of 'wastes' spread on land (Gendebien et al., 2001). However, the actual amounts of these materials applied to land in the UK are not precisely known except for paper sludge, and approximate loadings have been used to calculate metal inputs from this diverse range of materials. Median chemical composition values were taken from Davis and Rudd (1998) based on 10 years of measurements on different types of 'wastes'. These data represent only a limited number of UK 'waste' sources, but provide a general indication of 'waste' composition. There are no published records available on the land areas treated with industrial 'wastes'.

2.8. Composts

Recent statistics on the quantity of composted materials produced in the UK and their end-uses are reported by Slater et al. (2001). These mostly comprise municipal waste composts derived from green wastes (89%) and a limited amount of domestic solid waste composts (7.5%). Information on the amounts of compost used for different purposes (soil conditioning, mulching) and the heavy metal contents of composted 'wastes' produced in the UK are also available (Slater et al., 2001; Anon, 1998).

2.9. Other sources

A number of other potential sources of heavy metal inputs to agricultural land were identified as being of local importance, but were not included in the inventory because of difficulties in estimating their contribution to overall metal inputs. These included flooding events, where material rich in heavy metals may be carried from an upstream source and be re-deposited on flooded land further downstream. Corrosion of metal farm buildings, fencing, gates and electrical installations could also be a significant source of some metals; for example, Lijzen and Ekelenkamp (1995) estimated that approximately 40% of total Zn inputs to soils in the Netherlands was from corrosion. However, the contamination is likely to remain localised in the immediate vicinity of the structures, rather than influencing metal concentrations of wider areas of agricultural land. Run-off or spray may contribute to the heavy metal burden of soils close to major roads. Abrasion of the machinery used to cultivate agricultural land has also been suggested as a potential (if minor) source of heavy metals.

3. Results and discussion

3.1. Atmospheric deposition

The most important sources of heavy metals in the atmosphere include energy production, mining, metal smelting and refining, manufacturing processes, transport and waste incineration (Nriagu, 1990). The transfer of particles containing these metals from the atmosphere to the earth's surface may occur by dry, wet or occult deposition, onto soil or vegetation surfaces (Haygarth and Jones, 1992). Metals deposited on the soil surface will gradually become incorporated into the soil and will contribute to overall soil concentrations. However, metals falling onto vegetation may remain on the leaf surface, be absorbed by the plant or be washed off into the soil by rainfall.

Atmospheric deposition is ubiquitous, although deposition rates vary depending on proximity to point sources of pollution such as heavy industry or major roads. There has been considerable effort devoted to measuring deposition in UK urban areas (e.g. Harrison, 1993). However, until recently, the measurement of atmospheric deposition rates to agricultural soils has received comparatively little attention. Cawse (1987) reported on a network of 7 rural sites, but these were not representative of the country as a whole, and the two inland sites were potentially influenced by industrial sources of metals. Deposition in rain gauges at ADAS Experimental Centres was reported by Wadsworth and Webber (1977), but was probably influenced by zinc contamination and did not account for dry deposition. Subsequently, specific studies conducted at various locations have measured atmospheric deposition but with specific objectives and different methodologies. Moreover, metal emissions to the atmosphere are likely to have changed markedly (mainly decreasing) over recent decades as a result of changes in the nature and distribution of industries and the introduction of pollution abatement regulations. Hence, it was recognised that a more comprehensive estimate of atmospheric deposition to agricultural land was required. The 'frisbee' monitoring network established by Alloway et al. (2000) collected total deposition data at 34 sites in England and Wales, providing baseline information on inputs to lowland agricultural soils and on national variations in diffuse sources of metal loadings to soils.

Zinc was the metal deposited on soil in the largest amounts from the atmosphere in England and Wales, followed by Cu and Pb (Table 2). The rate of Zn deposition was relatively consistent across all the monitoring stations (126–356 g/ha/yr) indicating that this element was probably emitted to the atmosphere from many different sources and may also be subject to long-range, trans-boundary transport. Deposition rates of the other elements were much more variable than for Zn and differed by up to an order of magnitude, probably indicative of local differences in conditions and releases to the atmosphere.

