The Defra “Agricultural Soil Heavy Metal Inventory” for 2008

Report 3 for Defra Project SP0569

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EXECUTIVE SUMMARY

Controlling heavy metal inputs to soils is of great importance because of their persistence once they are present. Soil contamination by cadmium, lead and mercury may present a risk to human health if sufficient quantities were to enter the foodchain. Similarly, soil contamination by zinc and copper may have serious implications for long-term soil fertility and the potential for soils to support microbial populations, and food and fibre production.

Reducing heavy metal inputs to soils is a strategic aim of soil protection policies in the UK and the EU. "Safeguarding our Soils: A Strategy for England" published in September 2009 (Defra, 2009a) provides approaches to protecting soils in the long-term and acknowledges the need to reduce the levels of pollutants entering soils from materials spread to land. However, in order to achieve this aim information on the significance and extent of soil pollution 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 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 both the national scale and field-level, and for estimating the temporal capacity of soils to accept heavy metal inputs.

Heavy metal concentrations in livestock manures were measured to update measurements from the 1990s, particularly on Zn and Cu., This aimed to take account of reductions in the maximum permitted levels of trace element supplementation in livestock feeds introduced in 2004. Also, up-to-date information on the metal contents and quantities of other organic materials recycled to agricultural land, including sewage sludge (biosolids), compost, paper crumble, digestate, food and industrial 'wastes' etc. was collated. 'New' materials such as ash from the incineration of poultry litter and paper crumble, water treatment cake and food 'wastes' were also included in the inventory.

Whilst atmospheric deposition was shown to be a major source of heavy metals inputs to agricultural land at the *national level* (24-35% of total inputs for Zn, Cu, Ni, Cd, Pb and As, and 80% for Hg), livestock manures (*c*.30% of Zn, Cu and As inputs) and biosolids (10-41% of metal inputs) were also important sources because of the large quantities applied. Additionally, the results showed that metal addition rates at the *field-level* from some pig and poultry manures and green compost were similar to (and sometimes greater than) from biosolids. Moreover, metal addition rates from materials which are increasingly being applied to agricultural land (e.g. unprocessed food 'wastes' applied under an exemption from the Environmental Permitting Regulations and in compliance with current maximum permitted soil metal concentrations), were sometimes greater than those from biosolids.

‘Worst-case’ scenario estimates were made of the temporal capacity of a ‘typical’ topsoil for heavy metals (based on current maximum permitted soil metal concentrations where biosolids are applied and for a topsoil currently at background metal concentrations), assuming that the materials were applied every year to the same field, which would not often be the case in practice (particularly for biosolids and paper crumble).The ‘typical’ topsoil temporal capacity for Zn was estimated to be reached after less than 200 years of annual biosolids, pig slurry, compost and water treatment cake additions. In comparison, it was estimated to take >1,000 years of annual cattle farmyard manure applications to raise ‘typical’ topsoil Zn concentrations to the maximum soil limits. For unprocessed food ‘wastes’, the limiting metal was generally Cd, with the maximum soil concentration estimated to be reached after *c.*300 years of annual application.

This study has provided baseline information for the development of strategies to reduce heavy metal inputs to agricultural land and to effectively target any future policies for minimising long-term metal accumulation in soils.

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1. OBJECTIVE

The objectives of this work were:

- To collect up-to-date data on the heavy metal content of different types of livestock manures (including pigs, poultry and cattle).
- To collate more recent data on the metal content of other organic materials going to land and determine if the atmospheric deposition data need to be updated.
- To re-run the Defra “Agricultural Soil Heavy Metal Inventory” and establish any differences from the previous (2004) inventory.
- To calculate the temporal capacity (in years) of soils to reach current maximum permissible soil metal concentrations as specified in the Code of Practice for Agricultural Use of Sewage Sludge.
- To calculate the temporal capacity of soils (in years) to reach a range of maximum permissible soil metal concentrations.

2. INTRODUCTION

Controlling heavy metal inputs to soils is of great importance because of their persistence once they are present. Soil contamination by cadmium (Cd), lead (Pb) and mercury (Hg) may present a risk to human health if sufficient quantities of these elements were to enter the foodchain. Similarly, soil contamination by zinc (Zn) and copper (Cu) may have serious implications for long-term soil fertility and the potential for soils to support microbial populations, and food and fibre production.

Reducing heavy metal inputs to soils is a strategic aim of soil protection policies in the UK (Defra, 2004; Defra 2009a) and the EU (EC, 2002). “Safeguarding our Soils: A Strategy for England” published in 2009 (Defra, 2009a) provides approaches to protecting soils in the long-term and acknowledges the need to reduce the levels of pollutants entering soils from materials spread to land. However, in order to achieve this aim information on the significance and extent of soil pollution 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, nickel - Ni, chromium - Cr, Pb, Cd, Hg and arsenic - 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 national and catchment scales and at the field-level, and for estimating the temporal capacity of soils to accept heavy metal inputs.

