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SP0547: Sources and Impacts of Past, Current and Future Contamination of Soil

Appendix 1 : Heavy metals

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1.1 Introduction

This group of potentially toxic elements (PTEs) includes zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As) and mercury (Hg). Potentially significant emerging metals include the platinum group elements (PGEs), uranium (U) and vanadium (V). Whilst PTEs display a range of properties in soils, leaching losses and plant uptake are usually relatively small compared with the total quantities entering the soil from different diffuse and agricultural sources. As a consequence, they tend to slowly accumulate in topsoils over time. This could have long-term implications for the quality of agricultural soils, including phytotoxicity at high concentrations, the maintenance of soil microbial processes (e.g. nitrogen fixation, biological activity), and the transfer of zootoxic elements to the human diet from increased crop uptake or soil ingestion by grazing livestock (e.g. cadmium and lead).

Some heavy metals (e.g. Cd, Pb, Hg) have no known biological function and can cause serious health problems if they enter the human food chain. Others (e.g. Zn, Cu) are trace elements essential to the functioning of biological systems, although at elevated concentrations they can become toxic. To assess the relative importance of soil contamination by different heavy metals, it is important to consider their toxicity to different receptors namely humans, animals, plants and soil biota.

1.1.1. Highly toxic metals with no known biological function

Cadmium can cause a range of chronic human health problems and as a consequence, it is one of a small group of metals for which the FAO/WHO have set a provisional limit for daily intake by humans. The European Union has also introduced legislation defining the maximum permissible concentration (MPC) of Cd in a range of foodstuffs (EC, 2001).

Cadmium has been shown to accumulate in the organs of livestock grazing on land where phosphate fertilisers or sewage sludge have been applied over a number of years (e.g. Lee *et al*., 1994; Hill *et al*., 1998). Cd is also toxic to plants at high concentrations, although heavy metal tolerance can develop in certain species or populations (e.g. Turner, 1996). In addition, adverse effects on soil organisms and microbial processes have been demonstrated (e.g. McGrath, 1996). Cd is highly labile in soils (especially at low soil pH), and soils with high concentrations must be managed appropriately to avoid transfer into the human food chain.

Mercury is one of the most toxic elements to humans and higher animals, with the different forms (in particular methyl mercury) exhibiting a variety of symptoms including teratogenic, carcinogenic and mutagenic effects. The main sources of human exposure to Hg are from dental amalgam and in the diet. Indeed, the FAO/WHO have jointly set a provisional tolerable weekly intake (PTWI) of Hg in the diet of 0.3 mg, of which no more than 0.2 mg should be organic mercury. Hg is toxic to soil organisms and microbial processes (e.g. Muller *et al*., 2001). Moreover it can be released from the soil by volatilisation or transformed by methylation into more toxic forms.

Lead poisoning, especially in young children, is a global environmental and public health hazard (Adriano, 2001), which has led to the prohibition of Pb additives in petrol and paint in many countries. Pb is also covered by the recent European Union legislation defining the MPC in a range of foodstuffs (EC, 2001). Pb is less labile in soils than Cd, and even at high concentrations uptake by plants is usually small.

1.1.2. Metals with some (or poorly understood) biological function

Inorganic forms of As are highly toxic to humans and animals, and the JECFA has set a provisional tolerable weekly intake for inorganic arsenic (but not for organic or for total arsenic). However, there is some evidence of As requirement by livestock (Underwood and Suttle, 1999). Nickel and Cr are essential for human, animal and plant metabolism, although the WHO has set a Tolerable Daily Intake (TDI) for Ni. Arsenic, Ni and Cr are moderately labile in soils but phytotoxic only on contaminated soils.

1.1.3. Essential trace elements

Zinc and Cu are essential trace elements for humans, animals and higher plants, although both elements have been assigned a provisional maximum TDI by the WHO.

Copper deficiency in grazing ruminants is widely reported in many parts of the world, often due to interaction with a high level of soil Mo. In contrast, sheep are sensitive to Cu toxicity and may experience problems if grazed on pastures with high soil Cu concentrations. Crops such as cereals are sensitive to Cu deficiency, and in some areas of the country Cu is applied as a trace element fertiliser. Nevertheless, both Zn and Cu can be phytotoxic at high soil concentrations and have been shown to have adverse affects on soil microorganisms & microbial processes (e.g. McGrath, 1996; Lock and Janssen, 2005).

1.1.4. Other metals

Uranium (U) has a tendency to accumulate in bones or to cause functional disturbances of the liver, kidneys and lungs, as well as cancer and mutations. The concentration of U normally found in soils depends on the parent rock material, although contamination through emissions from the nuclear industry are clearly a major concern (see Appendix 3). The soluble fraction is readily absorbed by plants and in excess can lead to phytotoxicty. There is no clear evidence to support the essentiality (or otherwise) of vanadium (V) for plant growth, although phytotoxicty was demonstrated in early studies on phosphate fertilisers.

There have been concerns that Pt emitted by catalytic converters and inhaled with roadside dust could operate as an allergen, with obvious implications for the health of people living in urban environments or along major highways. However, the Pt emitted by catalytic converters is largely in the metallic form, which is considered to be biologically inert and non-allergenic so its sensitising potential is probably very low (Farago *et al*., 1998).

1.1.5.Summary

Controlling inputs of heavy metals to soils is of great importance because of their persistence in soils once they are present. Soil contamination by Cd, Hg and Pb presents a significant problem because of the seriousness of the human health effects if these elements are allowed to enter the foodchain. Similarly, soil contamination particularly by Zn and Cu may have serious implications for long-term soil fertility and the potential for soils to support microbial populations and crop growth.

1.2. The heavy metal inventory methodology

Reducing heavy metal inputs to soils is a strategic aim of soil protection policies in the UK (Defra, 2004) and the EU (EC, 2002). 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 soils. A quantitative inventory of heavy metal (Zn, Cu, Ni, Cr, Pb, Cd, Hg, As) inputs to agricultural soils can determine the scale and relative importance of different sources of metals, either deposited from the atmosphere or applied to agricultural land. Information on heavy metal inputs is also useful for estimating accumulation rates in soils at the national, catchment and field scale.

It is important to be aware that in its current form the inventory is not sensitive to all changes in farming practices and legislation because not all the appropriate data is available. A good example is the estimates of metal inputs from livestock manures, which are derived in part from animal numbers in the 2004 Agricultural Census. Thus, changes in the composition of the livestock sector since 2000 (e.g. due to foot and mouth disease or economic pressures) will be reflected in the inventory. But the estimate also relies on typical manure metal concentrations from data collected in the mid-1990s and will clearly not capture the more recent reductions in the maximum permitted levels of Zn and Cu in certain livestock feeds (EC, 2003). Suggestions for improving the inventory data and methodology are given in Section 11.

The inventory methodology was by necessity based on total heavy metal inputs. However, when interpreting the pressures from total metal loading rates it should be noted that metal bioavailability, especially uptake by plants, varies considerably depending on the form of the metal entering the soil, the soil physico-chemical conditions and the genotype of the crop plant. Moreover, climate change effects, such as changes in rainfall patterns, average temperatures and extremes may increase the rate of soil organic matter oxidation through extending the proportion of the year with warm wet soils, and thereby increase metal bioavailability to plants and micro-organisms. This will be particularly so with metal inputs from sewage sludge, livestock manures and composts etc. where the amounts added to individual fields can be large in comparison with the relatively small amounts added per hectare by atmospheric deposition.

1.3 Sources of heavy metals to agricultural soils

1.3.1 Atmospheric deposition

The most important emission sources of heavy metals to the atmosphere include energy production, mining, metal smelting and refining, manufacturing processes, transport and waste incineration (Nriagu, 1990). Metals deposited on the soil surface will gradually become incorporated into the soil and will contribute to overall soil concentrations. Atmospheric deposition is ubiquitous, although deposition rates vary depending on proximity to point sources of pollution, such as heavy industry or major roads.

A 'frisbee' monitoring network was established by Alloway *et al*. (2000) to collect total deposition (wet plus dry) data at 34 sites in England and Wales for a period of 42 months (1995-1998). This provided baseline information on inputs to lowland agricultural soils and on national variations in diffuse sources of metal loadings to soils. Total metal deposition was estimated in the inventory from the average deposition rate of each metal and the total area of land on agricultural holdings in England and Wales, as specified in the June Agricultural Census for 2004 (Defra, 2004).

Zinc was the metal deposited on soil in the largest amounts from the atmosphere in England and Wales, followed by Cu and Pb (Table A1.1). 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 emissions to the atmosphere.

A recent study comparing different methods for estimating atmospheric heavy metal (Cd, Pb, Cu and Zn) deposition in the UK found that estimates from the 'frisbee' network were greater than those estimated using moss surveys or using an emission inventory and atmospheric transport model (Nemitz *et al*., 2000). For example, the total deposition of Zn to England and Wales was calculated to be 5552 t using the 'frisbee' results, 2985-4591 t using the moss surveys and 389 t using the modelling approach (*Nemitz et al*., 2000). The reasons for these apparent discrepancies are unclear. However, analysis of the soluble and insoluble fractions of the 'frisbee' deposition samples showed that 75% of the Zn, 77% of the Cu and 67% of the Cd was present in a soluble form, indicating that the source was unlikely to have been local soil suspension and redeposition in the frisbees.

A preliminary comparison of the results with atmospheric deposition data from 12 other European countries (Table A1.1) showed that for most metals (Zn, Ni, Cd, Cr) the rate of input from the atmosphere in England and Wales was in the middle of the range measured in the other countries. Deposition of Cu and Pb in England and Wales was higher than many other EU countries, but similar to the rates measured in Germany and Italy. Whilst this agreement is reassuring, interpretation of these data should still be undertaken with care as the monitoring methods and network design were not the same in all countries.

1.3.2 Sewage sludge (biosolids)

Heavy metals are present in 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 (Gendebien *et al*., 1999). This has meant 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 most recent survey of sludge production, quality, reuse and disposal was for the period 1996/7 (Gendebien *et al*., 1999). During 1996/7, 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 in sludge used in agriculture (i.e. weighted on the basis of the quantity of sludge applied of different concentrations) and the total quantity of

Table A1.1. Heavy metals deposition rates (g/ha/yr) in selected European countries[a]

Country		Zn	Cu	Ni	Pb	Cd	Cr	As	Hg	Date	Method	Comments
England & Wales										1995-8	Bulk deposition	34 rural sites
	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	nd	nd		Moss	Data from several studies
Belgium		62	7	2.5	24	<0.1	nd	nd	nd		Not stated	Data from several studies
Denmark		80	8	2.1	10.4	0.3	1.3	1.1	nd	1999	Bulk deposition	7 evenly spread sites
Finland		20	5	1.5	5.7	0.2	0.5	0.7	nd	1997-9	Bulk deposition	8 background sites
Germany		540	53	11.0	57.2	2.5	7.0	nd	nd		Various	Data from several studies
Hungary		219	62	24.7	101.9	9.9		nd	nd		Bulk deposition	3 sites
Ireland		235	13	1.6	13.3	0.6	0.7	nd	nd	1997-8	Rainfall	2 sites
Italy		289	60	35.0	58.1	3.3	45.6	nd	nd	1997	Surrogate dry deposition	1 rural site
Norway		68	12	6.0	16.1	0.6	1.7	nd	nd		Not stated	Agricultural sites
Poland		540	40	20.0	100.0	2.0	30.0	nd	nd		Not stated	Data from several studies
Sweden		118	15	0.5	6.3	0.8	5.0	nd	0.1		Moss	
Switzerland		119	18	11.0	28.0	0.8	3.7	nd	nd	1999	Not stated	16 sites
The Netherlands		162	27	10.6	47	1.3	2.5	3.2	0.7		Not stated	

[a]Sources : Alloway et al. 2000; Eckel et al. 2001. nd = no data

Table A1.2. Concentrations of heavy metals in different materials applied to agricultural soils for crop production and quantities applied annually in England and Wales (see text for full details of data age and provenance).

Source	Quantity applied (Mt ds)	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
					(mg/kg ds)				
Sewage sludge[a]	0.48	802	565	59	221	3.4	163	6	2.3
Septic tank sludge[b]	0.01	649	nd	nd	nd	nd	nd	nd	nd
Livestock manures[c]									
Cattle slurry	1.51	170	45	6.0	7.0	0.3	6.0	2.0	nd
Pig slurry	0.20	650	470	14.0	8.0	0.4	7.0	2.0	nd
Cattle FYM[d]	8.01	68	16	2.8	2.4	0.2	2.0	1.2	nd
Pig FYM	1.05	240	168	5.2	3.2	0.2	2.4	0.8	nd
Layer manure	0.29	583	90	10.0	9	1.3	5.7	0.3	nd
Broiler litter[e]	1.33	217	32	4.0	3.3	0.6	2.0	0.5	nd
Inorganic fertilisers									
Nitrogen	0.99	14	10	1.4	4.6	0.9	3.4	0.9	0.03
Phosphate	0.23	654	94	63	10.5	30.6	319	22	0.1
Potash	0.31	8	6	0.8	2.7	0.5	2	0.5	0.02
Lime	2.70	11	2	5.1	2.0	0.3	6	nd	nd
Industrial 'wastes'									
Paper sludge[f]									
- primary + secondary physically/chemically treated	0.20	51-115	38-57	2.8-3.3	7.8-8.4	0.1	4.9-6.8	nd	0.1
-secondary biologically treated	0.06	136	108	10.3	28.6	0.7	17.9	nd	0.2
Food industry waste – general[g]	0.07	110	26	0.1	<22	<6	<22	nd	<0.2
Textile waste – dyers and bleachers[g]	<0.01	276	253	3.2	13	<7	8	nd	<0.3
Compost[h]	0.29	182	46	17	96	0.6	19.8	nd	0.2
Dredgings[i]	0.78	308	43	39	76	1.0	4.0	11	0.2

nd – no data

[a]Weighted average metal concentrations for sludge used on agricultural land in England and Wales in 1996/7 (Gendebien *et al*. 1999).