A recent study comparing different methods for estimating atmospheric heavy metal (Cd, Pb, Cu and Zn) deposition to the UK found that estimates from the 'frisbee' network were large compared to estimates using moss analysis or using an emission inventory and atmospheric transport model (Nemitz et al., 2000). The reasons for this apparent discrepancy are unclear, but could be due to the high particle collection efficiency of the 'frisbees' or local resuspension of soil particles. However, when the results were compared with atmospheric deposition data for 12 other European countries (Table 2), for most metals (Zn, Ni, Cd and Cr)

Table 2
Heavy metals deposition rates (g/ha/yr) in selected European countries

Country	Measurement										
	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg	Date	Method	Comments
England and Wales									1995–1998	Bulk deposition	34 rural sites (see text for details)
Mean	221	57	16	54	1.9	7.5	3.1	1.0			
Range	126–356	32–247	6–47	19–139	0.7–6.1	2.9–20	0.9–10	0.5–8.5			
Austria	500	100	2.1	8.5	2.7	6.2				Moss	Data from several studies
Belgium	62	7	2.5	24	<0.1						Data from several studies
Denmark	80	8	2.1	10.4	0.3	1.3	1.1		1999	Bulk deposition	7 evenly spread sites
Finland	20	5	1.5	5.7	0.2	0.5	0.7		1997–1999	Bulk deposition	8 background sites
Germany	540	53	11.0	57.2	2.5	7.0				Various	Data from several studies
Hungary	219	62	24.7	101.9	9.9					Bulk deposition	3 sites
Ireland	235	13	1.6	13.3	0.6	0.7			1997–1998	Rainfall	2 sites
Italy	289	60	35.0	58.1	3.3	45.6			1997	Surrogate dry deposition	1 rural site
Norway	68	12	6.0	16.1	0.6	1.7					Agricultural sites
Poland	540	40	20.0	100.0	2.0	30.0					Data from several studies
Sweden	118	15	0.5	6.3	0.8	5.0		0.1		Moss	
Switzerland	119	18	11.0	28.0	0.8	3.7			1999		16 sites
The Netherlands	162	27	10.6	47	1.3	2.5	3.2	0.7			
European average	227	34	10	38	1.9	9.3	2.0	0.6			

Sources: Alloway et al. (2000) and Eckel et al. (2001).

Table 3
Concentrations of heavy metals in different materials applied to agricultural soils for crop production and quantities applied annually in England and Wales

Source	Quantity applied (Mt ds)	Zn (mg/kg ds)	Cu	Ni	Pb	Cd	Cr	As	Hg
Sewage sludge[a]	0.44	802	565	59	221	3.4	163	6	2.3
Livestock manures[b]									
Cattle slurry	1.74	170	45	6.0	7.0	0.3	6.0	2.0	nd
Pig slurry	0.27	650	470	14.0	8.0	0.4	7.0	2.0	nd
Cattle FYM[c]	8.45	68	16	2.8	2.4	0.2	2.0	1.2	nd
Pig FYM	1.37	240	168	5.2	3.2	0.2	2.4	0.8	nd
Layer manure	0.30	583	90	10.0	9	1.3	5.7	0.3	nd
Broiler litter[d]	1.35	217	32	4.0	3.3	0.6	2.0	0.5	nd
Inorganic fertilisers									
Nitrogen	1.30	14	10	1.4	4.6	0.9	3.4	0.9	0.03
Phosphate	0.33	654	94	63	10.5	30.6	319	22	0.1
Potash	0.41	8	6	0.8	2.7	0.5	2	0.5	0.02
Lime	2.87	11	2	5.1	2.0	0.3	6	nd	nd
Industrial 'wastes'									
Paper sludge[e]	0.07	64	59	4.7	2.1	<1.2	6.9	nd	<0.05
Food industry waste—general[e]	0.07	110	26	0.1	<22	<6	<22	nd	<0.2
Textile waste—dyers and bleachers[e]	<0.01	276	253	3.2	13	<7	8	nd	<0.3
Compost[f]	0.06	75	25	10	65	0.7	50	nd	0.2

nd, No data.
[a] Weighted average metal concentrations for sludge used on agricultural land in England and Wales (Gendebien et al., 1999).
[b] Typical concentrations in manures (Nicholson et al., 1999).
[c] Includes sheep FYM.
[d] Includes broilers, pullets, other hens and other poultry.
[e] Assumes dry solids contents of 22, 5 and 4% for sewage sludge, food industry waste—general and textile waste—dyers and bleachers, respectively (Gendebien et al., 2001).
[f] Assumes a 40% dry solids content (Anon, 1998).

the rate of input from the atmosphere in England and Wales was similar to the European average. Deposition of Cu and Pb in England and Wales was higher than the average European value, but similar to the rates measured in Germany and Italy.