In this project, livestock manure metal concentrations were measured (building upon a previous sampling exercise undertaken in the 1990s) to provide up-to-date estimates of metal inputs (particularly Zn and Cu) from manures, following reductions in the maximum permitted levels of trace element supplementation in livestock feeds introduced in 2004 (EC, 2003). Also, up-to-date information on the metal content and quantities of other organic materials recycled to agricultural land, including sewage sludge (biosolids), compost, paper crumble, digestate and industrial ‘wastes’ etc. was collated, using published data sources and ADAS’ contacts within the agricultural and recycling industries. ‘New’ materials such as ash from the incineration of poultry litter and paper crumble, water treatment cake and food ‘wastes’ were included in the inventory. It was hoped to include fluorine (F), selenium (Se) and molybdenum (Mo) in the Inventory, however, very little data was available on the concentration of these elements in materials applied to land, and so inclusion in the Inventory at this stage would not have provided any meaningful information.

The Defra “Agricultural Soil Heavy Metal Inventory” for 2004 (Nicholson *et al.*, 2008) showed that atmospheric deposition was an important source of metal inputs to agricultural soils in terms of total inputs to England and Wales, although at a field-level inputs were low. Atmospheric deposition data in the 2004 Inventory were based on measurements made during the period 1995-

98, at 28 sites, using the “frisbee” technique (Alloway *et al*., 2000). However, Nemitz *et al*. (2000) highlighted that there can be discrepancies between different methods of estimating atmospheric heavy metal deposition (i.e. “frisbees”, moss samples, emission inventories and deposition modelling). Hence, an important part of this project was to review the latest Defra-funded research on atmospheric heavy metal deposition, with a view to revising (if appropriate) the figures previously used in the 2004 Inventory.

The updated Defra “Agricultural Soil Heavy Metal Inventory” for 2008 (compiled in this project) was used to identify where there had been changes in metal inputs to land from different sources, in comparison with the 2004 Inventory. In particular, the impact of reductions in the maximum permitted concentrations of Zn and Cu in livestock feeds on the contribution of livestock manures to overall metal inputs was assessed. Also, using the mean heavy metal content of soils in England and Wales (McGrath and Loveland, 1992), the length of time it would take for a ‘typical’ soil to reach the current maximum permissible metal concentrations as specified in the Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996) was determined. Additionally, using the same methodology, the length of time it would take for soils to reach a range of maximum permitted metal concentrations e.g. those calculated by the EA/EU Risk Assessment Approach (EA, 2008) or in the EC “Working Document on Sludge 3rd Draft” (EC, 2000) was estimated.

3. SOURCES OF HEAVY METALS TO AGRICULTURAL SOILS

3.1 Atmospheric deposition

Metals deposited from the atmosphere on to the soil surface will gradually become incorporated into the soil and will contribute to overall soil concentrations. Whilst atmospheric deposition is ubiquitous, deposition rates depend on proximity to point sources of pollution, such as heavy industry or major roads.

In previous iterations of the Inventory, data on heavy metal inputs to lowland agricultural soils were based on the Reading University “frisbee” monitoring network established by Alloway *et al*. (2000). However, this data is now around 15 years old and there have been more recent reductions in emissions, implying that the atmospheric deposition of metals was probably overestimated in the previous Inventories. Moreover, concerns have been raised that the “frisbee” methodology overestimated metal deposition in comparison with techniques used in other monitoring networks. For these reasons, this project reviewed the deposition data from the Reading network, along with data from the CEH “Rural Heavy Metal Monitoring Network”, to derive new estimates of heavy metal deposition to agricultural land.

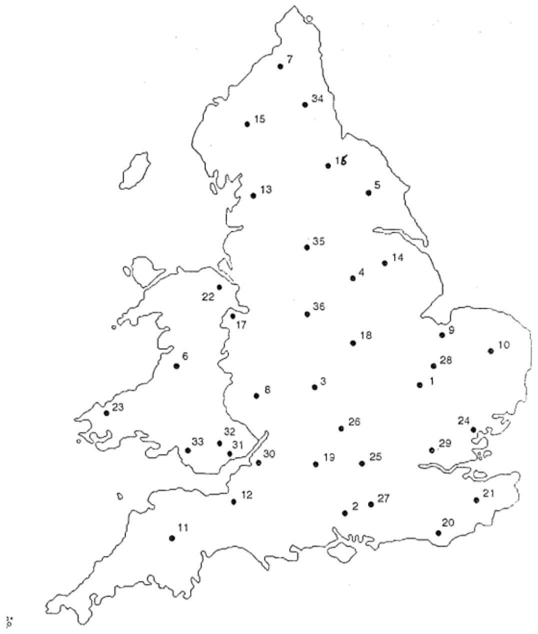
3.1.1 Measurements of metal deposition in the UK

Reading Network. This network was set up by Reading University at 35 sites in England and Wales as part of a MAFF-funded project (Alloway *et al*., 2000), Figure 1. Most sites were on agricultural land, with a bias towards lowland arable and grassland rather than upland rough grazing or forestry, and included a site near the Avonmouth zinc smelter. Total deposition was collected using Warren Springs Laboratory inverted “frisbees” at a height of 1.8m above the ground in duplicate pairs. Frisbees are recognised to collect ‘large’ dust particles (mainly 20-50μm), as well as ‘small’ particles in wet deposition. Samples were analysed to determine a soluble fraction (<0.45μm) and an insoluble fraction. All samples were analysed for metals; including As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The network operated for 42 months between 1995 and 1998.

CEH Network. CEH set up a “Rural Heavy Metal Monitoring Network” consisting of 15 sites across the UK (10 in England and Wales), Figure 2. Bulk precipitation samplers are used at all sites, with cloud collection at two upland sites. Particulates (PM_{10} i.e. <10μm) are collected at 10 sites, using ESM Anderson samplers, which can be equated to background rates of dry deposition. All samples are analysed for metals; including As, Cd, Cr, Cu, Mo, Ni, Pb, Se and Zn. Sampling started in 2004 and is ongoing.