[b]Quantitiy applied is a broad estimate (see text for details). Concentrations are for 11 samples taken in 1995

[c]Typical concentrations in manures sampled in the mid-1990s (Nicholson *et al*.,1999)

[d]Includes sheep FYM

[e]Includes broilers, turkeys, pullets, other hens and other poultry

[f]Data for 2003. Assumes dry solids contents of 43, 28 and 40% respectively.(Gibbs *et al*., 2005)

[g]Assumes dry solids contents of 5 and 4% for food industry waste – general and textile waste – dyers and bleachers, respectively (Gendebien *et al*., 2001)

[h]Concentrations are averages of data from 1995-2004 from WRAP (2004) and The Composting Association (E. Nicolls, pers. comm.). Assumes a dry solids content of 65%.

[i]Concentrations are averages of samples collected in 2004/5 by ADAS (S.Royle, pers. comm.). Assumes a dry solids content of 40%

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. The weighted average metal concentrations reported for sludge used on agricultural land are shown in Table A1.2.

Estimated input rates of heavy metals to soil with 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 A1.3), but higher than those from most of the other sources at a field level (Table A1.4). In normal 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.

Table A1.3. 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).

1.3.3 Septic tank sludge

There are no published data on the quantities or composition of septic tank sludge applied to agricultural land in the UK. However, it has been estimated that there are about 800,000 septic tanks in the UK (www.chestercc.gov.uk). Tanks for domestic purposes should have a minimum volume of 2700 litres for a family of 4 people (www.barnsley.gov.uk). In our calculations it was assumed that most tanks were for domestic households and all tanks were emptied at least once a year (as recommended), which equates to a total volume of septic tank sludge of 2.16 million m^3 per year. Data on the chemical composition of septic tank sludge were obtained from 11 samples taken in 1995 from a commercial company operating in the South West of England. These data indicated that the Zn content of septic tank sludge was c.650 mg/kg ds (compared with typically 802 mg/kg ds for sewage sludge). This equates to a total annual input of 9 tonnes Zn in England and Wales assuming that all septic tank sludge is all applied directly to agricultural land. If the septic tank sludge was applied to land at a rate equivalent to 250 kg N/ha, then the Zn addition rate would be c.4000 g/ha/yr, which is just lower than the rate from sewage sludge (4557 g Zn/ha/yr). There was no information for the other heavy metals.

Table A1.4. Heavy metal addition rates (g/ha/yr) to agricultural land in England and Wales from different sources, and the area (000 ha) receiving inputs from each source.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg	Area
Atmospheric deposition[a]	221	57	16	54	1.9	7.5	3.1	1.0	11228
Sewage sludge[a]	4557	3210	335	1256	19	926	34	13	73
Livestock manures[b]									
Dairy cattle slurry	1063	281	38	44	1.9	35	14	0.2	nd
Beef cattle slurry	1214	321	43	50	2.1	40	16	0.2	nd
Pig slurry	2321	1679	50	29	1.4	24	7.5	0.1	nd
Cattle FYM[c]	718	168	28	27	2.7	20	12	0.2	nd
Pig FYM	2120	1488	48	27	2.0	22	8.7	0.1	nd
Layer manure	2734	422	47	42	6.1	27	2.2	0.1	nd
Broiler litter[d]	1142	175	20	18	2.6	11	1.9	0.1	nd
Inorganic fertilisers									
Nitrogen	2.0	1.5	0.2	0.6	0.1	0.5	0.1	<0.1	8961
Phosphate	29	4.1	2.8	0.5	1.3	14	1.0	<0.1	8961
Potash	0.5	0.4	0.0	0.2	0.0	0.1	0.0	<0.1	8961
Lime[e]	56	12	26	10	1.5	31	0.0	0.0	8961
Irrigation water	39	16	1.6	0.8	0.1	0.1	1.2	nd	129
Paper sludge									
- primary treated	1511	1139	83	248	3	145	nd	3	nd
-secondary biologically treated	1257	1000	96	264	7	165	nd	2	nd
- secondary physically/chemically treated	3167	1580	90	214	3	186	nd	3	nd
Compost[b]	4221	1077	405	2233	14	459	0	6	nd
Dredgings	159900	22230	20020	39520	520	21580	5590	117	nd
Fungicides									
Hops	12888	2732							2
Fruit	125	1260							1
Arable	45								461
Lead shot				1900000					6
Corrosion[a]	5.2								11228

nd – no data
[a]Assumes an even distribution across the whole agricultural land area
[b]Rate of metal addition assuming an application rate equivalent to 250 kg N/ha/yr
[c]Includes sheep FYM
[c]dncludes broilers, pullets, other hens and other poultry
[e]Typically applied every 5 years to non-calcareous soils

Septic tank sludge is not covered by the the 'Safe Sludge Matrix'. However there are several options for its disposal/use :

- Spreading under the Sludge Regulations 1989 on land growing commercial food crops including for stock rearing purposes.
- Taken to a sewage treatment works (STW) under a paragraph 10A exemption.
- Taken to an appropriately licensed/authorised waste facility.
- Spread to land under a Waste Management License.

It is likely that most septic tank sludge is disposed of at sewage treatment works and not applied directly to agricultural land. The metals in septic tank sludge have therefore not been included as a separate item in the inventory.

1.3.4 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, 2000). 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 heavy metals consumed in feed are excreted in the faeces or urine, and will thus be present in livestock manure that is subsequently applied to land.

Manures 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 some 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 cattle and these should be disposed of into manure stores, thus contributing to the heavy metal content of manures spread to land (see section 2.2.12 below).

Typical heavy metals concentrations 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 A1.2. The highest concentrations of Zn and Cu were in pig slurry and laying hen manure, reflecting the levels of dietary supplementation.

Total heavy metal inputs to agricultural land from livestock manures were estimated from the livestock numbers reported in the June 2004 Agricultural Census (Defra, 2004), excreta production quantities (Anon, 2000a) 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 the 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 as a statutory requirement in Nitrate Vulnerable Zones (Defra, 2002), and the typical N content of livestock manures (Anon, 2000b).

Approximately 1700t of Zn and 540t of Cu were estimated to be applied with livestock manures to agricultural land in England and Wales in 2004. This was considerably lower than the 1900t of Zn and 650t Cu estimated for 2000 as a result of reductions in livestock numbers (mainly pigs and dairy cattle). The majority (>60%) of most metals (Ni, Cr, Pb, Cd, As, Hg) applied were in cattle manures, due to the large quantities produced (*c.*9.5 Mt ds) rather than elevated metal contents (Table A1.2). In contrast, smaller quantities of pig and poultry manures were produced (*c.2.9* Mt ds), but these supplied 51 and 63% of the total Zn and Cu inputs, respectively, due elevated manure concentrations. Concentrations of Ni, Cr, Cd, Pb, As and Hg in livestock manures were generally much lower than those in sewage sludge and compost applied to land (Table A1.2).

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 A1.4. A proportion of the metal inputs from handled manures (particularly cattle 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 accounted for in this inventory, hence Table A1.4 represents gross rather than net inputs from livestock manures and actual soil heavy metal accumulation rates will be lower. Also, on extensive livestock farms manure application rates will be lower than 250 kg/ha N. Nevertheless, Table A1.4 provides a useful basis to compare metal inputs from livestock manures with those from sewage sludges and composts applied at an equivalent rate.

Table A1.5. Previous (SI, 2000) and current (EC, 2003) maximum permitted levels of zinc and copper in livestock feeds (mg/kg complete feed)

Livestock category	Zinc		Copper	
	Previous	Current	Previous	Current
Pigs				
Up to 16 weeks	-	-	175	-
Up to 12 weeks	-	-	-	170
17 weeks – 6 months	-	-	100	25
Other pigs	-	-	35	25
All pigs	250	150	-	-
Poultry				
Layer	250	150	35	25
Broiler grower	250	150	35	25
Broiler finisher	250	150	35	25
Ruminants				
Pre rumination	-	200	-	15
Dairy and beef cattle	250	150	35	35
Sheep	250	150	15	15

Recent legislation which came into force in January 2004 (EC, 2003) has reduced the maximum permitted level of Zn and Cu supplementation in livestock diets to minimise their subsequent environmental impact in land applied manures. Table A1.5 shows the previous and current levels of Zn and Cu permitted in livestock diets. It can be inferred that considerable reductions in manure Zn and Cu concentrations will result as farmers implement this legislation. A projection of the likely effects of this reduction in feed Zn and Cu supplementation on soil metal inputs has been made in section 2.3.1. However, it should be noted that estimates of manure metal concentrations based solely on feed input data may be flawed as farmers can use metals (e.g. Zn) under veterinary prescription and similarly Cu inputs in cattle feeds enhance fertility.

1.3.5 Fertilisers and lime

Heavy metals are present in varying amounts in inorganic fertilisers (nitrogen, phosphate, potash) and in liming materials. The most widely recognised contamination of inorganic fertilisers is associated with Cd present in the rock phosphate feedstock of all phosphate fertiliser materials. Concerns over 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 voluntarily changing the source of raw materials to reduce inputs. The EU has also commissioned research on possible levy systems to reduce Cd inputs from this source (Oosterhuis *et al*., 2000).

Detailed statistics on inorganic fertiliser use on farms in England and Wales are provided in the Survey of Fertiliser Practice (Goodlass and Welch, 2005). Heavy metal concentrations in phosphate and other fertilisers used in the UK were most recently surveyed by Marks (1996). However, there was only limited and historical information on metal concentrations in liming materials (Chater and Williams, 1974).

As expected, phosphate fertilisers were an important source of heavy metals entering agricultural soils, particularly for Zn, Cd, Cr and As (Table A1.6). It is also interesting to note that Cd input rates with lime were similar to those from phosphate fertilisers (Table A1.2), although clearly the accompanying increase in soil pH on lime application would tend to decrease the availability of Cd for plant uptake and leaching.

In considering heavy metal loadings to agricultural land it should be borne in mind that Cu deficiency can be associated with sandy, shallow soils over chalk and peaty soils. Around 5% of the cereal growing area in England and Wales has been estimated to be deficient in soil copper for cereal crops (Chalmers *et al.,* 1999). Of the trace element fertilisers used in England and Wales, only Cu (as $CuSO_4$ or CuO) 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). Advisory experience indicates that foliar Cu sprays are widely used in preference to soil based dressings but that the majority of the spray will ultimately reach the soil.

1.3.6 Agrochemicals

The agricultural use of pesticides containing Hg and As 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, potatoes, top fruit and hops (e.g. Mancozeb, Zineb), whilst Cu (as copper oxychloride) is used as a fungicide for top fruit and hops.

The amounts of Zn and Cu applied to land in England and Wales were derived from published data on pesticide usage (Garthwaite and Thomas, 2001; Garthwaite and Thomas, 2002; Dean *et al*., 2002) and information on the heavy metal contents of the active ingredients (Whitehead, 2001). A total input of 22 t of Zn and 5 t of Cu was estimated to be applied annually with agrochemical products in England and Wales (Table A1.6). Metal input rates were based on the effective area receiving fungicide (i.e. the total spray hectares divided by the average number of spray passes). Input rates of Zn and Cu to land growing hops were very high (Table A1.4) because the crop receives an average of 8.7 spray passes, although the area receiving these high rates is small (<2000 ha). Top fruit can also receive relatively high rates of Cu inputs, but again the land area affected is small (<500ha).

The quantities of heavy metals entering soil in England and Wales 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 5,500 t of Cu are applied annually in Italy and around 3,500 t annually in France (Eckel *et al*., 2001). Other products used to control disease in vineyards may also contain As with, for example, 800-900 t of As estimated to be applied annually in France (Eckel *et al*., 2001).

One possible effect of climate change would be to encourage further UK wine production, which would probably increase the usage of the Cu containing products described above. Careful monitoring would be required to avoid the build up of Cu in these soils.

1.3.7 Irrigation water

In England and Wales, irrigation is only widely practised in certain regions (e.g. central, eastern and south-east England), mainly on light soils and for high value crops (e.g. salads, vegetables, potatoes, sugar beet). The 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, 101 million m^3 of irrigation water was applied to an area of 129,000 ha over the period 1984-1995 (equivalent to 783 m^3/ha/yr).

The majority of irrigation water supplies come 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 (c. 30 μg/l) and Cu (c. 4 μg/l) concentrations between the two water sources. Irrigation water was a relatively minor source of heavy metals to agricultural land at an individual field level (Table A1.6).

Climate change could greatly increase the area of UK crops requiring irrigation, however water abstraction licensing restrictions and the low metal concentrations present in water supplies mean that irrigation water is unlikely to become a major source of heavy metals.

1.3.8 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 England and Wales, landspreading of industrial wastes is normally carried out under exemptions from Waste Management Licensing Regulations - WMLR (SI, 2005) which implement the Wastes Framework Directive (EC, 1975). Under these regulations, 'waste' materials applied to farmland must be shown to result in 'benefit to agriculture or ecological improvement'. Materials commonly applied include by-products from the food industry (e.g. meat and dairy processing, brewery and soft drinks manufacture), abattoirs, paper and textile production, tanneries and pharmaceutical/chemical processing.

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). The heavy metal contents of these industrial ‘wastes’ varied greatly depending on the source, with some typical examples shown in Table A1.2. The actual amounts of these materials applied to land in England and Wales are not precisely known and approximate loadings have been used to calculate metal inputs from this diverse range of materials.

The carbon content and liming properties of paper sludge make it a valuable soil conditioner particularly on acidic soils. To support the reuse of paper sludge on agricultural land, the paper industry have produced a Code of Practice for Landspreading Paper Mill Sludges (Paper Federation of Great Britain, 1998). A recent study on the production and land spreading of paper wastes (Gibbs *et al*., 2005) provided comprehensive information on the heavy metal content of paper wastes and the quantities applied to agricultural land.

The quantities of paper sludge applied to land increased from an estimated 322,000 tonnes fresh weight (c. 20% dry matter) in the 2000 inventory to *c*.700,000 fresh weight (c. 39% dry matter) in the 2004 inventory, which have in combination resulted in the estimated total metal inputs from this source increasing 4-5 fold. Application rates in the 2004 inventory are 69 t/ha for primary treated and secondary chemical/physical treated materials, and 33 t/ha for secondary biological treated material, lower than the assumption of 100 t/ha made in the 2000 inventory. Heavy metal input rates (Table A1.4) were considerably lower than the maximum permitted values for sewage sludge application (Table A1.3).

There was insufficient information to calculate metal input rates from other types of industrial ‘wastes’, however, as many of these materials are liquids it is unlikely that metal loading rates would be high.