3.2. Sewage sludge

Heavy metals are present in UK sewage sludge as a result of domestic, road run-off and industrial inputs to the urban wastewater collection system (IC Consultants, 2001). Controls on industrial discharges of heavy metals and changes in industrial practices in the UK have markedly reduced the metal content of sewage sludge, so that diffuse inputs from domestic sources (particularly Cu associated with leaching from plumbing materials and use of Zn in body care products) have increased in relative importance (Comber and Gunn, 1996). The weighted average metal concentrations reported for sludge used on agricultural land are shown in Table 3.

Estimated input rates of heavy metals to soil in sewage sludge assuming an application rate of 250 kg N/ha/yr were lower than the maximum permitted rates of addition for the agricultural use of sludges (Table 1), but higher than those from any of the other sources at a field level (Table 4). In practice, the 'average actual' rate of sludge application is equivalent to 289 kg N/ha/yr (Gendebien et al., 1999) and so 'average actual' rates of metal additions would be proportionately higher than those given in Table 4. Nevertheless, in normal

Table 4
Heavy metal addition rates (g/ha/yr) to agricultural land in England and Wales from different sources

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	221	57	16	54	1.9	7.5	3.1	1.0
Sewage sludge[a]	4557	3210	335	1256	19	926	34	13
Livestock manures[a]								
Dairy cattle slurry	1063	281	38	44	1.9	35	13.8	0.2
Beef cattle slurry	1214	321	43	50	2.1	40	15.7	0.2
Pig slurry	2321	1679	50	29	1.4	24	7.5	0.1
Cattle FYM[b]	718	168	28	27	2.7	20	11.9	0.2
Pig FYM	2120	1488	48	27	2.0	22	8.7	0.1
Layer manure	2734	422	47	42	6.1	27	2.2	0.1
Broiler litter[c]	1142	175	20	18	2.6	11	1.9	0.1
Inorganic fertilisers								
Nitrogen	2.2	1.6	0.2	0.7	0.1	0.5	0.1	<0.1
Phosphate	34	4.9	3.3	0.5	1.6	17	1.1	<0.1
Potash	0.5	0.4	0.1	0.2	0.0	0.1	0.0	<0.1
Lime[d]	53	12	25	10	1.4	29	0.0	0.0
Irrigation water	39	16	1.6	0.8	0.1	0.1	1.2	nd
Paper sludge	1380	1270	102	45	12.5	150	nd	0.5

nd, No data.
[a] Rate of metal addition assuming an application rate equivalent to 250 kg N/ha/yr.
[b] Includes sheep FYM.
[c] Includes broilers, pullets, other hens and other poultry.
[d] Typically applied every 5 years to non-calcareous soils.

operational practice rates of sludge application are generally adjusted on the basis of nitrogen content and are not restricted by heavy metals.

Despite marked improvements in sludge quality, industrial inputs still typically represent up to 50% of the total metal loads in sewage sludge (IC Consultants, 2001). Large variations in metal concentrations are also apparent in sludges produced by different treatment works of comparable size (Gendebien et al., 1999) reflecting localised metal discharges to the urban wastewater collection system. This emphasises the importance of continued vigilance by the water industry in reducing metal discharges in industrial effluents to support the long-term operational and environmental sustainability of sludge recycling in agriculture.

3.3. Livestock manures

Heavy metals are present in livestock diets at background concentrations and may be added to certain feeds as supplementary trace elements for health and welfare reasons, or as growth promoters. Copper is added to growing pig diets as a cost-effective method of enhancing performance, and is thought to act as an anti-bacterial agent in the gut (Rosen and Roberts, 1996). Zinc is also used in weaner pig diets for the control of post-weaning scours (Holm, 1990). Both Zn and Cu are required in trace amounts as poultry enzyme co-factors (Underwood and Suttle, 1999). Small amounts of these heavy metals are naturally present in basal diets (e.g. cereals, soya), although supplements are added in mineral form to fully meet the birds' requirements. Other heavy metals may be present in livestock diets as a result of contamination of mineral supplements (e.g. some limestone added to laying hen feeds may contain relatively high levels of Cd). For all livestock, the majority of most heavy metals consumed in feed is excreted in the faeces or urine, and will thus be present in manure that is subsequently applied to land.