A summary of the main differences between the two networks is given in Table 1.

Figure 1. Reading Network monitoring sites



Site No	Location
1	Boxworth
2	Bridgets
3	Drayton
4	Gleadthorpe
5	High Mowthorpe
6	Pwllpeiran
7	Redesdale
8	Rosemaund
9	Terrington
10	Morley
11	North Wyke
12	Taunton
13	Lancaster
14	North Lincs
15	Penrith
16	Northallerton
17	Ellesmere
18	Leicester
19	Marlborough
20	Uckfield
21	Ashford
22	Ruthin
23	Pembroke
24	Colchester
25	Sonning
26	Wytham
27	Alice Holt
28	Arthur Rickwood
29	Brentowood
30	Avonmouth
31	Usk
32	Monmouth
33	Cowbridge
34	Hexham
35	Harewood
36	Ashbourne

Figure 2. CEH “Rural Heavy Metal Monitoring Network” sites

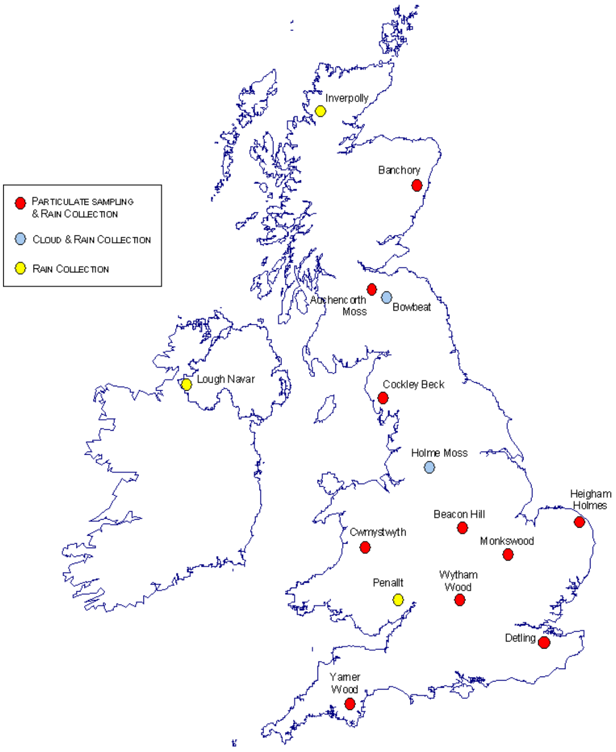


Table 1. Differences between the Reading and CEH networks

Reading	CEH
34 sites.	15 sites.
England and Wales.	UK.
Predominantly agricultural land (bias towards lowland arable and grassland).	Predominantly remote rural/upland.
42 months data (1995-8).	Ongoing (4 years available from 2004).
Samples collected monthly	Samples collected weekly or monthly depending on the site
Used Warren Spring Laboratory “frisbees” to collect ‘total deposition’ (wet + dry).	Uses bulk rainfall collectors at all sites, plus particulate and cloud deposition collectors at selected sites.
Total deposition calculated for agricultural land area only.	Total deposition calculated for whole land area.
Mercury measured using same method as other metals.	Mercury measured using a method to reduce diffusion to/from atmosphere.
Se and Mo not measured.	Se and Mo measured

3.1.2 Comparison of data from the two networks

Deposition rate measurements from the Reading network were higher than those reported by CEH for all eight of the metals measured by each network (Table 2).

Table 2. Comparison of metal deposition rates (g/ha/yr) from the Reading and CEH networks

Metal	Reading[1]	CEH[2]			
		2004	2005	2006	2007
Zn	221	83	79	69	42
Cu	57	12	12	11	8.7
Ni	16	3.9	5.6	4.4	2.6
Pb	54	18	14	12	8.8
Cd	1.9	0.37	0.36	0.34	0.22
Cr	7.5	2.2	1.9	2.2	2.2
As	3.1	2.8	2.6	2.8	2.3
Hg	1.0	-	0.07	0.08	0.09

[1] 34 sites over 42 months from 1995-98 (England and Wales), excluding Avonmouth Arithmetic mean.

[2] Mean of data extrapolated from the 15 monitoring sites to *c.*11,000 mapping points (UK). Data for Hg not provided for 2004.

The Reading network sites were mainly located on lowland arable and grassland, and whilst care was taken to locate them >500m from major roads, >1km from motorways and >5km from industrial point sources, they were still nearer to industrial/urban sources of heavy metal pollution than the remote upland sites selected by CEH. There is therefore a strong argument that the Reading measurements are more representative of actual deposition onto *agricultural* land than the CEH measurements, which were designed to measure *background* metal concentrations and deposition. Indeed, comparison with other international data has shown that the Reading network deposition rates were similar to those measured in 12 other European countries (Nicholson *et al*., 2003). Fowler *et al*. (2006) also compared total annual metal deposition calculated from a range of sources (National Atmospheric Emission Inventory-NAEI from 1995 to 2003; European Monitoring and Evaluation Programme-EMEP deposition values; moss deposition data; the Reading data and the FRAME model) and found some large differences. In general, total emissions estimated using the emission approach (NAEI) were up to an order of magnitude smaller than from the deposition network measurements. Notably, the Reading network produced higher total deposition estimates than either the moss survey or the CEH network, but this was most probably (in part) due to the location of the sampling sites as discussed above.