1.3.9 Compost

Like industrial wastes, source separated composts may be applied to agricultural land under an exemption from the WMLR (SI, 2005). Composted municipal solid waste (MSW) is unlikely to spread to agricultural land as a licence is need unless the material has been source separated. The potential use of composted MSW in land restoration is dealt with in section 2.6.3.

Recent statistics on the quantities of composted materials produced in the UK (Slater *et al*., 2005) show that around 290,000 tonnes ds of compost were spread to agricultural land in England and Wales in 2003/4 (Table A1.2), a large increase on the estimate of 57,000 t ds used in the 2000 inventory. These materials mostly comprise composts derived from green wastes and a limited amount of domestic solid waste compost. Information on the heavy metal content of *c.*200 green waste composts was taken from WRAP (2004) and supplemented by data from the Composting Association from 130 samples tested for compliance with the PAS100 composting quality standard (E. Nicholls, pers comm). Together, this new information increased the estimated total heavy metal inputs from compost by up to *c*.14-fold compared with the 2000 inventory. Using a maximum permitted application rate of 36 t/ha (based on 250 kg/ha N and an N content of 7.0 kg/t), metal loading rates from compost were similar to those from sewage sludge.

Currently, composts still represent a relatively minor source of total heavy metals to agricultural land compared with other inputs (Table A1.6) and the recommended compost quality standards (PAS100) will continue to restrict metal inputs from this source. However, the anticipated expansion of the composting industry in response to European and national policies encouraging the diversion of organic wastes from landfill disposal will further increase the recycling of composted materials to agricultural land in the future.

1.3.10 Dredgings

Information on heavy metal concentrations in canal dredgings was available for 80-100 samples taken from different stretches of canals mainly in the Midlands and North West England in 2004/5 (S. Royle, ADAS, pers comm). The median metal analysis was used in the inventory. The total quantity of dredgings applied to agricultural land was more difficult to estimate as no central records are kept. However, a figure of 5,000,000 tonnes fresh weight was used in the inventory based on an estimate provided by the Environment Agency (J. Lees, pers. comm.).

Heavy metal concentrations in the dredged materials were relatively high (Table A1.2) and estimates of the total quantities applied to agricultural land showed them to be a major source (>20% of total inputs) of some heavy metals (in particular Ni, Cr and As). Application rates calculated on a per hectare basis were extremely high and exceeded the maximum permissible average annual addition rates for sewage sludge (Table A1.3). However comparisons of this type can be somewhat misleading because when organic manures (e.g. sewage sludge, livestock manure, composts, food wastes etc) are added to the soil, microbial activity causes the organic matter to break down so that these materials have only a limited long-term effect on the soil volume. Analysis of canal sediment samples show that they comprised *c.*96 % mineral material, similar to mineral topsoils (Davies *et al*., 1977) and add significantly to the soil volume. Thus spreading dredgings can be compared to spreading a mineral topsoil, as they both add to the volume of the existing soil. Hence it is important to distinguish between the application of organic manures and dredging materials which comprise largely inorganic material.

Topsoil heavy metal concentrations following spreading and the incorporation of dredgings are calculated from the mixing ratio of the dredgings and field soil. For example, if the field topsoil had a Zn content of 50 mg/kg and the dredgings a content of 150 mg/kg, and the two were thoroughly mixed in a 1:1 ratio, the mixed material would have a zinc content of (150 + 50)/2 = 100 mg/kg. Calculations of this type are performed to obtain acceptable mixing ratios and to ensure that total soil concentrations do not exceed maximum permitted levels in topsoils where sewage sludge is applied to agricultural land (DoE, 1996).

The land area receiving dredgings annually (calculated from the total quantity produced and the typical spreading rate) was estimated to be <4000 ha, with such applications made under a Paragraph 7A exemption from the WMLR (SI, 2005). The maximum quantity that can be spread is 5000 t/ha

It should also be noted that dredging materials currently applied to land are likely to be *less* contaminated than in the past because of the introduction of cleaner technologies etc. For this reason and because historical dredging applications would have ben subject to less stringent controls, sites with a history of dredgings applications could be contaminated with heavy metals (and other contaminants) and may warrant further investigation if they are to be used for food crop production.

1.3.11 Corrosion

Corrosion of Zn from pylons and galvanised materials used in agriculture was estimated using information on the quantities of galvanised steel produced each year and the percentage used in agriculture provided by the Galvanisers Association (W. Piatkiewicz, pers comm). This was combined with the corrosion rate formula reported by WS Atkins (2000), using the concentration of SO_2 in urban air (18.08 $\mu g/m^3$) in 1996. Factors influencing the rate of corrosion of galvanised structures and hence the likely soil Zn concentration include the age of the structure, the date it was painted (if at all) and the atmospheric SO_2 concentration. The estimates indicated that corrosion was a minor contributor to total Zn inputs to agricultural soils (*c*.1% of total inputs).

Nevertheless, inputs local to such a source can be high, with some researchers even using soils collected around galvanised electricity transmission towers for use in experiments where contaminated soils were required (e.g. Smolders *et al*., 2003). These authors reported soil Zn concentrations of 226-595 mg/kg near pylons compared with background soil values of 25-82 mg/kg, although Zn concentrations decreased sharply 10-20 m from the pylons. Fava (2002) reported Zn concentrations up to *c.*8000 mg/kg under pylon bases in Italy, but with near background levels (<33 mg/kg) only 50cm from the pylon base.

1.3.12. Livestock footbaths

The use of cattle footbaths can help reduce the incidence of foot lameness, particularly that caused by foul of the foot, heel erosion and digital dermatitis (Defra, 2005a). The main types of footbath solutions in use are formalin and zinc or copper sulphate. Defra recommend that footbaths should be used throughout periods of risk (i.e. during the winter housing period and in spring and autumn). Footbaths should be constructed in such a way that they can be emptied directly into a suitable collection facility (i.e. a slurry or manure store) and not find their way into a watercourse or groundwater.

An estimate of Zn and Cu sulphate footbath usage by dairy and beef farmers in England and Wales was made using data on livestock numbers, assuming that 50% of farmers would use a Zn/Cu based product. It was also assumed that a typical footbath volume would be 300 l, it would be filled with a 10% solution of Zn sulphate or 7.5% solution of Cu sulphate and would be changed monthly. Using these figures, the annual usage of Zn and Cu in cattle footbaths was estimated to be 121 and 103t, respectively, which equates to c. 16% of estimated total Zn inputs with cattle manures and 54% of the Cu inputs. These quantities are somewhat larger than expected and may imply that either i) footbath usage was overestimated, ii) farmers are not disposing of spent footbaths into slurry/solid manure stores or iii) that the manures in the survey of heavy metal concentrations (Nicholson *et al.*, 1999) were not representative of farms where regular footbathing occurs.

On lowland sheep farms, Defra recommend that footbathing should be routinely carried out about 5 times a year and more frequently if foot rot is a serious problem (Defra, 2005b). Formalin and Zn sulphate are the most commonly used products (Cu sulphate is not used due to the sensitivity of sheep to Cu). The Defra booklet states that "the contents of footbaths should be carefully disposed of after use, well away from watercourses to prevent environmental pollution". Nevertheless, if the same area is used for disposal each time (for convenience) then high soil Zn concentrations could build up.

An estimate of Zn sulphate footbath usage by sheep farmers in England and Wales was made using data on livestock numbers, assuming that 50% of farmers would use a Zn based product. It was also assumed that a typical footbath volume would be *c.*100 l, it would be filled with a 10% solution of Zn sulphate and would be changed 4 times a year. The total amount of Zn estimated to be used in sheep footbaths alone and disposed of directly onto soil was *c.*380 t/yr, which represents around 7% of the total Zn input to soils in England and Wales.

1.3.13 Lead shot

The use of lead shot in shotgun cartridges at clay pigeon shoots and other shooting activities was estimated using data supplied by Mellor and McCartney (1994) and updated using information published on the Clay Pigeon Association website (CPSA, 2005).

Estimates of the use of lead shot in shotgun cartridges showed that this was the single most important source of Pb inputs to soils in England and Wales, with around 15,000 t deposited each year. The Clay Pigeon Association currently lists *c.*400 shooting grounds in England and Wales. Illustrative Pb input rates at these sites were calculated assuming that each ground was 15 ha in size. Hence, Pb loading rates were extremely high (*c*.1.9 t/ha) on these relatively small areas of land (Table A1.4). Other sources have indicated that on some longstanding shooting grounds Pb has been deposited in excess of 150 tons/acre (S. Richardson, ADAS, pers. comm.). Cartridges containing lead shot are also used for hunting, although their use in wetland sites of Special Scientific Interest has been prohibited due to the risk of poisoning waterfowl (SI, 1999). Thus the total amount of Pb deposited to land could be much greater than the estimate which is based only on clay pigeon shooting inputs.

Previous research (Mellor and McCartney, 1994) showed that topsoil total Pb concentrations at a clay pigeon shooting site in northern England commonly exceeded 5000 mg/kg. This is much greater than the maximum permitted level of 300 mg/kg for land where sewage sludge is applied. It also exceeds the ICRCL trigger value (2000 mg/kg for open space), which indicates that remedial action should be taken especially if contamination is continuing. Indeed a policy to allow for the regular and efficient recovery of lead shot from such soils has been proposed in the past (R. Unwin, Defra, pers comm.). Also, previous attempts have been made to develop machinery to extract shotgun pellets from soils, although the extent to which this technology has been taken up by the industry is not known (S. Richardson, ADAS, pers. comm.).

Lead pellets deposited on soils only deteriorate slowly providing they are left undisturbed. However, if the pellets are disturbed then the oxide shell will disintegrate and be dissipated into the soil. Lead from shot may be directly ingested by soil fauna, wildlife and livestock, as well as being taken up by plants and into the food chain (Thomas, 1997). Mellor and McCartney (1994) found that topsoil bioavailable Pb and plant concentrations were elevated at the clay pigeon site in northern England, supporting the data from similar studies in New Zealand (Rooney *et al*., 1999) and the US (e.g. Hardison *et al*., 2004; Cao *et al*., 2003).

Alternatives to Pb shot include bismuth, steel, tin, tungsten-iron, tungsten-matrix, or tungsten-polymer materials. A lead gunshot cartridge costs approximately 11p, steel around 16p and bismuth/tungsten matrix around 50p. These alternatives have different properties and ballistics than lead shot. Steel is regarded as less effective than other types of shot, and is potentially dangerous when used in wooded areas because it is more likely to ricochet off trees. Shooters do not therefore generally favour steel, but switching to bismuth or tungsten, for example, could significantly increase their costs. Moreover, whilst undisturbed lead shot will retain its form for many tens of years, alternatives such as steel will in some acidic soils deteriorate within 18 months and release iron oxides and other contaminants into the soil. The environmental impacts of tungsten and tungsten alloys as replacements for lead shot and other munitions (e.g. depleted uranium) have been recently comprehensively reviewed (Harrison and Bradley, 2005).

Note that Denmark and The Netherlands have banned all uses of lead shot.

1.3.14 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 total 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. This issue is examined in greater detail in Appendix 5.

In addition, highways run–off or spray may contribute to the heavy metal burden of agricultural soils close to major roads. Heavy metal inputs to roadside soils from traffic related sources are discussed further in section 2.6.4. Abrasion of machinery (e.g. ploughs, discs, tines etc.) used to cultivate agricultural land has also been suggested as a potential (if minor) source of heavy metals.

1.4 The importance of the different heavy metal sources

Annual heavy metal inputs to agricultural land in England and Wales (2004) from all the sources considered are summarised in Table A1.6. Compared with the 2000 inventory, total inputs of most metals had increased due to the inclusion of new sources such as footbaths, dredgings and lead shot. Only inputs of Cu had decreased mainly due to reductions in livestock numbers (especially pigs).

Table A1.6 : Annual heavy metal inputs (t) to agricultural land in England and Wales for the year 2004

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	2485	638	180	611	22	84	35	11
Livestock manures	1666	541	47	44	4	32	15	<1
Sewage sludge	385	271	28	106	2	78	3	1
Industrial ‘wastes’	65	25	4	7	1	6	nd	<1
Inorganic fertilisers	199	67	30	13	9	94	6	<1
-Phosphate fertilisers	*152*	*22*	*15*	*2.4*	*7.1*	*74*	*5.1*	*<0.1*
Agrochemicals	22	5	0	0	0	0	0	0
Irrigation water	5	2	0	0	0	0	0	nd
Composts	52	13	5	28	<1	6	nd	<1
Corrosion	59							
Dredgings	615	86	77	152	2	83	22	<1
Lead shot				18000				
Footbaths	381	0						
Total	5934	1648	371	18960	39	383	80	13

nd = no data

For Zn and Cu, approximately 30% of the total annual inputs to agricultural land were derived from livestock manures, which were a much less important source of the other metals. Around 90% of total Pb inputs were accounted for by lead shot, whilst dredgings were shown to be an important source of Ni, Cr and As (22-27% of total inputs). For Cd, 56% of inputs were from atmospheric deposition and 23% from inorganic fertilisers (mainly phosphate fertilisers) and lime. Over 85% of Hg inputs were from atmospheric deposition.

Atmospheric deposition was an important source of many heavy metals to agricultural land in terms of total quantities on a national scale. However, input rates on an individual field basis were small compared with those associated with sewage sludge, composts and livestock manures applied for crop production (Table A1.4). Excluding dredgings and lead shot, the highest input rates of most metals were from sewage sludge and composts (applied at 250 kg total N/ha/yr). However, sewage sludge generally represented <25% and compost <1% of the total metal inputs and the land area receiving these materials annually was relatively small (Table A1.4; <1% of agricultural land receives sewage sludge; 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 (probably due to supplementation of dairy cattle diets to maintain fertility and possibly Zn from footbaths) and As (probably as a result of inadvertent contamination of feeds with other mineral supplements).

1.4.1 Effects of reduced Zn and Cu supplementation in livestock feeds

The effects of reducing Zn and Cu supplementation in livestock diets (principally pig and poultry feeds) on manure metal concentrations and soil loadings were assessed by comparing the heavy metal concentrations of manures at the previous (pre-January 2004) levels of supplementation with calculated concentrations for diets reduced to the current maximum values (see section 2.2.4).