Manure will also contain heavy metals that have been ingested in drinking water or have been added with bedding materials (e.g. straw). Corrosion of the galvanised metal use to construct

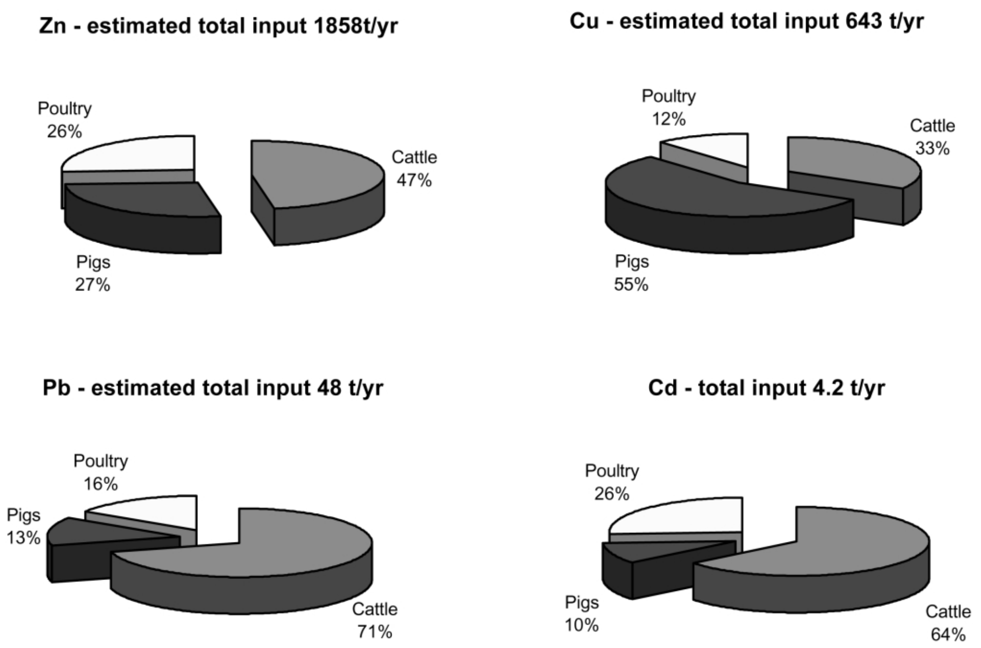

Fig. 1. Contribution of different animal types to selected total metal (Zn, Cu, Pb and Cd) inputs to agricultural land in livestock manures.

livestock housing and the licking and biting of metal housing components is a potential source of Zn in some manures. Footbaths containing Cu or Zn may be used as hoof disinfectants for sheep and cattle and these may be disposed of into manure stores thus contributing to the heavy metal content of manures spread to land.

Typical concentrations of heavy metals in livestock manures from a survey of 85 samples collected from commercial farms in England and Wales in the mid-1990s (Nicholson et al., 1999) are shown in Table 3. The highest concentrations of Zn and Cu were in pig slurry and laying hen manure, reflecting dietary supplementation. Approximately 1900 t of Zn and 650 t of Cu were applied in livestock manures to agricultural land in England and Wales in 2000. The majority ($>$ 60%) of most metals (Ni, Cr, Pb, Cd, As and Hg) applied were in cattle manures, due to the large quantities produced (c.10 Mt ds) rather than elevated metal contents (Table 3). In contrast, smaller quantities of pig and poultry manures were produced (c.3.3 Mt ds), but these supplied 53% of the Zn and 67% of the Cu inputs from livestock manures (Fig. 1), due to the elevated concentrations in the manure. Concentrations of Ni, Cr, Cd, Pb, As and Hg in livestock manures were much lower than those in sewage sludge. A recent EU initiative has proposed a reduction in the concentrations of heavy metals (particularly Zn and Cu) in livestock diets to minimise their subsequent environmental impact in land applied manures (CEC, 2000). However, this decision needs to be based on an objective assessment of the environmental, economic and animal welfare issues related to dietary supplementation compared with the impacts of alternative approaches available for animal production.