It has been argued (Nemitz *et al*., 2000; Fowler *et al*., 2006) that due to the design of the “frisbee” samplers, the Reading network captured a substantial proportion of locally suspended and redeposited dust/soil particles, and therefore the results were not truly representative of heavy metal deposition rates derived solely from the atmosphere. There is some evidence from the Reading data to support this argument. For example, the site at Ashbourne (Derbyshire) was located in an area of old lead mine workings, with high soil Pb concentrations (142 mg/kg) and recorded the second highest level of Pb deposition (the highest being at Avonmouth). Similarly, the site at North Wyke (Devon) had high levels of Pb deposition, which most probably reflected the presence of former Pb mines on Dartmoor.

A comparison was made between the CEH bulk collection samplers and the “frisbee” samplers (Nemitz *et al*., 2000). Fowler *et al*. (2006) commenting on the study of Nemitz *et al*. (2006) stated that “Comparing the metal deposition at Redesdale, close to the Scotland–England border with values at Auchencorth Moss, in the Scottish Borders, a site with similar annual precipitation, deposition values were substantially larger for the “frisbee” network by between 30% and a factor of two, depending on the metal”. However, such inferred differences cannot be considered a true comparison as there may be important local influences on deposition rates at each site. Also, Fowler *et al*. (2006) stated that “A six-month comparison at Auchencorth Moss of a wet only collector and the “frisbee” collector confirmed these results. The most likely cause of the larger values from the “frisbee” collector was the capture of locally re-suspended particulate matter, which was not sampled so efficiently by the wet collector. Due to their aerodynamic characteristics, the capture efficiency of the “frisbee” collectors for coarse particles probably exceeded that of vegetation.”

It is also possible that the “frisbee” design may have collected too much or too little rainfall, due to splash effects. However, Reading University compared the rainfall volumes collected by the “frisbees” with Meteorological Office rainfall data measured at weather stations close to the “frisbee” monitoring sites (Alloway *et al*., 2000). Generally, the amounts of rainfall collected by the “frisbees” agreed well with the weather stations, with a discrepancy (underestimate) of only around 10%. The national average annual rainfall collected with the “frisbees” was 654 mm, which was 87% of the national average of Meteorological Office rainfall (751 mm).

It would be expected that metals derived from soil/dust particles would be largely present in an *insoluble* form. Data from the Reading network showed that for Zn, Cu, Cd, Ni, As and Hg *at least 60% of the total deposition was in a soluble form* (i.e. passing through a 0.45µm filter), indicating that metal deposition was largely derived from rainfall inputs (Table 3). For Pb and Cr, <50% of deposition was in a soluble form suggesting that dust/soil was a relatively more important source of these metals. The CEH network also measured the greatest proportion (>60%) of metals in wet deposition (Table 3), although the samplers also collected some dry deposition (i.e. fine particulate material <10µm).

In summary, these data indicate that an important proportion of total metal deposition is in the form of small particulates which reach the soil as dry deposition, and that the Reading network may have over-estimated this fraction due to the capture of some ‘large’ locally suspended and redeposited dust/soil particles, which were not measured by the CEH samplers.

Table 3. Proportion (%) of metal in soluble and insoluble fractions (Reading) or deposited as wet, dry and cloud deposition (CEH)

	Reading		CEH		
Metal	Soluble	Insoluble	Wet	Dry*	Cloud
Zn	72	28	82	17	1
Cu	70	30	69	29	2
Ni	68	32	69	29	2
Pb	44	56	69	30	1
Cd	60	40	73	25	2
Cr	34	66	65	33	2
As	62	38	69	30	1
Hg	62	38	nd	nd	nd
Se	nd	nd	81	16	3
Mo	nd	nd	nd	nd	nd

*Particulate material <10µm
nd = no data

3.1.3 Adjusting metal deposition rates for use in the Inventory

This project needed to make a decision on which dataset was most appropriate for use in the updated inventory of metal inputs to agricultural land. On balance, the project team (and Steering Group) considered that it would be most appropriate to continue to use the Reading measurements, as these were specifically designed to measure deposition to *agricultural* land rather than the CEH measurements, which related to deposition to largely remote upland sites. However, we adjusted the Reading measurements as follows:

1. The soluble deposition component of the Reading measurements equates to metal inputs in wet deposition and provides a robust estimate of rainfall derived metal deposition. The proportion of dry deposition from the CEH data (Table 3) was then used to estimate total deposition for the Reading network data (i.e. wet plus dry deposition). This had the effect of reducing the total deposition rate for most metals, and in particular for Cr and Pb (Table 4).
2. The CEH data showed a clear trend of decreasing total metal deposition over time for most metals, with the exceptions of Cr and Hg (Table 2). This trend was supported by longer term results from moss survey data from 28 European countries, which showed a decrease in moss heavy metal concentration from 1990 for the majority of metals (Harmens and Norris, 2008; Harmens *et al*., 2007; Harmens *et al*. 2008). These temporal trends in moss heavy metal concentrations are in agreement with trends in EMEP emission data for As, Cd, Cu, Pb, Hg, Ni and Zn. As it is now more than 10 years since the Reading data were collected, we considered that it would be appropriate to make adjustments to estimated deposition rates based on reported temporal trends. The decline in UK moss heavy metal concentrations between 1995 and 2005 (a period which roughly corresponds to the time since the Reading measurement were made) is shown in Table 4.