Most of the Zn and Cu ingested by livestock is excreted in the urine and faeces. It has also been shown (Nicholson *et al*., 2001) that altering the Zn and Cu content of pig and poultry diets has a predictable effect on manure metal concentrations (i.e. the manure metal concentration can be predicted from the feed metal concentration using a simple concentration factor calculation). Therefore, for this study, an estimate of manure metal concentrations from animals with the current maximum Zn and Cu supplemented diets (i.e. post January 2004) was made on a pro-rata basis from feed concentrations.

A number of example diets were compiled. For pigs, this was based on a 400 sow mixed unit, assuming usage of 2,500 mg/kg Zn on veterinary prescription to control post-weaning scours for up to 14 days. For poultry, typical broiler and laying hen flocks were considered. For cattle, an autumn calving dairy herd producing 6000 kg milk per lactation and a grass-silage beef system were used. The calculations assumed that concentrates formed only a proportion of the complete cattle diet, with the metal concentration of the other dietary constituents (i.e. silage, grazed grass) remaining unchanged. A comparison between manure Zn and Cu concentrations at pre- and post-2004 maximum rates is shown in Table A1.7.

Table A1.7. Manure Zn and Cu concentrations (g/t or m^3 fw) at pre-2004 and the predicted effects of current reduced dietary supplementation rates.

	Zinc		Copper	
Manure type	Pre-2004[1]	Current reduced level[2]	Pre-2004[1]	Current reduced level[2]
Pigs				
Pig slurry[4]	65	43	47	36
Poultry				
Laying hens	175	=	27	=
Broilers	130	=	19	16
Turkeys	130	=	19	=
Cattle				
Dairy slurry[5]	17	=	5	4
Beef slurry[6]	17	16	5	=

[1]Typical concentrations from Nicholson *et al.* (1999).
[2]Concentrations predicted using revised maximum permitted limits in EC (2003)
[4]A 400 sow mixed unit.
[5]Autumn calving dairy herd.
[6]Grass silage beef.
= Manure metal concentration unchanged

To calculate net soil Zn and Cu loadings, the manure were assumed to have typical total nitrogen (N) contents as specified in Anon (2000) and to be applied at a maximum rate of 250 kg N/ha/yr. It was also assumed that the soil received inputs from atmospheric deposition at the mean rate measured for agricultural land in England and Wales (Alloway *et al*., 2000). Estimates of crop Zn and Cu offtakes were made assuming the land was in cereal cropping, and using typical yields and straw/grain metal concentrations. Leaching loss data was from Keller *et al*. (2002). As a proportion of the metal inputs in 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, the results represent gross rather than net inputs to the soil from this source.

For poultry and cattle manures, concentrations were assessed as unlikely to change greatly as the feed Zn and Cu concentrations measured by Nicholson *et al* (1999) were already similar to or below the post-2004 maximum levels. However, reducing Zn and Cu inputs in pig feeds from pre-2004 levels to the current maximums was predicted to reduce soil loadings by 37 and 20%, respectively. Total annual Zn and Cu inputs to agricultural soils from livestock manures were recalculated assuming that feed Zn and Cu concentrations were reduced to the current maximum rate. Total Zn inputs were predicted to decrease from 1666 to 1504 t/yr, a reduction of 10%. Similarly, total Cu inputs were predicted to fall from 541 to 451 t/yr, a reduction of 9%. However, there may be circumstances where reduced feed concentrations are balanced by increased Zn use on veterinary prescription.

These results indicate that reducing Zn and Cu supplementation in livestock feeds would substantially reduce manure Zn and Cu concentrations, and hence decrease total inputs to agricultural land and loadings to individual fields. However, further information is required to confirm and quantify the actual effects of reduced dietary supplementation introduced in January 2004 on manure metal concentrations and soil loadings.

1.5 Implications for agricultural soil quality and function

1.5.1 Effects on agricultural soil quality

The heavy metal input rates were used to estimate the 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 advisory limits for heavy metals where sewage sludge is applied to agricultural land (Table A1.3). It was assumed that all fields received inputs from atmospheric deposition. Losses of metals via crop offtake were based on typical yields and metal concentrations in cereal grain and straw (Alloway *et al*., 2000), and leaching losses on figures taken from Keller *et al*. (2002) for a loamy sand soil where sewage sludge had been applied.

Soil Zn would be raised to the limit value (200 mg Zn/kg dry soil) after approximately 87 years of sewage sludge additions compared with 94 years for composts and 149-177 years for pig slurry or laying hen manure applied annually at rates of 250 kg/ha total N (Table A1.8). Annual applications of paper sludge would also raise soils to the Zn limits value after 128-313 years. Repeat applications of dredgings are unlikely in the short-term and would not be allowed once soils have reached maximum permitted heavy metal concentrations.

Note that these times would be decreased if soil Zn concentrations were already elevated above background values or if application rates or Zn concentrations were higher than those assumed here. In comparison, it would take >1000 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 A1.8.

This inventory of heavy metal inputs to agricultural land demonstrates that agricultural soils are at risk from heavy metal accumulation through the application of organic manures, in particular from pig and poultry manures, sewage sludge, composts and paper sludge. Hence, it may be appropriate to consider the introduction of maximum permissible soil metal concentrations to protect agricultural land from long-term heavy metal accumulation for all organic manures (similar to the controls currently in place for sewage sludge applications), unless strategies can be found to further reduce their metal content.

Table A1.8. Time (years) required to raise soil metals concentrations from background[a] to limit[b] concentrations, assuming annual applications of each material.

Source	Zn	Cu	Ni	Pb	Cd	Cr
Sewage sludge	87	118	495	650	366	>1000
Layer manure	149	882	>1000	>1000	>1000	>1000
Pig slurry	177	225	>1000	>1000	>1000	>1000
Pig FYM	196	255	>1000	>1000	>1000	>1000
Broiler litter	390	>1000	>1000	>1000	>1000	>1000
Cattle slurry	392	>1000	>1000	>1000	>1000	>1000
Cattle FYM	687	>1000	>1000	>1000	>1000	>1000
Atmospheric deposition	>1000	>1000	>1000	>1000	>1000	>1000
Paper sludge (primary + bio treated)	313	352	>1000	>1000	>1000	>1000
Paper sludge (chem/phys treated)	128	239	>1000	>1000	>1000	>1000
Fertilisers (NPK) and lime	Net decrease	>1000	>1000	>1000	>1000	>1000
Irrigation water	Net decrease	>1000	>1000	>1000	>1000	>1000
Composts	94	350	411	371	486	>1000
Agrochemicals (hops)	30	139	>1000	>1000	>1000	>1000
Dredgings	2	17	8	21	14	54

[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)
Calculations assume a soil density of 1.3 g/cm^3 and a cultivation depth of 25cm.
Net decrease: the rate of metal removal exceeds the rate of metal input

1.5.2 Effects on soil function

Soil is an extremely effective filter and buffer for heavy metals. The great majority of most heavy metals entering agricultural soils is retained in the soil matrix by adsorption on mineral particles or by forming stable complexes with soil organic matter. This means that only a small proportion of the heavy metals entering the soil will eventually reach the wider environment via leaching or plant uptake. Although the uptake of metals by plants is small in terms of the total quantities involved, the effects can be profound and there has been much research on this topic. However, there is a relative lack of information on the concentration of metals in soil leachates or in by-pass flow from cracking clay soils, both of which have the potential to affect the quality of surface or ground waters. This could have implications for the quality of waters for freshwater fish where limits on Zn and Cu concentrations have been set under the Fresh Water Fish Directive (EC, 1978).

Heavy metal additions can have a direct impact on the ability of a soil to support food crop production. For example, the EU has set maximum limits for the concentration of Pb and Cd permitted in wheat and barley grain. Recent research has shown that the Pb in cereal grain is likely to originate mainly from atmospheric deposition and other routes of surface contamination during harvest and storage rather than as a direct result of crop uptake from the soil (Zhao *et al*, 2004). However, grain Cd concentrations were shown to be correlated with soil Cd concentrations (Adams *et al*, 2004) so that a soil with elevated Cd levels may, if not properly managed, become unable to produce grain that will be allowed into the human food chain. This would have serious economic consequences for the individual farmer and the country as a whole if this was to occur on a wider scale.

In addition, soils with elevated levels of Cd and Pb could adversely affect the quality of offal from animals grazing the land (e.g. Lee *et al*., 1994; Hill *et al*., 1998). Ruminants are known to ingest relatively large amounts of soil when grazing. The metals in this soil combined with those in the forage could increase the metal concentration of offal to above the defined limits.

Biomass and fibre production can be affected by soil heavy metals through phytotoxicity where elevated levels can cause yield reductions. Some biomass crops such as willow (*Salix* spp.) have been studied as potential phytoremediation crops for Cd and Zn (e.g. Watson *et al*., 1999), however, the timescales for metal removal are large (i.e. decades, centuries). Also, biomass crops with high metal concentrations may be less suitable for use in power generation. It would not be an economic proposition to recover these metals from incinerator ashes and they would probably be buried in landfill sites where conditions may be such that metal-containing leachates could enter the environment.

Over time, the proportion of soils In England and Wales with metal concentrations exceeding the maximum permissible limits for sewage sludge reuse will increase. Thus the area of land available for the recycling of sewage sludge (and by inference other metal-containing organic manures and composts) will slowly decrease. This could affect our ability to reuse these materials and create the need for costly alternative disposal solutions. In the shorter term, one could envisage certain areas of the country becoming net exporters of organic materials, with the need to develop an infrastructure to support this.

Probably, the least understood impact of soil heavy metal additions is their effects on soil microbial processes which impact on broader soil functions such as biomass, food and fibre production and environmental interaction. The effects of heavy metals from sewage sludge on soil microbes in agricultural ecosystems were summarised by McGrath (1996). He concluded that whilst soil respiration rates and the soil microbial biomass were both affected by metals (especially Zn), microbially mediated processes such and C and N mineralisation were relatively insensitive at the metal concentrations normally found in agricultural soils. Also, the fixation of atmospheric nitrogen was more sensitive to metals (particularly Zn), which may decrease the numbers of free-living bacteria and cyanobacteria in soil, and symbiotic nitrogen fixation by legumes with rhizobia. More recently, studies have shown that elevated soil Zn can affect the functional diversity of microbial communities (Moffett *et al*., 2003; Lock and Janssen, 2005).

Alterations to soil processes may have economic impacts. Where soil processes are disturbed, the release of nutrients from that soil may be impacted (e.g. nitrogen mineralisation). If N availability was increased, nitrate leaching losses may also increase, particularly if increased mobility was co-incident with periods of high rainfall and/or low plant uptake. A reduction of soil organic matter content through reduced crop growth in response to metal phytotoxicity would impact on the ability of soil to retain nutrients and resist soil water erosion, and on crop yields at harvest. If soils are unable to support crop growth or to produce crops that meet market place quality needs, the latent financial value of the land will be compromised.

1.6. Inputs of other metals to agricultural soils

The continued application of phosphate fertiliser to soils over many years can increase the soil uranium (U) content, with the quantity added depending on the rock phosphate source, the fertiliser processing method and the application rate. Research in Germany showed that triple superphosphate fertilisers contain 85-191 mg U/kg compared with 13-75 mg U/kg in rock phosphate. Rothbaum *et al*. (1979) showed that virtually all of the U applied in phosphate fertiliser remained in the soil surface horizons, although other authors have found increased U in surface waters draining intensively fertilised land in the south-west USA and Yugoslavia (Zielinski *et al*., 1997); Barisic *et al*., 1992). Ryan (1981) has argued that the U added to agricultural land with P fertilisers does not significantly affect the radiation dose to the general public. However, continued application over *c.*100 years could lead to a 50% increase in the U content of agricultural soils.

Phosphate is sometimes added to livestock feeds as a mineral supplement and if contaminated with U, could lead to increased U in food products and excreta. German researchers measured levels of U in cattle FYM and slurry which generally did not exceed 2 mg/kg dm. If cattle slurry containing U at 2 mg/kg dry matter was applied at a rate of 250 kg N/ha (equivalent to 63 m^3/ha for a slurry with 4 kg/m^3 total N), then the U addition rate would be *c.*13 g/ha. This is double that applied in triple superphosphate fertiliser with a typical U concentration of *c.*100 mg/kg ds (or 217 mg/kg P_2O_5) and applied at a rate of 30 kg P_2O_5/ha, where the U addition rate would be only *c.*6.5 g/ha. Whilst maximum limits for permitted concentrations of Cd and As in phosphate feed supplements are specified in Schedule 7 of The Livestock Feedstuffs Regulations, no such limits exist for U.

The major anthropogenic source of vanadium (V) to the environment is from the combustion of fossil fuels. There is some debate as to whether V is essential for normal plant growth, although V phytotoxicity was recognised in early studies on phosphate fertilisers. Current opinion is that the environmental threat posed by V is slight (Jones *et al*., 1995).

1.7 Heavy metal inputs in organic farming systems

Organic farming systems are of growing importance to European agriculture and are often claimed to have lower metal inputs than conventional systems (Eckel *et al*., 2005). Fertilisers permitted for use on organic farms are specified in the UKROFS standards and some (e.g. composted household waste) must meet specified levels of heavy metals (UKROFS, 2003). The use of rock phosphate fertiliser is permitted providing the Cd content is less than 90 mg/kg P_2O_5. Note that the median value for phosphate fertilisers used in 'conventional' agriculture is 31 mg/kg P_2O_5, Marks (1996). In practice, most nutrients added to soils on organic farms are from livestock manures, which must be sourced from organically or extensively managed livestock systems - manures from 'factory farming' are not permitted. Organic farmers still use copper for disease control on certain crops (e.g. potatoes).

We are not aware of any published information on the differences in heavy metal concentrations between manures from organically or conventionally managed farms. However, according to the UKROFS standards, mineral supplementation in livestock diets should be rendered unnecessary through sound agricultural practice. For trace elements, restricted supplements may be used following prior approval by the certification body, where there is evidence of a suspected dietary deficiency. Management practices should limit animal health problems so that they can be managed mainly by prevention. Phytotherapeutic (e.g. plant extracts, essences, etc.) or homeopathic products (e.g. plant, animal or mineral substances) should be used in preference to chemically-synthesised veterinary medicinal products or antibiotics. Zinc and Cu containing footbaths are permitted on organic farms where there is a disease control problem to be addressed.

Although organic farming only comprises a small proportion of the agricultural land in England and Wales, it would be prudent to establish whether there are any differences in terms of soil heavy metal inputs.

1.8. Heavy metals inputs to other soil uses

A summary of the available information on metal inputs to land uses other than agriculture is provided below.