Heavy metal input rates to soils in England and Wales where handled livestock manures were applied at a rate of 250 kg total N/ha/yr are shown in Table 4. A proportion of the metal inputs from handled manures, as well as those excreted directly onto grazing land, are recycled through the agricultural system in animal feeds grown and fed on-farm. This recycling process is not account-

Table 5
Annual heavy metal inputs (t) to agricultural land in England and Wales for the year 2000

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	2457	631	178	604	21	83	35	11
Livestock manures	1858	643	53	48	4.2	36	16	0.3
Sewage sludge	385	271	28	106	1.6	78	2.9	1.1
Industrial 'wastes'	45	13	3	3	0.9	3.9	nd	0.1
Nitrogen	19	13	2	6	1.2	4	1.2	<0.1
Phosphate	213	30	21	3	10.0	104	7.2	<0.1
Potash	3	2	<1	1	0.2	1	0.2	<0.1
Lime	32	7	15	6	0.9	17	nd	nd
Total inorganic fertilisers	266	53	37	16	12	126	8.5	0.1
Agrochemicals	21	8	0	0	0	0	0	0
Irrigation water	5	2	<1	<1	<0.1	<1	0.1	nd
Composts	<1	<1	<1	<1	<0.1	<1	nd	<0.1
Total	5038	1621	299	778	40	327	62	13

nd, No data.

ed for in this inventory, hence Table 4 represents gross rather than net inputs from livestock manures and actual heavy metal soil accumulation rates will be lower. Also, there is evidence to suggest a manure application rate of 250 kg total N/ha/yr may not be representative of what occurs in practice on some farms. On pig and poultry farms with a limited land area, manure application rates may exceed 250 kg total N/ha/yr, however, on extensive grassland farms application rates may be much lower. Hence, the 'average actual' metal application rates on a particular farm may be proportionately higher or lower than those quoted in Table 4. Nevertheless, Table 4 provides a useful basis to compare metal inputs from livestock manures with those from sewage sludges applied at an equivalent rate.

3.4. Fertilisers and lime

The most widely recognised contamination of inorganic fertilisers is associated with Cd present in the rock phosphate feedstock of all phosphate fertiliser materials. Concerns relating to the potential consequences for human health from the accumulation of Cd in the environment (e.g. Jarup et al., 1998) have led to fertiliser manufacturers changing the source of raw materials to reduce inputs, and to the EU commissioning research on possible levy systems to reduce Cd inputs from this source (Oosterhuis et al., 2000). Heavy metals are also present in varying amounts in other inorganic fertilisers (nitrogen, potash) and in liming materials.

As expected, phosphate fertilisers in particular, were an important source of heavy metals entering agricultural soils, particularly for Zn, Cu and Cd (Table 5). Heavy metal inputs with lime were also relatively high, but this was largely due to the large quantities (2.9 Mt in 2000) applied, rather than elevated heavy metal concentrations (Table 3).

Copper deficiency is associated with sandy, shallow soils over chalk and peaty soils. Approximately 5% of the cereal growing area in England and Wales, and 30% in Scotland has been estimated to be deficient in soil copper for cereal crops (Chalmers et al., 1999). Zn deficiency can arise where there is a low total content in soils, or more commonly where soil conditions reduce its availability (e.g. high pH). Of the trace element fertilisers used in England and Wales, only Cu is regularly applied, with c.2% of the total cropping area reported to receive a foliar Cu spray in 1991 at rates of 70–600 g/ha (ADAS, 1992). We were unable to locate any reported data on soil application rates of Cu or the application of other trace element fertilisers.

3.5. Agrochemicals

The agricultural use of mercury and arsenic containing pesticides is no longer permitted in the UK, and only a small number of approved pesticides contain other heavy metals. Zinc is a minor constituent of some fungicides that are applied to winter wheat and potatoes, whilst Cu is used as a fungicide for top fruit and hops. A total input of 21 t of Zn and 8 t of Cu was estimated to be applied annually in agrochemical products to agricultural land in England and Wales (Table 5).

These quantities are much lower than those in countries with extensive viticulture where inorganic fungicides with a high Cu content (e.g. Bordeaux mixture) are regularly applied to vineyards. For example, estimates suggest that at least 5500 t of Cu are applied annually in Italy and approximately 3500 t annually in France (Eckel et al., 2001). Other products used to control disease in vineyards may contain As with, for example, 800–900 t of As applied annually in France (Eckel et al., 2001).