Table 4. Reading network adjusted deposition rates based on CEH dry deposition proportions and temporal trends from UK moss surveys

	Reading deposition data			CEH	*Total deposition*	UK moss concentration		Reduction	**Total deposition**
Metal	Mean total	Soluble fraction	Wet	Dry deposition	*(adjusted for dry deposition)*	1995	2005		**(adjusted for time)**
	g/ha[1]	%[1]	g/ha	%[2]	*g/ha*	mg/kg[3]		%	**g/ha**
Zn	221	72	159	17	*192*	34.2	20.0	42	**112**
Cu	57	70	40	29	*56*	5.4	3.6	34	**37**
Ni	16	68	11	29	*15*	1.5	0.8	49	**8**
Pb	54	44	24	30	*34*	8.3	2.6	69	**11**
Cd	1.9	60	1.1	25	*1.5*	0.2	0.1	51	**0.7**
Cr	7.5	34	2.6	33	*3.8*	1.4	0.8	41	**2.2**
As	3.1	62	1.9	30	*2.7*	0.4	0.1	68	**0.9**
Hg	1	62	0.6	Nd	*0.62*	nd	nd	nd	**1**

nd = no data

[1] Alloway *et al*. (2000)

[2] Fowler *et al*. (2006)

[3] Harmens *et al*. (2007); Harmens *et al*. (2008)

Table 5. Previous and revised metal deposition rates for use in the "Heavy Metal Inventory for Agricultural Soils" (and comparison with 2007 CEH data)

	Previous deposition rate* (g/ha)	Revised deposition rate (g/ha)	Reduction (%)	CEH 2007 (g/ha)
Zn	221	112	49	42
Cu	57	37	35	8.7
Ni	16	8	50	2.6
Pb	54	11	80	8.8
Cd	1.9	0.7	63	0.22
Cr	7.5	2.2	71	2.2
As	3.1	0.9	71	2.3
Hg	1.0	1.0	nd	0.09

nd = no data
*Alloway *et al*. (2000)

The net effect of these adjustments was to reduce metal deposition rates in the 2008 Inventory by between 35 and 71% compared with the 2004 Inventory, with the greatest reductions for Pb, Cr and As (Table 5). Nevertheless, the revised metal deposition rates (with the exception of Cr and As) were still up to 4-fold higher than total deposition rates reported by CEH for 2007 (with the exception of Hg).

3.1.4 Changes to total metal deposition estimates

Total metal deposition was estimated in the inventory from the mean deposition rate of each metal and the total area of agricultural land in England and Wales in 2008 (9.1 million hectares). As other metal input sources (e.g. livestock manures, biosolids, compost, fertilisers etc.) are not applied to rough grazing or woodland, these areas were excluded from the agricultural land area used to calculate total metal deposition.

The net effect of all these changes was to substantially decrease total atmospheric inputs of all heavy metals to agricultural land in England and Wales. For example, total Zn inputs decreased from *c.*2500 t/y in the 2004 Inventory to *c.*1000 t/yr in the 2008 Inventory, and Pb inputs decreased from *c.*600 t/y to *c.*100 t/yr.

3.2 Biosolids

Biosolids (sewage sludge) are a valuable source of nitrogen (N), phosphorus (P) and organic matter to agricultural soils. In the EU, the recycling of biosolids in agriculture is controlled by Directive 86/278/EEC, which aims to “to regulate the use of sewage sludge in agriculture in such a way as to prevent harmful effects on soil, vegetation, animals and man, thereby encouraging the correct use of such sewage sludge” (CEC, 1986). This Directive is implemented in the UK through the Sludge (Use in Agriculture) Regulations 1989 (SI, 1989) and the Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996). It is a legislative requirement to monitor and control the application of biosolids to agricultural land to ensure that permitted levels of soil heavy metals are not exceeded (Table 6).

Table 6. Maximum permissible concentrations of heavy metals in soils after application of biosolids 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	300				15
Hg	1				0.1
Cr	400				15
Mo	4				0.2
Se	3				0.15
As	50				0.7
F	500				20

The 2004 Inventory (Nicholson *et al*., 2008) used biosolids data from the period 1996 to 1997 (Gendebien *et al*., 1999). At that time, approximately 50% of the sludge produced in England and Wales (480,000 tonnes of dry solids – tds) was applied to 73,000 ha of agricultural land. Data from the Environment Agency “Sewage Sludge Survey 2001 to 2007” (M. Davis, EA; pers. comm.) was used to update the Inventory and showed that in 2007 biosolids applications had increased to more than 1.1 million tds and were applied to an estimated 170,000 ha of agricultural land (assuming an application rate of 6.5 t/ha dry solids). Metal inputs to land were calculated using mean biosolids quality data for the period 2001 to 2007 (Table 7).

Table 7. Biosolids nitrogen and heavy metal concentrations

	Concentration (mg/kg dry solids-ds)	
Metal	1996/97[1]	Mean 2001-2007[2]
Nitrogen (% ds)	4.4	3.6
Zn	802	636
Cu	565	330
Ni	59	38
Pb	221	151
Cd	3	2
Cr	163	92
As	6	6[3]
Hg	2	1

[1] Gendebien *et al*. (1999). Used in the 2004 Inventory

[2] M. Davis (EA, pers. comm.). Used in the 2008 Inventory

[3] Arsenic value from Gendebien *et al*. (1999) also used in the 2008 Inventory as no new arsenic data was available

As a result of the increased quantity of biosolids applied to agricultural land, total heavy metal inputs also increased. For example, total Zn inputs increased from 385 to 701 tonnes and total Cu inputs increased from 271 to 364 tonnes between the 2004 and 2008 Inventories (Figure 3).