1.8.1. Forest soils

Sources of heavy metals to forest soils. The most important source of heavy metals to forest and woodland soils is atmospheric deposition. Heavy metal deposition rates are likely to be greater than for agricultural or 'natural' soils because tree foliage is efficient at trapping gases, particles and fog droplets. Trees (particularly conifers) also have a much larger leaf surface area than herbaceous vegetation per unit ground area. Windspeeds are reduced in woodlands, resulting in greater deposition of the particulate metal burden. These factors increase the metal content of the leaf litter, which eventually becomes incorporated in the upper soil horizons, augmenting total metal concentrations. In addition, rainfall leaches metals and other cations from the leaves, and stem flow and canopy drip may transfer the metals to the forest floor (Imperial College, unpublished report).

Sewage sludge is sometimes applied to forested land (or land being prepared for woodland cover) with the quantity in 1996/7 reported as 1000 t ds, equivalent to <1% of total sewage sludge production (Gendebien *et al*., 1999). Applications are made under and exemption as part of the WMLR, but should comply with the Manual of Good Practice for the Use of Sewage Sludge in Forestry (Wolstenholme *et al*., 1992). This effectively sets the same limits for metal loading rates as the Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996). Where sewage sludge is applied, it will be the major source of heavy metals.

Whilst composts can be applied to forestry, there was no reported use in 2001/2 (Davies, 2003). This situation may change as more composted materials are produced and, given the relatively high heavy metal concentrations of green waste composts, their use in forestry may justify similar monitoring and controls to those in place for sewage sludge.

Indeed the Forestry Commission has recently issued a draft information note on the use of sewage sludge, composts and other organic 'wastes' in forestry which updates the advice given in the Code of Practice based on policy, technical and legislation changes that have occurred since the 1990's (Moffat, 2005). It is likely that the limits for maximum permitted metal concentrations in sewage sludges destined for application to agricultural land will still be applicable for forest land.

Wood ash has also been used successfully as a fertiliser for nutrient poor forest soils. The environmental impacts associated with its use were extensively reviewed by the Forestry Commission (Pitman, undated) who found no problems associated with the heavy metal contents. There is no information on how widespread or otherwise the use of woodash is in the UK, although it has been used in Scandanavia and the USA.

Effects of heavy metals on forest soil quality and function. There is little information on the current heavy metal concentrations of forest soils in the UK. However, the Forestry Commission measured heavy metal concentrations in around 80 soils from different types of forest/woodland in 1994 as part of a survey for the EC (Moffat and Hutchings, 1996). The results are summarised in Table A1.9, and show that forest soil (O horizon) Zn, Cu, Ni and Cr concentrations were generally lower than the mean values for soils in England and Wales (McGrath and Loveland, 1992). However, concentrations of Pb and Cd were higher than the mean soil concentrations. There are several possible explanations for this, the most likely being that the forests were planted on land that was already high in these metals (e.g. close to old mines).

Table A1.9. Mean heavy metal concentrations (mg/kg) in 82 UK forest/woodland soils (1994) compared with mean concentrations in soils in England and Wales.

	Zn	Cu	Ni	Pb	Cd	Cr
Beech	54	12	10	51	1.3	12
Norway Spruce	61	15	12	139	1.0	12
Oak	54	18	18	88	0.9	25
Scots Pine	41	16	8	74	1.0	7
Soils in E&W	82	18	23	40	0.7	39

Source : A. Moffat (pers comm).

The complexes formed between some heavy metal cations and the humus layer of woodland soils are highly stable. This explains the high retention of heavy metals in woodland organic soil horizons in areas near pollution sources and implies that metals are relatively immobile in woodland soils (Davis *et al*., unpublished).

Heavy metals have a range of effects on forest and woodland ecosystems. Several studies have demonstrated reductions in leaf litter decomposition rates in woodland sites as the result of increased metal concentration. Opinion is divided as to the mechanisms of litter accumulation. Some authors suggest that it is due to the loss of certain groups of invertebrates (Martin and Bullock, 1994), while others maintain that litter accumulation is related to decreased microbial activity and decomposition. Reduced rates of decomposition have long-term implications for the ecosystem because of slower rates of remobilisation of essential nutrients leading to decreased ecosystem productivity (Davis *et al*., unpublished).

Less research has focused on the effects of metals on the microbial communities of woodland soils. Microbial activity in woodland / forest soils has a great impact on the growth of flora and fauna. In woods and forests with low microbial activity large amounts of nutrients accumulate in the mor layer in forms unavailable to vegetation. Phospholipid Fatty Acid Analysis (PLFA) of soil cores at increasing distances from a smelter demonstrated reduction in fatty acids associated with ectomycorrhizal fungi principally due to Cu contamination (Davis *et al*., unpublished).

It is difficult to control metal inputs to forest ecosystems as leaves are excellent scavengers of metal ions from the atmosphere. In the longer term, reforestation of brownfield/agricultural land could lead to an increased use of organic manures (e.g. biosolids) as preparative materials and subsequent mobilisation of heavy metals largely due to increases in soil acidity and land management practice changes.

1.8.2 Soils in the built environment

Sources of heavy metals to soils in the built environment*.* There has been considerable effort devoted to monitoring and reporting air quality in urban areas of England and Wales in response to the EU Air Quality Framework Directive (EC Directive 96/62/EC). This has shown that airborne heavy metal concentrations have decreased substantially over recent years, although for most metals urban concentrations exceed those at rural sites by a factor of two (Harrison *et al*., 1993). Whilst atmospheric Pb concentrations are monitored as part of the Air and Environmental Quality Research programme because of its use as an additive in petrol, there are few actual measurements of Pb (and other heavy metal deposition) to soils in the urban environment.

One of the most useful sources of information the models to estimate heavy metal deposition developed as part of the 'critical load' methodologies for toxic metals. The 'critical load' project devised an 'inferential' model linking annual mean deposition and air concentrations of heavy metals (Nemitz *et al*., 2000) and linked this with a model simulating the transport and deposition of metals across the UK (FRAME-HM). High resolution maps of Pb and Cd deposition produced using the model, clearly show 'hot spots' in the major urban conglomerations due to the proximity of point sources of pollution and the high volumes of traffic.

Crematoria and cemetries which are principally located in urban areas may be an important source of Hg emissions to some urban soils, derived principally from dental amalgam (Nieschmidt and Kim, 1997). Lee *et al*. (2000) reported that the distance Hg would travel in air after leaving a crematorium stack before grounding, or entering the sea, depended on the chemical species of Hg emitted as well as dispersion conditions near the stack. A consultation paper on Hg emissions from crematoria by the Environment Agency Local Authority Unit (EA, 2003) concluded that levels of Hg around crematoria are below those at which health concerns are believed to occur. The EA paper also concluded that, without intervention, Hg emissions from crematoria in the UK would increase by two-thirds between 2000 and 2020, and that by 2020 crematoria would emit between 11 and 31% of Hg emissions to air. Clearly there is a need for up-to-date information on Hg levels in soils and crops in the vicinity of crematoria and cemetries to provide a baseline against which changes in future emissions can be measured and monitored.

A wide range of industrial activities can be potential sources of gross heavy metal contamination to urban soils. These are generally point sources and are very heterogeneous in nature so it is difficult to generalise about inputs to urban soils as a whole. Corrosion of metals on industrial sites could also elevate soil Zn concentrations (see section 2.2.11.). Soil contamination is dealt with under contaminated land regulations, which specify levels above which remedial action needs to be taken if the land is to be fit for other purposes.

Other potential sources of heavy metals to soils in the built environment could be the local use of livestock manures, biosolids and composts etc. in parks, gardens and allotments, and as part of land reclamation/restoration schemes.

Effects of heavy metals on soils in the built environment*.* Risks to buildings, building materials and services from soil contamination are considered to stem mainly from the presence of aggressive substances, combustible materials, expansive slags or unstable fills (EA, 2001). However, heavy metal contamination of urban soils could affect the use of gardens and allotments for food production, and the role of soil as a filter for urban water. It could also affect its use as a 'platform for construction', since soils contaminated at above the CLEA 2002 (Contaminated Land Exposure Assessment) soil guideline value (SGV) may not be usable for certain land uses (residential, allotments, commercial/industrial) without further investigation and possibly remediation, which is likely to be costly.

1.8.3 Land restoration and reclamation

Sources of heavy metals to restored/reclaimed soils. Land restoration or reclamation is the process of returning underused, derelict or abandoned land to beneficial use. Examples of such land would include old collieries or quarries restored for amenity use, forestry and so on – a good example would be the Eden Project in Cornwall. Restoration will usually focus on restoring ecosystem functions such as nutrient cycling, hydrological balance and ecosystem resilience, although restoring the original flora may on occasions be a realistic and appropriate goal. Reclamation is the replacement of ecological functions by planting a different vegetation to that which previously grew. Best practice guidance on restoring sites is given in Williamson *et al*. (2003).

At many sites, the topsoil is of poor quality and needs to be supplied, supplemented or replaced. This can be achieved using 'waste' materials such as sewage sludge and compost to supply organic matter and nutrients. Applications are made under an exemption as part of the WMLR. Sites may be in NVZs but because they are not classed as agricultural land they will are not be subject to restrictions based on N loading.

In 1996/7, it was reported that 6% (58,000 t ds) of sewage sludge produced in England and Wales was used for land reclamation (Gendebien *et al*., 1999). There are comprehensive guidelines for the use of sewage sludge in land restoration (Hall and Wolstenholme, 1999). The volume applied needs to contain enough nitrogen, phosphorus and organic material to form a good growing medium but not exceeding safe limits for heavy metals. In this context the limit on soil heavy metal concentrations set out in the regulations on the use of sludge in agriculture (DoE, 1996) are normally applied to land restoration applications. Normal application rates range from about 500 tonnes/hectare to 1000 t/ha, depending upon the heavy metal content of the sludge and the host material. Higher levels may be used in site restoration if appropriate (Enviros, 2004).

Around 19,000 tonnes of compost are used in land restoration (which predominantly consists of green waste compost (Davies, 2003). However, research is currently being undertaken on the use of composted MSW as a medium for land restoration. Preliminary analysis of the finished compost produced from this project (50% MSW, 50% green waste) indicated that the heavy metals concentrations were generally about twice those in green waste compost, although still lower than the PAS100 standard for compost (S. Richardson, ADAS, pers. comm.). This compost could be applied at the remediation site at rates of up to 2000 t/ha, greatly exceeding the permitted average annual heavy metal application rates in the Sludge Code (over 200 kg/ha Zn and Pb in this case), although clearly these situations are 'one-off' applications and some mixing with the existing topsoil will usually occur.

Effects of heavy metals on restored soil function. Clearly the impact of heavy metals in restored soils will depend on the resulting soil concentrations and the target end use, be it amenity, agriculture, forestry etc. Restored soils can be returned to agricultural production following a 5 year lay off. If an organic 'waste' has been used at high rates with little mixing into the soil, then it is quite possible that the resulting topsoil concentrations would exceed the limits in the Code of Practice for the Agricultural Use of Sludge as the metal concentrations would not be reduced after 5 years. This may have implications for the functioning of that soil particularly in terms of the impact on soil processes.

1.8.4 Roadside soils

Sources of heavy metals to roadside soils. Estimates of heavy metal emissions specifically from traffic were recently reported in the EC funded POLMIT project, which looked at pollution of groundwaters and soils by road and traffic sources (TRL, 2002). Calculated total deposition rates (including wet deposition from runoff and vehicle splash and dry deposition from windblown particles) from 14 European monitoring sites were reported, although due to the lack of reliable data these were only broad scale estimates (Table A1.10). Soil heavy metal (Zn, Cu and Pb) input rates decreased rapidly more than c. 10m from the roadside, thus the rates in Table A1.10 are roughly equivalent to per hectare deposition rates and can be directly compared with atmospheric deposition rates to urban and agricultural soils. Metal emission rates were found to be primarily dependent on traffic volume. Data from the UK indicated that road transport contributes only very small amounts of Cd or Cr and small amounts of Cu (2%), but important amounts of Pb (59%) and Zn (23%) to total atmospheric metal emissions. The small contribution of traffic to Cd emission is somewhat surprising as Cd oxide is used as a curing agent for vehicle tyres, but similar findings were reported by Hol *et al*. (1997) and Zechmeister *et al* (2005). Nevertheless, Cd and Zn are found at elevated levels in highway runoff and contribute to the burden in sewage sludge (Water UK, 2001).

Table A1.10. Heavy metal emissions to roadside soils

Heavy metal	Calculated emission rate (g/km road/year)*
Cd	1 – 10
Cr	14 - 162
Cu	9,248 - 108,893
Pb	7,391 - 110,984
Zn	2,479 - 51,369

*One carriageway (downwind side) only
Source : TRL (2002).

The POLMIT project found that Pb concentration exceeded the soil intervention level of 530 mg/kg at two sites whilst the target level of 85 mg/kg was exceeded at most of the other sites. However, the area of soil polluted by Pb lay directly adjacent to the road, and in the surface 10 cm of soil. Concentrations rapidly decreased with increasing distance from the road edge and depth from the surface, reflecting the strong adsorption capacity of this element. Soils with high pH encouraged this adsorption process. Although soil intervention levels for Cd, Cu and Zn were not exceeded, many of the sites had concentrations of these metals above the target levels (0.8 mg/kg, 36 mg/kg and 140 mg/kg, respectively). Similarly to lead, these elevated concentrations were only found in surface soils adjacent to the road.

There has been some interest in recent years in emissions from catalytic converters of the platinum group elements (PGEs), including Platinum (Pt), Rhodium (Rh) and Palladium (Pd). Increased concentrations of PGEs have been reported in roadside soils and dusts, with higher Pt concentrations associated with higher traffic densities (Farago *et al*., 1998). The distribution of PGEs near to major roads has been shown to decrease rapidly away from the road, reflecting patterns shown by other traffic derived elements such as Zn and Pb (Jarvis *et al*., 2001). However, one study from the US indicated that Pt could potentially travel up to 50m from the roadside (Ely *et al*., 2001). Pt from road dusts can be solubilised and enter waters, soils and potentially be transferred to the food chain, although there is at present no evidence in the scientific literature of adverse health effects from Pt (Farago *et al*., 1998).