3.6. Irrigation water

In the UK, irrigation is practised only in certain regions, mainly on light soils and for high value crops (e.g. potatoes, sugar beet). The annual amount of irrigation water used in England and Wales varies greatly depending on the season, with greater amounts applied during dry conditions (Anon, 1997). On average, 85 million m^3 of irrigation water was applied to an area of 122 400 ha over the period 1984–1992 (equivalent to 694 m^3/ha/yr). The majority of irrigation water comes from rivers and streams (48%) or boreholes (29%). Analysis of 23 borehole supplies and 7 stream/river samples (ADAS, unpublished data) showed little difference in Zn (30 μg/l) and Cu (4 μg/l) concentrations between the two water sources. Irrigation water was a relatively minor source of heavy metals to agricultural land in England and Wales at an individual field level (Table 4).

3.7. Industrial 'wastes'

The recycling of industrial 'wastes' to agricultural land is an expanding practice as measures to reduce the disposal of organic 'wastes' to landfill are introduced (CEU, 1999). In the UK, landspreading of industrial wastes is normally carried out under exemptions from Waste Management Licensing Regulations (SI, 1994) which implement the Wastes Framework Directive. Under these regulations, 'waste' materials applied to farmland must be shown to confer 'agricultural benefit', which according to one suggested definition (Davis and Rudd, 1998) means that application should improve soil conditions for crop growth whilst ensuring the protection of environmental quality (for example, the material may be applied as a soil conditioner and/or source of plant nutrients). Materials commonly applied include by-products from the food industry (e.g. meat and dairy processing, breweries and soft drinks manufacture), abattoirs, paper and textile production, tanneries and pharmaceutical/chemical processing. Organic materials are the main sources of metals applied to soil in this category, as they represent $>$90% of the industrial 'wastes' applied to land (Gendebien et al., 2001). The heavy metal content of industrial 'wastes' varies greatly depending on the source, but some typical examples are shown in Table 3.

The carbon content and liming properties of paper sludge make it a valuable soil conditioner particularly for thin, acidic soils and the paper industry have produced a Code of Practice on best management practices for land (Paper Federation of Great Britain, 1998). At a typical application rate of 100 t/ha fresh weight, heavy metal input rates (Table 4) were considerably lower than the maximum permitted values for sewage sludge application (Table 1). There was insufficient information to calculate metal input rates from other types of industrial 'wastes'.

3.8. Composts

The total amount of compost produced in the UK in 1999 was 462 700 t and it was assumed in this inventory that 92% of this was generated in England and Wales, of which one third was applied to agricultural land as a soil conditioner (Slater et al., 2001). There was no information on the area of land receiving compost, so actual application rates could not be calculated.

Currently, composts represent a relatively minor source of heavy metals to agricultural land compared with other inputs (Table 5) and the recommended compost quality standards will continue to restrict metal inputs from this source (Composting Association, 2000). However, expansion of the composting industry is anticipated in response to European and national policies encouraging the diversion of organic wastes from landfill disposal, and this will increase the recycling of composted materials to farmland in the future.

3.9. An inventory of heavy metal inputs

Annual heavy metal inputs to agricultural land in England and Wales (2000) from all the sources considered are summarised in Table 5. For Zn and Cu, approximately 40% of total annual inputs to agricultural land were derived from livestock manures, 38–48% from atmospheric deposition and 8–16% from sewage sludge. In contrast, 55–77% of Ni, Pb and As inputs were from atmospheric deposition and only 6–27% from livestock manures. For Cd, 53% of inputs were from atmospheric deposition and 30% from inorganic fertilisers (mainly phosphate fertilisers) and lime, with 11% from animal manures. The major sources of Cr to agricultural land were phosphate fertilisers, sewage sludge and atmospheric deposition. Over 85% of Hg inputs were from atmospheric deposition.

Although atmospheric deposition was an important source of heavy metals to agricultural land in terms of total quantities on a national scale, input rates on an individual field basis were small compared with those associated with metal contamination of sewage sludge and livestock manures applied to agricultural soils for crop production (Table 4). The highest input rates of all metals were for sewage sludge (applied at 250 kg total N/ha/yr), although sewage sludge generally represented <25% of the total metal inputs and the land area receiving sludge annually was relatively small (<1% agricultural land; Gendebien et al., 1999). Zinc and Cu input rates from pig and poultry manures applied at an equivalent N rate (250 kg total N/ha/yr) were c.45% of the sewage sludge input rates for these metals. Metal input rates from cattle manures were generally low in comparison with sewage sludge and pig or poultry manures, except for some elevation for Zn (due to supplementation of dairy cattle diets to maintain fertility) and As (probably as a result of inadvertent contamination of feeds with other mineral supplements).