Metal addition rates from biosolids were also estimated at an application rate equivalent to 250 kg total N/ha, the maximum field rate limit in Nitrate Vulnerable Zones - NVZs (Defra, 2008), using the mean total N concentration in biosolids from 2001-2007 of 3.6% dry solids (ds). In contrast to the increase in total metal inputs, the rate of metal addition (at 250 kg N/ha) at the *field-rate* was reduced due to the decrease in dry solids metal concentrations (Table 7 and Figure 4).

Figure 3. Total quantities of metals applied to agricultural land in England and Wales from biosolids in the previous (2004) and current (2008) Inventories.

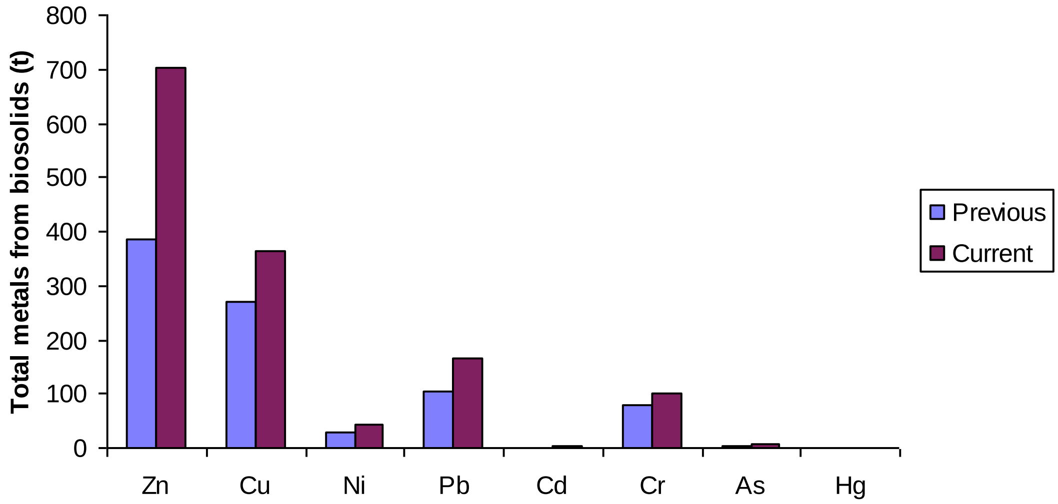
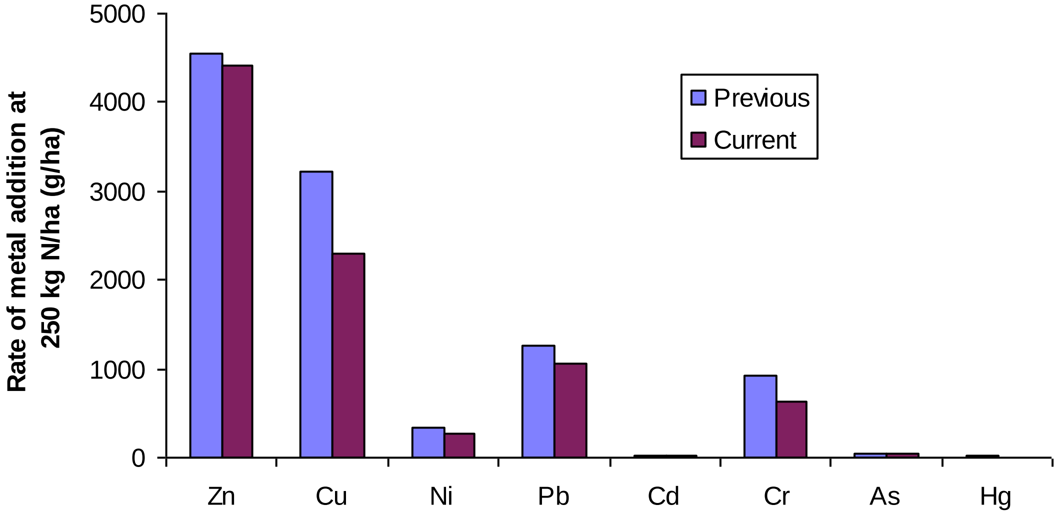


Figure 4. Heavy metal addition rates (at 250 kg N/ha) to agricultural land in England and Wales from biosolids in the previous (2004) and current (2008) Inventories.



3.3 Livestock manures

The 2004 Inventory used ‘typical’ livestock manure metal concentrations measured in samples collected in the 1990s (Nicholson *et al*., 1999) and hence did not capture the effects of recent reductions in maximum permitted levels of Zn and Cu in certain livestock feeds (Table 8). To update the Inventory on metal concentrations in livestock manures, new data was obtained from samples collected between 2007 and 2009 for this project.