Effects of heavy metals on roadside soil function. Heavy metal contamination is not likely to impact on roadside soil function *per se* unless concnetrations were so high that plant growth was limjited, but is clearly of concern to people living and working near to major roads in terms of the potential health risks and the metal levels in foods grown near roads.

1.8.5. Natural soils

Sources of heavy metals to natural soils. Inputs of heavy metals to natural and semi-natural soils (e.g. moorlands, wetlands) are likely to be exclusively from atmospheric deposition. Deposition rates in such areas are best estimated using the methodology developed for the 'critical loads' studies described above in section 2.1.1.

There may be some input of Pb from lead shot where shooting is permitted, although this has now been prohibited over wetland sites of special scientific interest to prevent the poisoning of waterfowl which may ingest the lead shot (SI, 1999). Further investigation of the input and affects of lead shot has already been recommended in section 2.1.13.

Effects of heavy metals on natural soil function. Heavy metal inputs to natural and semi-natural soils could have implications for their ability to support of ecosystems, habitats and biodiversity. The impact of metals on soil microbes and microbial activity has been discussed above in terms of agricultural and forest soils, but the effects of such disturbances on sensitive natural ecosystems could be profound, especially if metal inputs occur in conjunction with acidification or eutrophication.

There are, however, a numbers of sites designated as SSSIs due to their elevated heavy metal concentrations (e.g. in former mining areas of Cornwall, Devon, north Pennines etc). Although not strictly natural soils in that the metals originate from historic mining activities, the anthropogenic activities largely ceased in the 19th Century so that the local ecology has had sufficient time to adapt to the conditions. These sites demonstrate that it is possible for ecosystems to recover and flourish in seemingly adverse environments, and although the original ecology of the sites has been lost a new and equally interesting habitat has developed.

1.9 Modelling heavy metal inputs to soils

The modelling of individual heavy metal inputs to soils has concentrated on atmospheric deposition loadings. The EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) was set up to support the Convention on Long Range Transboundary Air Pollution. The main tasks of EMEP in the field of heavy metals are to provide monitoring and modelling data on concentrations, depositions and transboundary fluxes of heavy metals over Europe. Deposition of Cd, Pb and Hg is modelled using the MSCE (Meteorological Synthesizing Centre East) emission/transport based model. This approach has been adopted and refined as part of the 'critical loads' methodology described earlier (Nemitz *et al*., 2000), with the recognised problem that modelled deposition estimates for the UK do not agree particularly well with those measured using 'frisbees', although rather better agreement was obtained with moss bag measurements. Nevertheless, these models overestimate deposition compared with emissions inventory in particular for Cd. This discrepancy still needs to be resolved.

In the UK, the FRAME model (Fine Resolution Atmospheric Multi-pollutant Exchange, Singles *et al*., 1998), originally developed to simulate the transport and deposition of reduced-N species, has been extended to include heavy metals, although no information is currently available on model performance or results. Models such as the MSCE emission/transport model and the FRAME model rely on spatial emissions data. This is commonly provided, in the UK, by systems such as the National Atmospheric Emissions Inventory (NAEI) which provide estimates of emissions to the atmosphere from the UK for a multitude of pollutants (see, for example, Dore *et al.*, 2004). However, spatial variations in emissions are often not quantified, or quantified only within a limited spatial domain, leading to uncertainties in emissions estimates and corresponding uncertainties in model predictions of deposition.

There are a number of studies which have derived models to predict the accumulation of metals in a particular soil (or soils) over time based on known sources, constant metal input rates, and the dynamics of metal behaviour in that soil (e.g. Moolenaar, 1997). UK studies have concentrated on developing a model for the soil accumulation of Cd from phosphate fertilisers. Work has also been undertaken in the Netherlands to model Cd accumulation at a regional scale (Tiktak *et al*., 1998) using a process based model called SOACAS. This considered inputs from atmospheric deposition, fertiliser and livestock manures, and losses via leaching and plant offtake. These were then combined with a Cd soil sorption model and incorporated into a Geographical Information System (GIS) to predict Cd concentrations in topsoil at a regional level. Towers and Paterson (1997) used a simpler approach for Scottish soils, employing a 'rule-based' classification of soils to assess their sensitivity to heavy metal inputs from sewage sludge. In previous work for Defra (Alloway *et al*., 2000) an initial attempt was made to produce partial metal flux maps for agricultural soils, although soil sorption models or sensitivity classes were not included. However, this was successful at identifying potential 'hotspots' for metal inputs which were largely related to areas of concentrated pig and poultry farming (Zn and Cu) or atmospheric deposition.

There is now considerable scope to expand this approach to develop a policy tool which could predict soil metal concentrations on a spatial and temporal basis as a result of for example changes in legislation (e.g. reduced livestock feed trace element concentrations) or other factors (e.g. falling animal numbers). This could be extended by overlaying the data onto soil metal concentration maps, which would enable the identification of soils that were particularly vulnerable to additional metal inputs either because they already had high soil metal concentrations or because they supported sensitive ecosystems.

1.10 The legislative framework

Most legal and voluntary measures relevant to heavy metal seek to control inputs to agricultural soils, although there are some Codes of Practice in place which cover other soil uses (e.g. forestry, land restoration). The measures can also be broadly divided into those which directly seek to limit or control heavy metal inputs to soil and those which have an indirect effect (i.e. measures which have implications for heavy metal inputs to soil without this being their primary purpose). A summary of the measures is provided in Appendix 6.

1.10.1 Agricultural soils

Organic manures. Direct measures are limited to those controlling metal inputs to soils with some organic materials. EU Directive 86/278/EEC on the protection of soil where sewage sludge is used in agriculture defines quality standards for sewage sludge including limit values for PTEs in soil to which sludge is applied and maximum annual quantities of PTEs which may be applied to the soil. This has been implemented in the UK by the Sludge (Use in Agriculture) Regulations 1989 (SI, 1989), as amended in 1990, and is supported by a Code of Practice for Agriculture Use of Sewage Sludge (DoE, 1996).

The regulations on agricultural use of sewage sludge currently represent the only statutory based mechanism specifically for controlling heavy metal inputs to agricultural soils in the UK. However, a voluntary certification scheme (PAS100) has recently been introduced for source segregated composted 'wastes' specifying limits on heavy metal concentrations in materials that are ready for sale or distribution (BSI, 2002) and compost producers are strongly urged to comply by the Composting Association. The Landfill Directive (EC, 1999) sets national targets for reducing the amount of biodegradable waste being disposed to landfill and the Waste Strategy 2000 tasks WRAP with taking measures to increase composting. As a consequence the amount of waste being composted and applied to land is likely to increase in future, with the effect that heavy metal additions to soils from this source will also increase.

Composts and other 'waste' materials (e.g. dredgings) can be applied to agricultural land under an exemption from the Waste Management Licensing regulations (SI, 2005), providing they can be shown to provide 'agricultural benefit or ecological improvement' and that heavy metal additions should be shown not to cause a disbenefit. This is usually effected by demonstrating that the application will not exceed the soil heavy metal limits specified in the Sludge Regulations. Indeed there is a Code of Practices for the application of paper sludge (Paper Federation of Great Britain, 1998) and guidelines for dredgings applied to agricultural land. The exemption process is regulated in England and Wales by the Environment Agency.

The heavy metal content of livestock manures largely reflects concentrations in the feed and the efficiency of feed conversion by the animal, although for some livestock there may be significant inputs of metals given on veterinary prescription (pigs) or used in footbaths (sheep and cattle). Clearly, a reduction in the heavy metal content of livestock feeds would lead to an associated reduction in excretal outputs and hence metal inputs to soils. Zinc and Cu are permitted additives to livestock feeds and concentrations in complete feeding stuffs for different livestock classes are currently controlled under the EU Feeding Stuffs Directive and implemented in the UK by the Feeding Stuffs Regulations (SI, 2000). It has been suggested that there is scope for reducing maximum permitted levels (MPLs) of Zn and Cu in livestock feeds closer to suggested nutritional requirements. The EC has recently reviewed the position with regard to a number of trace elements in animal feeding stuffs, and in some cases has recommended reductions. These recommendations have been reviewed by the EC Scientific Committee on Animal Nutrition (SCAN) and reductions to MPLs of some trace elements (including Zn and Cu) in certain livestock feeds have recently been agreed. The effects of these reductions on heavy metal inputs to soils with manures now need to be determined.

Inputs of heavy metals with livestock and other organic manures will be indirectly limited by compliance with published guidance on manure management and land application available in the Water Code (MAFF, 1998). More specifically Nitrate Vulnerable Zone (NVZ) legislation (Defra, 2002) limits the quantity and timing of manure applications in NVZs based on their nitrogen content and will also limit heavy metal application rates in these areas.

Fertilisers, plant protection and irrigation. The EC has recently issued a draft proposal relating to Cd in fertilisers, where a reduction of the maximum Cd concentration from 60 to 20 mg Cd/kg P_2O_5 over a period of 15 years was proposed. These values were based on Cd risk assessments and soil mass balance calculations by the Scientific Committee of Toxicology, Ecotoxicity and the Environment (SCTEE), utilising data reported from the Member states. However, this proposal was rejected and a new approach is being prepared at the moment. At the current state of consultation, the limit of 60 mg Cd/kg P_2O_5 is proposed to be fixed, with a labelling system for phosphate with a lower Cd content. Note that the median value for phosphate fertilisers used in UK agriculture is 31 mg Cd/kg P_2O_5, Marks (1996), so the introduction of such a limit would have minimal impact on Cd inputs to soils in England and Wales. In the interim, Austria, Sweden and Finland have already introduced national limits for permissible amounts of Cd in phosphate fertilisers.

In terms of plant protection products, The Water Resource Act (1991) currently prohibits the use of products containing Cd or Hg. Use of fungicides containing Zn or Cu is not restricted and can lead to high metal input rates to soils growing certain crops (e.g. hops).

There is no legislation relating to the quality of irrigation water, although there are guidelines recommending maximum heavy metal concentrations in irrigation water to prevent crop phytotoxicity (ADAS, 1981).

Organic farming. On organic farms, compliance with UKROFS standards may mean that heavy metal inputs to soils are lower than for conventional agriculture, but at present we have no data to support this hypothesis.

Overarching measures. There are two recent pieces of legislation, which whilst not directly tackling heavy metal inputs to or concentrations in soils, could have an important impact on agricultural practice. These are the Water Framework Directive (EC, 2000) and the Fresh Water Fish Directive (EC, 1978). The Water Framework Directive sets environmental quality standards for water, including limits for Cd, Cu, Hg and As concentrations in water. The Freshwater Fish Directive has set limits for Zn and Cu concentration in freshwaters where fish are present. Compliance with these directives will mean that potential sources of selected metals to water will need to be assessed. This could have implications for organic manure spreading where heavy metals could enter surface waters via leaching, bypass flow on cracking clay soils, or by overland flow in association with sediment losses.

Furthermore, the CAP reform package means that farmers will only receive the Single Payment if they achieve ‘cross-compliance’ (i.e. they comply with a number of existing directives including the Nitrates, Groundwater and Sewage Sludge Directives) and maintain their land in ‘good agricultural and environmental condition’ (GAEC). These requirements will encourage farmers to better understand the importance of protecting their soil resources from contamination.

1.10.2 Other soils

Atmospheric deposition. One of the major sources of heavy metal inputs to all soils is atmospheric deposition. Deposition will usually comprise a greater proportion of total inputs on urban, forest or natural soils than on agricultural soils, where metals can be input from many other sources. It is not practical to directly limit the amounts of metals that are deposited to soils. However, it is possible to control emissions to the atmosphere, and hence minimise atmospheric metal concentrations and ultimately metal deposition to soils. There are a number of relevant pieces of legislation.

In the UK, the Pollution Prevention and Control (PPC) regulations implement the Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC) and aim to prevent or reduce emissions and to air, land and water and waste production from a range of industries. The incidence of waste incineration as a primary waste management mechanism will increase as the cost of landfill tax and restrictions on the land application of waste increase. The Waste Incineration Directive will be the mechanism by which emissions from such facilities are minimised. However, since there will be an increased number of facilities, dispersed more widely across the country, the pattern of distribution of contaminants arising from waste incineration will differ from that which has been previously studied. The Large Combustion Plant Directive should also bring about a change in contaminant dispersal from these types of point sources. Road transport policy also has the capacity to influence contaminant inputs to soil. Increased use of cleaner fuels, more fuel efficient vehicles and development of clean technologies such as fuel cells, will contribute to reducing the incidence of contaminant release from the transport sector.

In the international context, the convention on Long-Range Transboundary Air Pollution (LRTAP) seeks to control emissions of air pollutants, with the Aarhus Protocol on Heavy Metals aiming to set targets for reduced emissions of Cd, Pb and Hg. Under the LRTAP, air pollution in Europe is monitored under the Co-operative Programme for Monitoring and

Evaluation of the Long Range Transmission of Air Pollutants (EMEP). This comprises ongoing monitoring of emissions, measurements of air and precipitation quality and development of a deposition model, although only selected metals (Cd, Pb) are covered. The EU Air Quality Framework Directive (96/62/EEC) first daughter directive sets critical levels for Pb in the air, but future directives will set levels for Cd, As, Ni and Hg.

Organic manures. There is no legislation directly controlling inputs of metals with sewage sludge or other organic materials to forest soil or land reclamation sites. However, there are Codes of Practice in place (Hall and Wolstenholme, 1999; Wolstenholme *et al*., 1992), which essentially apply the same principals and limits as those in the Code of Practice for the Agricultural Use of Sewage Sludge. Advice on the use of organic manures in forestry has recently been updated (Moffat, 2005).

Other inputs. The only other major source of metal to natural soils (and some agricultural soils) is with lead shot from shooting. The use of lead shot in wetland sites of special scientific interest has been prohibited to prevent the poisoning of waterfowl, which may ingest the shot (SI, 1999).

1.10.3. Summary

Most of the legal and voluntary measures relevant to heavy metals seek to control inputs to agricultural soils. The use of sewage sludge in agriculture is effectively regulated. However, measures to control heavy metal inputs in other organic manures are either voluntary (e.g. the PAS100 standard for composts) or indirect (e.g. the restrictions on manure application rates in NVZs). We suggest that it would be prudent to harmonise policy relating to heavy metal inputs from <u>all</u> organic materials applied to land. There should be a clear differentiation between materials applied as fertilisers (e.g. organic manure) and those acting a growing medium (e.g. dredgings).