3.10. Implications for soil quality

The heavy metal input rates were used to estimate the time (number of years) required to raise topsoil concentrations from background values (mean concentrations in England and Wales taken from McGrath and Loveland, 1992) to the maximum permissible limits for heavy metals stipulated in the controls on the agricultural use of sewage sludge (Table 1), assuming all fields received inputs from atmospheric deposition and there were no losses of metals (e.g. via crop offtake or leaching). Soil Zn would be raised to the limit value (200 mg Zn/kg dry soil) after approximately 80 years of sewage sludge additions compared with 130–164 years if pig or laying hen manures were applied annually at rates of 250 kg/ha total N (Table 6). However, these times would be decreased if soil Zn concentrations were already elevated above background values, if more than one material was applied to a field each year or if application rates or Zn concentrations were higher than those assumed here. In comparison, it would take >1700 years for atmospheric deposition alone to raise topsoil Zn to the limit concentrations. Similar estimates for other metals (Cu, Ni, Pb, Cd and Cr) are provided in Table 6.

This inventory of heavy metal inputs to agricultural land demonstrates that agricultural soils are potentially at risk of heavy metal accumulation from the application of pig and poultry manures. It may become necessary to introduce maximum permissible soil metal concentrations to protect agricultural land from long-term heavy metal accumulation from these types of livestock manures (similar to the controls currently in place for sewage sludge applications), unless strategies can

Table 6
Time (years) required to raise soil metals concentrations from background[a] to limit[b] concentrations

Source	Zn	Cu	Ni	Pb	Cd	Cr
Sewage sludge	80	116	485	645	352	1256
Layer manure	130	794	2709	8749	933	> 10 000
Pig slurry	151	219	2580	> 10 000	2232	> 10 000
Pig FYM	164	246	2667	> 10 000	1892	> 10 000
Broiler litter	281	1642	4705	> 10 000	1648	> 10 000
Cattle slurry	358	1348	> 10 000	9452	2186	> 10 000
Cattle FYM	408	1688	3881	> 10 000	1621	> 10 000
Atmospheric deposition	1733	6689	> 10 000	> 10 000	3893	> 10 000
Paper sludge	239	286	1443	8501	518	7444
Fertilisers and lime	1234	5055	3868	> 10 000	1459	> 10 000
Irrigation water	1473	6689	> 10 000	> 10 000	3893	> 10 000

Calculations assume a soil density of 1.3 g/cm^3 and a cultivation depth of 25 cm.
[a] Mean soil concentration in England and Wales (McGrath and Loveland, 1992).
[b] Maximum permissible soil concentration (at soil pH 6.0–7.0 for Zn, Cu and Ni) where sewage sludge is applied (DoE, 1996).

be found to reduce the metal content of these manures.

This inventory has been based on total heavy metal inputs, but it is widely recognised that their bioavailability, especially uptake by plants, will vary considerably depending on the form of the metal entering the soil, the soil physico-chemical conditions and the genotype of the crop plant (Alloway, 1995). These variables are too complex to take into consideration in a national inventory, but it must be remembered that the impact of the metals in a soil will vary between sites. This will be particularly so with metal inputs from sewage sludge and livestock manures where the amounts added to individual fields can be relatively large in the long-term, in comparison with the relatively small amounts added per hectare by atmospheric deposition. Some authors have already attempted to develop risk assessment methods that use soil physico-chemical characteristics to estimate soil sensitivity to heavy metal inputs at both the site scale (Blume and Brummer, 1991) and at a national scale in relation to sewage sludge applications (Towers and Paterson, 1997).

4. Conclusions

In response to concerns over the impact of heavy metal on long-term soil fertility and the potential transfer of certain metals to human diets, an inventory of heavy metal inputs to agricultural soils was developed for England and Wales (for the year 2000). The known major sources of heavy metals considered included atmospheric deposition, sewage sludge, livestock manures, inorganic fertilisers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts. Atmospheric deposition was the main source of most metals entering agricultural land, with livestock manures and sewage sludge also locally important sources. The highest rates of heavy metal inputs on an individual field basis were from sewage sludge, although this practice is regulated and monitored within carefully controlled limits. Inputs of Zn and Cu from pig and poultry manures, which are applied to larger areas of farmland, were c.45% of those from sewage sludge. This study will assist in the development of strategies for reducing heavy metal inputs to agricultural land and to effectively target policies for preserving long-term soil quality.

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