Table 8. Previous and current maximum permitted levels of Zn and Cu in livestock feeds (mg/kg complete feed)

Livestock category		Zinc		Copper	
		Previous[1]	Current[2]	Previous[1]	Current[2]
Pigs					
	Up to 16 weeks	na	na	175	na
	Up to 12 weeks	na	na	na	170
	17 weeks – 6 months	na	na	100	25
	Other pigs[3]	na	na	35	25
	All pigs	250	150	na	na
Poultry					
	Layer	250	150	35	25
	Broilers (grower & finisher)	250	150	35	25
Ruminants					
	Pre-rumination	na	200	na	15
	Dairy and beef cattle	250	150	35	35
	Sheep	250	150	15	15

[1] SI (2000)
[2] EC (2003)
[3] Pigs over 6 months and breeding pigs
na = not applicable (i.e. no maximum permitted level specified for this livestock category)

3.3.1 Method

Sampling programme. The sampling programme was designed to provide robust data on the metal content of a range of livestock manure types, with a proportionately greater emphasis on pig and poultry manures, reflecting their greater contribution to Zn and Cu loadings to agricultural soils. Samples from free range hens were also collected, as these now represent *c.*50% of UK egg production and have a higher N output than caged-hens (Defra, 2007a), which could affect metal loading rates at the *field-level*. One hundred and ninety livestock manure samples were collected from commercial farms in England and Wales between 2007 and 2009 (Table 9), with the sampling programme utilising samples already collected as part of LINK project LK0988 (Reducing the risk of diffuse pollution by improved assessment of the nutrient content in farm manures and biosolids via Near Infrared Reflectance Spectroscopy (NIRS)). In addition, for each manure sample information was collected on the livestock type, diet, bedding type and quantity used, as well as the manure management system employed.

Table 9. Livestock manure type and sample number

Manure type	Sample number
Dairy slurry	24
Dairy farmyard manure (FYM)	18
Beef slurry	11
Beef FYM	15
Pig slurry	49
Pig FYM	26
Layer manure[1]	17 (10 free range)
Broiler/turkey litter[2]	19
Sheep FYM	6
Duck FYM	5
Total	*190*

[1] Manure produced by egg-laying hens

[2] Manure (including litter) produced by chickens and turkeys raised for meat production

Sample collection and analysis. Slurry and solid manure samples were collected in accordance with ADAS standard operating procedures (Anon, 2000; Chambers *et al*., 2001). The samples were analysed to determine dry matter, total nitrogen (N), Zn, Cu, Ni, Pb, Cd, Hg and Cr concentrations. Additionally the poultry manure samples were analysed for As. Metal concentrations in dried samples were determined by aqua-regia digestion and analysis using ICP-MS.

The Mann Whitney test was used to compare ‘current’ (this project) and ‘previous’ (Nicholson *et al*., 1999) manure metal concentrations.

3.3.2 Manure metal concentrations

Poultry. Zn concentrations in layer manure decreased between the ‘previous’ and ‘current’ sampling dates ($P<0.01$; Figure 4), most probably reflecting the decrease in maximum permitted levels in feeds from 250 to 150 mg/kg (Table 8). However, Zn concentrations in broiler litter (*c*.360 mg/kg dry matter - dm) did not differ ($P>0.05$) between the two sampling dates. Also, the ‘current’ sampling programme measured higher ($P<0.05$) Zn concentrations in layer manure from caged hens (349 mg/kg dm) than free-range hens (244 mg/kg dm), although the reasons for this difference are not readily apparent, as free-range hens are known to excrete more nitrogen than caged hens (Defra, 2007a). Corrosion of the metal cages in which battery hens are kept is unlikely to account for all of the difference.

There were no changes in layer manure or broiler litter Cu concentrations between the ‘previous’ and ‘current’ sampling dates (Figure 5). Duck FYM (only sampled in 2008/2009) had a Cu concentration of 65 mg/kg dm which was broadly in line with layer manure concentrations.

The highest Cd concentrations were in layer manure in both the ‘previous’ (1.1 mg/kg dm) and ‘current’ (0.7 mg/kg dm) sampling programmes. In the case of As, there were no differences in manure concentrations between the two sampling dates, although for broiler litter the concentration was reduced from 9.0 to 0.7 mg/kg dm (Table 10).

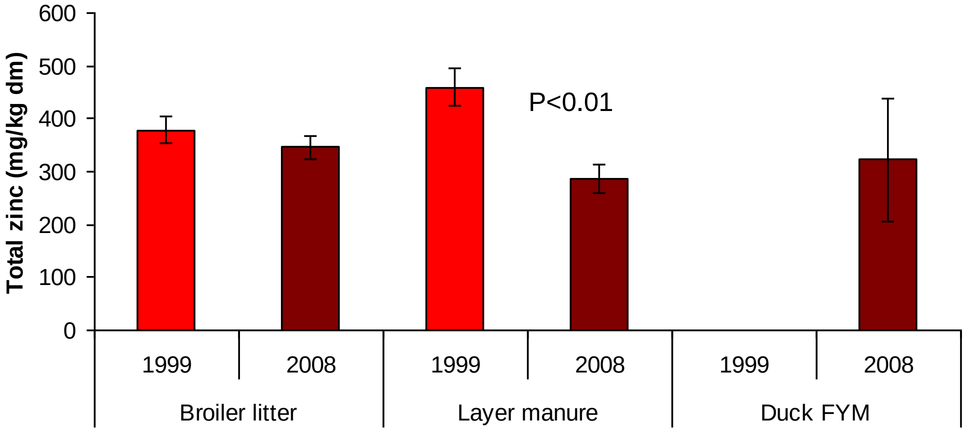
Pigs. Zn concentrations in both pig FYM and slurry increased between the ‘previous’ and ‘current’ sampling dates (Figure 4), which was most probably a result of the increased use of Zn on veterinary prescription (to control post-weaning scours) to compensate for the reduction in maximum permitted Cu levels in feeds (Table 8). Although numerically large (*c*.250 mg/kg dm), the increase was not statistically significant (P>0.05), most probably because the pig manure samples were taken from a wide range of rearing units where use of Zn on prescription (and to a lesser extent in feeds) may have varied greatly depending on the age and type of stock. Unfortunately, it was not possible to interrogate the data further to determine the nature of differences between the pig rearing units.