1.11 Recommendations for further work

1.11.1 Policy requirements

- There is a need to *rationalise policy approaches* to control heavy metal inputs from <u>all</u> organic materials applied to land. There should be a clear differentiation between materials applied as fertilisers (e.g. manure) and those where additions act as a growing medium (e.g. canal dredgings). This should be supported by research to compare the behaviour in soils of heavy metals from different organic and other material additions, and their effects on long-term soil function.

- There would be benefit in *developing a policy tool to predict soil metal concentrations on a spatial and temporal basis* based on changes in legislation or other factors. The data could be overlaid with information from soil maps, to allow the identification of soils that are particularly vulnerable to additional metal inputs either because of inherently elevated soil metal concentrations or the ecosystems they support.

1.11.2 Information gaps

- A *re-survey of livestock feeds and manure metal concentrations* in England and Wales needs to be undertaken to provide up to date estimates of manure metal inputs (particularly Zn and Cu) following reductions in the permitted levels of trace element supplementation of livestock feeds introduced in January 2004.

- Current *on-farm practice for the use and disposal of Zn and Cu based footbaths* should be investigated.

- *Up-to-date information on the types and quantities of sewage sludge materials being applied to land* in England and Wales is needed to reflect the use of new sludge treatment processes, changes in outlets etc.

- More robust information on *the heavy metal content of MSW composts etc.* should be obtained to support their increasing use both in land restoration and in agriculture (where source segregated).

- We recommend that a *re-survey of Cd concentrations in phosphatic fertilisers* used on farms in England and Wales is undertaken to quantify the effect of the voluntary switch made by manufacturers to ‘low’ Cd rock phosphate sources.

- We recommend that *U concentrations in phosphate feed supplements and livestock manures* are quantified to provide underpinning data to assess the implications for animal health and welfare.

- There is a need for *up-to-date information on Hg levels in soils and crops in the vicinity of crematoria and cemetries* to provide a baseline against which changes in future emissions can be measured and monitored.

1.11.3 Research requirements

- There is an urgent need for up-to-date work on the *trace element requirements* of all livestock types, taking account of changes in genotype and management practices since the previous recommendations were published. These studies should encompass interactions between trace elements and other dietary constituents, as well as differences in the bioavailability of different mineral forms. In terms of reducing Zn and Cu loadings to agricultural soils, the studies should focus on *pigs* (weaners and finishers) and *poultry* (broilers and laying hens).

- The *discrepancy between different methods of estimating atmospheric heavy metal deposition* (‘frisbee’, moss samples, emission inventories and deposition modelling) needs to be resolved to derive a robust estimate of metal inputs from this source.

- There is a lack of information on *metal concentrations in soil leachates or in by-pass flow from cracking clay soils*, both of which may affect surface or ground water quality. This could have implications for compliance with the Freshwater Fish Directive where limits on Zn and Cu concentrations have been set. Such data are also valuable in compiling robust input-output balances for agricultural soils and farming systems.

- A number of representative *clay pigeon shoots and other shooting sites* should be studied to fully assess the scale, extent and implications of the Pb contamination problems, and if appropriate to identify potential remediation solutions.

- There is a need to investigate the effects of heavy metal inputs from atmospheric deposition on soil processes in *sensitive natural ecosystems*, which may also be experiencing acidification or eutrophication.

References (Heavy metals)

Adams ML, Zhao FJ, McGrath SP, Nicholson FA & Chambers BJ (2004). Predicting cadmium concentrations in wheat and barley grain using soil properties. *Journal of Environmental Quality* 33, 532-541.

ADAS (1981). Water Quality for Crop Irrigation : Guidelines on Chemical Criteria. ADAS/MAFF leaflet 776.

ADAS (1992). Soil Science Newsletter. SS/92/1. ADAS, Wolverhampton.

ADAS (2001). *The Safe Sludge Matrix : Guidelines for the Application of Sewage Sludge to Agricultural Land*, 3rd Edition. ADAS, Wolverhampton. Website : http://www.adas.co.uk/matrix

Adriano DC (2001). *Trace Elements in Terrestrial Environments: Biogeochmistry, Bioavailability, and Risks of Metals*. Springer-Verlag, New York.

Alloway BJ (1995) Soil processes and the behaviour of metals. In : Alloway B.J. (editor). *Heavy Metals in Soils* (2nd edition). Blackie Academic and Professional, London, pp. 11-37.

Alloway B J, Zhang P, Mott C, Chambers BJ, Nicholson FA, Smith SR, Carlton-Smith C, Andrews AJ (2000) *The Vulnerability of Soils to Pollution by Heavy Metals*. Final Report for MAFF Contract SP0127. MAFF, London.

Anon (1997). Survey of Irrigation of Outdoor Crops in 1995, England. HMSO, London.

Anon (1998). Compost Quality : The UK Standard. CON9801. Henry Doubleday Research Association Publications, Ryton, Coventry.

Anon (2000). Fertiliser Recommendations for Agricultural and Horticultural Crops (RB209), Seventh Edition. The Stationery Office Norwich 177pp.

Anon (2002). Germany to reduce pollutants in fertilisers. *Environment Daily* 1229, 5 June 2002.

Anon (2003). Fertiliser makers slam draft cadmium limits. *Environment Daily*, 1491, 5 August 2003

Barisic D, Lulic S & Miletic P (1992). Radium and Uranium in phosphate fertilisers and their impact on the radioactivity of waters. *Water Research (United Kingdom) Scope* 26:5, 607-611.

Blume HP & Brummer G (1991) Prediction of heavy metal behaviour in soil by means of simple field tests. *Ecotoxicological and Environmental Safety* 22, 164-174.

BSI (2005); *British Standards Institution. Specification for Composted Materials*. PAS100:2005. 2nd Edition. BSI, London.

Cao X, Ma LQ, Chen M, Hardison DW & Harris WG (2003). Lead transformation and distribution in soils of shooting ranges in Florida, USA. *Science of the Total Environment* 307, 179-189.

Cawse PA (1987). Trace and major elements in the atmosphere at rural locations in Great Britain 1972-1981. In : Coughtrey P, editor. *Pollutant Transport and Fate in Ecosystems*. Blackwell Scientific Publications.

CEC (1986); Commission of the European Communities. *Council Directive of 12 June 1986 on the protection of the environment and in particular of the soil, when sewage sludge is used in agriculture*. Official Journal of the European Communities, Directive 86/278/EEC, No L 181/6-12.

CEC (2000) *Directive 2000/86/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste*, Official Journal of the European Communities L332 (28.12.02)

CEC (2000). Commission Regulation Amending Directive 70/524 Concerning Additives in Feeding Stuffs as Regards to Trace Elements (Draft). SANCO/367 rev2/2000.

CEC (2001) *Directive 2001/80/EC) of the European Parliament and of the Council of 23 October 2001 on the limitation of certain emissions into the air from large combustion plant*. OJ L 309 27.11.2001 p1.

CEU (1999); *Council of the European Union. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste*. Official Journal L182, 1-19

Chambers, B. J., Smith, K. A., Pain, B. F. (2000). Strategies to encourage better use of nitrogen in animal manures. *Soil Use and Management* 16, 157-161.

Chang, A.C., Page, A.L. and Asano, T. (1995) *Developing Human Health-Related Chemical Guidelines for Reclaimed Wastewater and Sewage Sludge Applications in Agriculture.* World Health Organization, Geneva.

Chater M, Williams RJB. (1974) The chemical composition of British agricultural liming materials. *Journal of Agricultural Science*; 82: 193-205
Comber, S.D.W. and Gunn, A.M. (1996) Heavy metals entering sewage treatment works from domestic sources. *Water and Environmental Management* 10, 137-142.
Composting Association (2000). *The Composting Association Standards for Composts : Working Document.* The Composting Association, Wellingborough.
CPSA (2005). Clay Pigeon Shooting Association. http://www.cpsa.co.uk
Critchley RF (1983). An Assessment of Trace Metal Inputs to Agricultural Land in the United Kingdom. WRc, Medmenham.
Davies, B., Eagle D. & Finney B. (1977) Soil Management, Farming Press Ltd..
Davis RD & Rudd C. (1998). Investigation of the criteria for and guidance on the landspreading of industrial wastes. Final Report to the Environment Agency. Environment Agency R&D Technical Report P193. Environment Agency, Swindon.
Davis MRH, Smith SR & Bell JNB (unpublished). The effects of atmospheric deposition of heavy metals on the microbial community of a woodland ecosystem. Imperial College (unpublished report)
Dean, S., Garthwaite, D. G, and Thomas, M.R. (2001). Pesticide Usage Survey Report 173 : Hops in Great Britain 2000. Defra Publications, London.
Defra (2002a) Guidelines for Farmers in NVZs – England. Defra Publicatiaons, London PB5505
Defra (2002b) Ammonia in the UK. Defra Publications, London. PB6865
Defra (2003). The June Agricultural Census, 2003. Website : http://farmstats.defra.gov.uk
Defra (2004). *The First Soil Action Plan for England : 2004-2006*. Defra publication PB 9441.
Defra (2005a). Lameness in Dairy Cattle. http://www.defra.gov.uk/animalh /welfare/farmed/cattle/pb4020
Defra (2005b). Lameness in Sheep. http://www.defra.gov.uk/animalh /welfare/farmed/sheep/pb1149
DoE (1996). *Code of Practice for Agriculture Use of Sewage Sludge*. DoE Publications.
DETR (2001); Department of the Environment, Transport and the Regions. *The Draft Soil Protection Strategy for England and Wales - A Consultation Pape*r. DETR, London.
Dore CJ, Watterson JD, Goodwin JWL, Murrells TP, Passant, NR, Hobson MM, Baggott SL, Thistlethwaite G, Coleman PJ, King KR, Adams M, Cumine PR (2004): *UK emissions of air pollutants 1970 to 2002*. 16th NAEI report, NETCEN, UK.
DTLR (2001). *Planning Policy Guidance 25 – Development and Flood Risk*. Department of Transport, Local Government and the Regions.
EA (1998) *Groundwater Regulations Process Handbook* Section 4.3.1 (CONTROL OF AGRICULTURAL ACTIVITIES) - Annex 3 (Other agricultural activities) - pt. 6. Footbaths
EA (2001). *Assessment and management of risks to buildings, building materials and services from land contamination*. R&D Technical Report P5-035/TR/01
EA (2003). *Mercury emission from crematoria*. Consultation on an assessment by the Environment Agency's Local Authority Unit.
EA (2004), *The State of Soils in England and Wales*. Environment Agency, Bristol.
EC (1970). *The Feedingstuffs Directive*. 70/524/EEC
EC (1975). *Framework Directive on Waste*. 75/442/EEC.
EC (1978). *The Freshwater Fish Directive on the Quality of Fresh Waters Needing Protection or Improvement in order to Support Fish Life*. 78/659/EEC.
EC (1999). *The Landfill Directive*. 99/31/EC.
EC (2000). *The Water Framework Directive*. 2000/60/EC
EC (2001a). *The Soil Protection Communication* - DG Environment Draft October 2001. Website: http:/europa.eu.int/comm/environment/agriculture /pdf/soilpaper2.pdf
EC (2001b). Commission Regulation (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Communities L77, 1-13.
EC (2001c). Directive 2001/80/EC) of the European Parliament and of the Council of 23 October 2001 on the limitation of certain emissions into the air from large combustion plant. OJ L 309 27.11.2001 p1.
EC (2002). *Towards a Thematic Strategy for Soil Protection*, Brussels 16.4.2002 COM (2002) 179 Final.

EC (2003a). *Opinion of the Scientific Committee for Animal Nutrition on the Use of Copper in Feedingstuffs*. Health and Consumer Protection Directorate - General, C2 - Management of Scientific Committees; scientific co-operation and networks, 19 February 2003

EC (2003b). *Opinion of the Scientific Committee for Animal Nutrition on the Use of Zinc in Feedingstuffs*. Health and Consumer Protection Directorate - General, C2 - Management of Scientific Committees; scientific co-operation and networks, 14 March 2003

EC (2003c). Commission Regulation (EC) No 1334/2003 of 25 July 2003 amending the conditions for authorisation of a number of additives in feedingstuffs belonging to the group of trace elements. Official Journal of the European Communities L187, p.11.

Eckel H, Dohler H, Roth U. (2001)Assessment and reduction of heavy metal inputs into agro-ecosystems (AROMIS). EU Concerted Action QLK5-2000-00670. Report of the first meeting. KTBL, Darmstadt.

Eckel, H., Roth, U., Nicholson, F. and Unwin, R. (Eds) (2005) *Assessment and reduction of heavy metal inputs into agro-ecosystems (AROMIS)*. Final Report of EU Concerted Action QLK5-2000-00670. KTBL, Darmstadt.

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA & Jain JC (2001). Implications of platinum-group element accumulation along US roads from catalytic-converter attrition. Environmental Science and Technology, 35, 3816-3822.

Enviros (2004). Benefits of recycling sewage sludge for land restoration. Briefing note for Water UK. Water UK.

Farago, ME., Kavanagh, P., Blanks, R. Kelly, J., Kazantzis G., Thornton, I., Simpson, P. R., Cook, J. M., Delves, H. T. and Hall, G. E. M. (1998). Platinum concentrations in urban and road dust and soil, and in blood and urine in the United Kingdom. *Analyst*, 123, 451-454.

Fava G, Fratesi R, Ruello ML & Sani D (2002). Soil zinc contamination from corrosion of galvanised structures. *Chemistry and Ecology* 18, 223-232

Fowler, D., Cape, J.N. and Leith I.D. (1985) Acid inputs from the atmosphere in the United Kingdom. *Soil Use and Management* 1, 3-5.

Garthwaite, D. G, and Thomas, M.R. (2001). *Pesticide Usage Survey Report 171 : Arable Crops in Great Britain 2000*. Defra Publications, London.

Garthwaite, D. G, and Thomas, M.R. (2002). *Pesticide Usage Survey Report 181 : Soft Fruit in Great Britain 2001*. Defra Publications, London.

Gendebien A, Carlton-Smith C, Izzo M & Hall JE (1999). *UK Sewage Sludge Survey : National Presentation*, R&D Technical Report P165, Environment Agency, Swindon.

Gendebien A, Ferguson R, Horth H, Sullivan M, Davis R, Brunet H, Dalimier F, Landrea B, Krack D, Perot J, Orsi C. (2001) *Survey of Wastes Spread to Land*. Final Report of DG Environment Study Contract B4-3040/99/110194/MAR/E3. Website : http://europa.eu.int/comm/environment/waste/landspreading.pdf.

Gibbs P, Muir I, Richardson S, Hickman G &Chambers B (2005). *Landspreading on Agricultural Land : Nature and Impact of Paper Wastes Applied in England and Wales*. Environment Agency Report for project P5-088.

Goodlass, G. and Welch, W.. (2005). *The British Survey of Fertiliser Practice : Fertiliser Use on Farm Crops for Crop Year 2004* The BSFP Authority, London.

Hall JE & Wolstenholme R (1999). *Manual of Good Practice for the Use of Sewage Sludge in Land Reclamation*. WRc.

Hardeson Jr DW, Ma LQ, Luongo T & Harris WG (2004). Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering. *Science of the Total Environment* 328, 175-183.

Harmsen K. (1992) Long-term behaviour of heavy metals in agricultural soils : a simple predictive model. In: Adriano D. (editor). *Biogeochemistry of Trace Metals*. Lewis Publishers, Boca Raton, pp. 217-247.

Harrison P & Bradley K (2005). *Possible Health and Environmental Impacts of Tungsten in Lead Replacement Shot*. An IEH client report for Defra.

Harrison RM, Luhana L & Smith DJT (1993). Urban air pollution by heavy metals : sources and trends. *Proceedings of the 9th International Conference on Heavy Metals in the Environment, Toronto, Canada*. p81-84.

Haygarth PM & Jones KC (1992). Atmospheric deposition of metals to agricultural surfaces. In : D. C. Adriano, editor. *Biogeochemistry of Trace Elements*. Lewis Publishers, Boca Raton, pp. 249-276.

HGCA (1997). *Cereals and Sulphur Deficiency*. Topic Sheet 1, March 1997. Home Grown Cereals Association London.

Hill J, Stark BA, Wilkinson JM, Curran MK, Lean IJ, Hall JE & Livesey CT (1998). Accumulation of potentially toxic elements by sheep given diets containing soil and sewage sludge. I. Effect of type of soil and level of sewage sludge in the diet. *Animal Science* 67, 73-86

Hol PJ, Gawron AJ; Hurst JM, Yeager AR, Van Galen DA & Isrenn R. (1997). Investigation of lead and cadmium levels in roadside rhododendron leaves in Bergen, Norway utilizing multivariate analysis. Microchemical Journal**,** 55, 169-178

Hulme, M. *et al.* (2002) *Climate Change Scenarios for the United Kingdom*: The UKCIP02 Scientific Report, Tyndall Centre for Climate Change Research, School of Environmental Sciences, University of East Anglia, Norwich, UK. 120pp.

IC Consultants (2001). *Pollutants in Urban Waste Water and Sewage Sludge*. Final Report to DG Environment, European Commission. IC Consultants Ltd. London.

Jarup L, Berglund M, Elinder CC, Nordberg C & Vahter M (1998). Health effects of cadmium exposure - a review of the literature and risk estimate. *Scandinavian Journal of Work and Environmental Health* 24, 1-51.

Jarvis KE, Parry SJ & Piper JM. (2001). Temporal and spatial studies of autocatalyst-derived platinum, rhodium and palladium and selected vehicle-derived elements in the environment. *Environmental Science and Technology*, 35, 1031-1036.

Jones KV, Lepp NW & Obbard JP (1995) Other metals and metalloids. In : Alloway B.J. (editor). *Heavy Metals in Soils* (2nd edition). Blackie Academic and Professional, London, pp. 11-37.

Keller C, McGrath SP & Dunham SJ (2002). Trace metal leaching through a soil-grassland system after sewage sludge application. *Journal of Environmental Quality* 31, 1550-1560.

Lee, J., Grace, N. D. and Rounce J. R. (1994). Cadmium accumulation in liver and kidney of sheep grazing ryegrass/white clover pastures. *Proceedings of the New Zealand Society of Animal Production*, 54, 31-34

Lee D, Nemitz E, Fowler D, Hill P, Clegg S & Kingdon R. (2000). Sources, Sinks and levels of Atmospheric Mercury in the UK. http://www.aeat.co.uk/netcen/airqual/reports/dera_hg/dera_hg1.pdf

Lijzen JPA & Ekelenkamp A (1995). *Sources of diffuse emissions to soil* (In Dutch with English summary). Report no. 950011007. National Institute of Public Health and the Environment (RIVM), Bilthoven, the Netherlands..

Lock K & Janssen CR. (2005). Influence of soil zinc concentrations on zinc sensitivity and functional diversity of microbial communities. *Environmental Pollution*, 136, 275-281.

MAFF (1998a). Ministry of Agriculture, Fisheries and Food. *Code of Good Agricultural Practice for the Protection of Water*. MAFF Publications, London

MAFF (1998b). Ministry of Agriculture, Fisheries and Food. *Code of Good Agricultural Practice for the Protection of Soil*. MAFF Publications, London

Marks M (1996). *Survey of the trace contaminants in phosphatic fertilisers*. Experiment Report for MAFF project CS0201/CS0202. MAFF, London.

Martin MH & Bullock RJ (1994). The impact and fate of heavy metakls in an oak woodland ecosystem. In: *Toxic Metals in Soil-Plant Systems*, ed. SM Ross, Wiley Chichester.

McGrath SP & Loveland PJ (1992). *The Soil Geochemical Atlas of England and Wales*. Blackie Academic and Professional, London,.

McGrath SP (1996). Effects of heavy metals from sewage sludge on soil microbes in agricultural ecosystems. In: *Toxic Metals in Soil-Plant Systems*, ed. SM Ross, Wiley Chichester.

Mellor A & McCartney C (1994). The effects of lead shot deposition on soild and crops at a clay pigeion shooting site in northern England. *Soil Use and Management* 10, 124-129.

Misselbrook TH, Chadwick DR, Chambers BJ, Smith K, Webb J, Demmers T & Sneath RW (2004). *Inventory of Ammonia Emissions from UK Agriculture – 2003*. Annual project report to Defra for contract AM0127.

Moffat A. (2005). *Use of sewage sludges, composts and other organic wastes in forestry*. Forestry Commission Draft Information Note.

Moffat, A.J. and Hutchings, T.R. (1996) *National Report: United Kingdom. Forest Soil Condition in Europe*. Report of a large scale soil survey. ICP UN ECE.

Moffett BF, Nicholson FA, Uwakwe NC, Chambers BJ, Harris JA & Hill TCJ (2003). Zinc contamination decreases the bacterial diversity of agricultural soil. *FEMS Microbiology Ecology* 43, 13-19.

Moolenaar, SW, van der Zee SEATM & Lexmond ThM (1997). Indicators of the sustainability of heavy metal management in agro-ecosystems. *The Science of the Total Environment* 201, 155-169.

Muller AK, Christensen S & Sorenson SJ (2001). The effect of long-term mercury pollution on the soil microbial community. *FEMS Microbiol Ecol* 36. 11-19.

Nemitz E, Fowler D, McDonald AG, Gallagher MW, Dorsey J, Harrison RM & Allen AG. (2000). *Development of critical loads methodologies for toxic metals in soils and surface waters - estimation of the UK deposition fields of Cd, Pb, Cu and Zn*. Final report for NERC Environmental Diagnostics GST/03/1709. Centre for Ecology and Hydrology, Edinburgh.

Nicholson F. A., Smith, S. R., Alloway B. J., Carlton-Smith, C. and Chambers, B. J. (2003). An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of the Total Environment* 311, 205-219.

Nicholson, F.A. and Chambers, B. J. (2003) *Heavy metal content of animal manures and implications for soil fertility*. Final Report for Defra Contract SP0516

Nicholson FA, Chambers BJ, Williams JR & Unwin RJ (1999). Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresource Technology* 70, 23-31.

Nieschmidt A & Kim N (1997). Effects of mercury release from amalgam dental restorations during cremation on soil mercury levels of three New Zealand crematoria. *Bulletin of Environmental Contamination and Toxicology* 58, 744-751.

Nriagu, J.O. (1990) Global metal pollution : poisoning the biosphere ? *Environment* 32, 7-33.

Oosterhuis FH, Brouwer FM & Wijnants HJ (2000). *A possible EU wide charge on cadmium in phosphate fertilisers : economic and environmental implications*. European Commission report number E-00/02.

Paper Federation of Great Britain (1998). Code of Practice for Landspreading Paper Mill Sludges. Paper Federation of Great Britain, Swindon.

Pitman R. (???) *Wood Ash use in forestry : A Review of the Environmental Impacts*. Forestry Commission.

Rooney CP, McLaren RG & Creswell RJ (1999). Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water Air and Soil Pollution* 116, 535-549

Rothbaum HP, McGaveston DA, Wall T, Johnston AE & Mattingly GEG (1979). *Journal of Soil Science,* 30, 147-153

Rosen GD & Roberts PA (1996). *Comprehensive Survey of the Response of Growing Pigs to Supplementary Copper in Feed*. Field Investigations and Nutrition Service Ltd., London.

Ryan (1981). *Nuclear Safety*, 22, 70-76

Singles R, Sutton MA & Weston KJ (1998): A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. *Atmospheric Environment*, 32, 3, 393-399.

SI (1989). *The Sludge (Use in Agriculture) Regulations 1989*, SI 1263, HMSO, London.

SI (1990). *The Sludge (Use in Agriculture) Regulations 1990*, SI 880, HMSO, London.

SI (1999). *The Environmental Protection (Restriction of the use of Lead Shot) (England) Regulations 1999*. SI 2170. HMSO, London.

SI (2000). *The Feeding Stuffs Regulations 2000*. SI 2481, The Stationary Office, Norwich.

SI (2005). *The Waste Management Licensing (England and Wales) (Amendment and Related Provisions) Regulations 2005*, SI 883. HMSO, London.

Slater R,. Davies P & Gilbert EJ (2005). *The State of Composting in the UK 2003/04*. The Composting Association Wellingborough.

Smith KA, Brewer AJ, Crabb J & Dauven A. (2000). A critical appraisal of animal manure management practice in England and Wales: I. Pig manure. *Soil Use & Management* 16: 124-132.

Smith KA, Brewer AJ, Crabb J & Dauven A. (2001). A critical appraisal of animal manure management practice in England and Wales: II. Poultry manure. *Soil Use & Management* 17: 48-56.

Smith KA, Brewer AJ, Crabb J & Dauven A (2001). A critical appraisal of animal manure management practice in England and Wales: III. Cattle manure from dairy and beef production. *Soil Use & Management*; 17: 77-87.

Smith SR (1996). Agricultural Recycling of Sewage Sludge and the Environment. CAB International, Oxford, 382 pp.

Smolders E, Leuven KU, Buekers J, Oliver I & McLaughlin MJ (2004). Soil properties affecting toxicity of zinc to soil microbial properties in laboratory-spiked and field-contaminated soil. *Environmental Toxicology and Chemistry* 23, 2633-2628.

Thomas MR & Wardman OL (1999). *Pesticide Usage Survey Report 150. Review of Usage of Pesticides in Agriculture and Horticulture throughout Great Britain 1986-1996*. MAFF Publications, London.

Thomas VG (1997). The environmental and ethical implications of lead shot contamination of rural lands in North America. *Journal of Environmental Ethics* 10, 41-55.

Tiktak A, Alkemade JRM, van Grinsven JJM & Makaske GB, (1998). Modelling cadmium accumulation at a regional scale in the Netherlands. *Nutrient Cycling in Agroecosystems* 50, 209-222.

Towers W. and Paterson E. (1997) Sewage sludge application to land - a preliminary assessment of the sensitivity of Scottish Soils to heavy metal inputs. *Soil Use and Management* 13, 149-155.

TRL (2002). *Pollution from Roads and Vehicles and Dispersal to the Local Environment*. Final Report of EC Project Pollution of Groundwater and Soil by Road and Traffic Sources: dispersal mechanisms, pathways and mitigation measures (POLMIT). Project no. RO-97-SC.1027

Turner AP (1996). The responses of plants to heavy metals. In : *Toxic Metals in Soil-Plant Systems* (Ed. SM Ross). Wiley, Chichester.

Underwood EJ & Suttle NF (1999). *The Mineral Nutrition of Livestock*, 3rd Edition. CABI Publishing Wallingford.

UKROFS (2003). *UKROFS Standards for Organic Food Production*.

US EPA; US Environmental Protection Agency (1992) *Technical Support Document for Land Application of Sewage Sludge*, Volume I. Eastern Research Group, Lexington.

Wadsworth GA & Webber J (1977). Deposition of minerals and trace elements in rainfall. In : Inorganic Pollution and Agriculture, MAFF Reference Book 326. HMSO, London.

Water UK (2001). *Cadmium briefing paper*. Website : http://www.water.org.uk.

Whitehead R (2001). The UK Pesticide Guide 2001. CABI Publishing, Wallingford

Williamson J, Rowe E, Rendell T, Healey J, Jones D & Nason M. (2003). *Restoring habitats of high conservation value after quarrying: best practice manual*. Institute of Environmental Science, University of Wales, Bangor.

Wolstenholme R, Dutch J, Moffat AJ, Bayes CD & Taylor CM (1992). *A manual of good practice for the use of sewage sludge in forestry*. Forestry Commission Bulletin 107. HMSO, London.

WRAP (2004). *To Support the Development of Standards for Compost by Investigating the Benefits and Efficacy of Compost Use in Different Applications*. WRAP Project code STA0015. WRAP Banbury.

WS Atkins (2000). *Environmental Impact of Metals : Review of Zinc in the UK*. Report for the Department of Environment, Transport and the Regions.

Zechmeister HG, Hohenwallner D, Riss A & Hanus-Illnar A (2005). Estimation of element deposition derived from road traffic sources by using mosses. *Environmental Pollution* 138, 238-249

Zhao FJ, Adams ML, Dumont C, McGrath SP, Nicholson FA, Chambers BJ & Sinclair AH (2004). Factors affecting the concentration of lead in British wheat and barley grain *Environmental Pollution* 131, 461-168.

Zielinski RA, Asher-Bolinder S, Meier AL, Johnson CS & Szabo BJ (1997) Natural or fertilizer-derived uranium in irrigation drainage : a case study in southeastern Colorado USA, *Applied Geochemistry*, 12, 9.