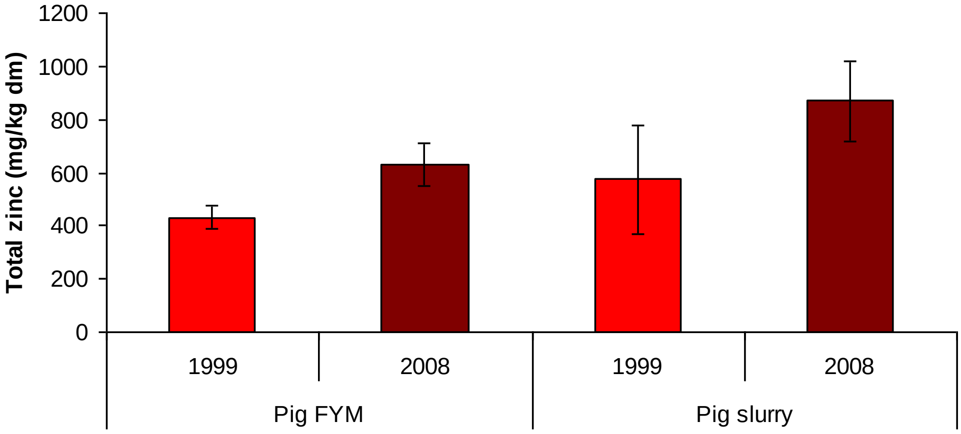
Pig FYM Cu concentrations decreased between the ‘previous’ and ‘current’ sampling dates (P=0.01) from 374 to 199 mg/kg dm. There was also a numerical decrease in pig slurry Cu concentrations (from 351 to 279 mg/kg dm), although this was not statistically significant (P>0.05), Figure 5. These data indicate that the reduction in pig feed Cu concentrations (Table 8) was reflected in reduced concentrations in pig FYM and slurry.

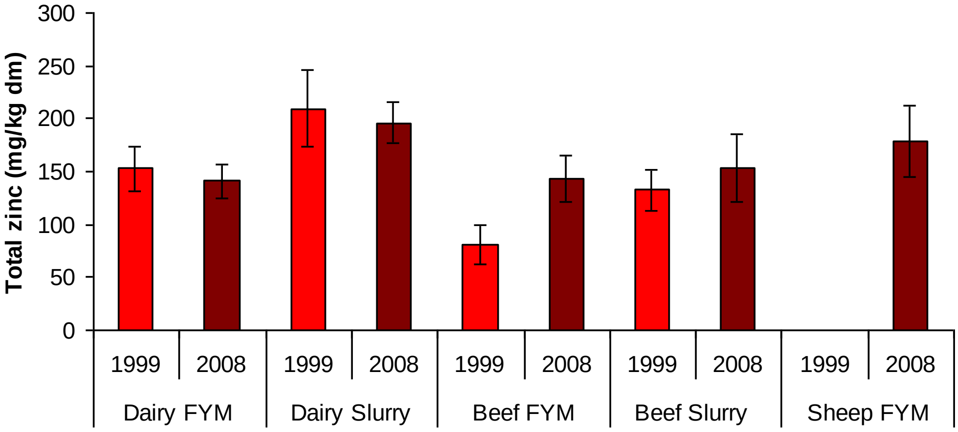
Cattle. Manure Zn (and Cu) concentrations were typically higher in dairy cattle manures than beef cattle manures, most likely due to the trace element enriched mineral supplements fed to dairy cattle to maintain high levels of milk production (Figure 5). Zn concentrations in dairy and beef FYM/slurry did not differ (P>0.05) between the two sampling dates.

There were no differences (P>0.05) in Cu concentrations in dairy FYM, beef FYM or beef slurry between the ‘previous’ and ‘current’ sampling dates (Figure 6). In contrast, dairy slurry Cu concentrations had increased (P<0.05) from 62 mg/kg to 137 mg/kg. This may be linked to increased milk production per cow (since the 1990s), which has been (partly) achieved through an increase in the amount of compound feed fed to dairy cattle. Copper has many functions associated with the immune status of dairy cows and is particularly associated with the prevention of mastitis. As productivity increases, the importance of ensuring adequate Cu (and other essential trace elements) also increases. Also, there has been greater awareness of the need for Cu in cattle diets, including the effects of Cu deficiency on health and fertility, and the binding effects of other elements (particularly molybdenum and iron). In addition, there has been an increase in the number of herds where cows are fed complete diets (in contrast to the more traditional feeding of silage/forage and compound feed separately).

Figure 5. Comparison of ‘previous’ (Nicholson *et al.*, 1999) and ‘current’ (2008) manure Zn concentrations

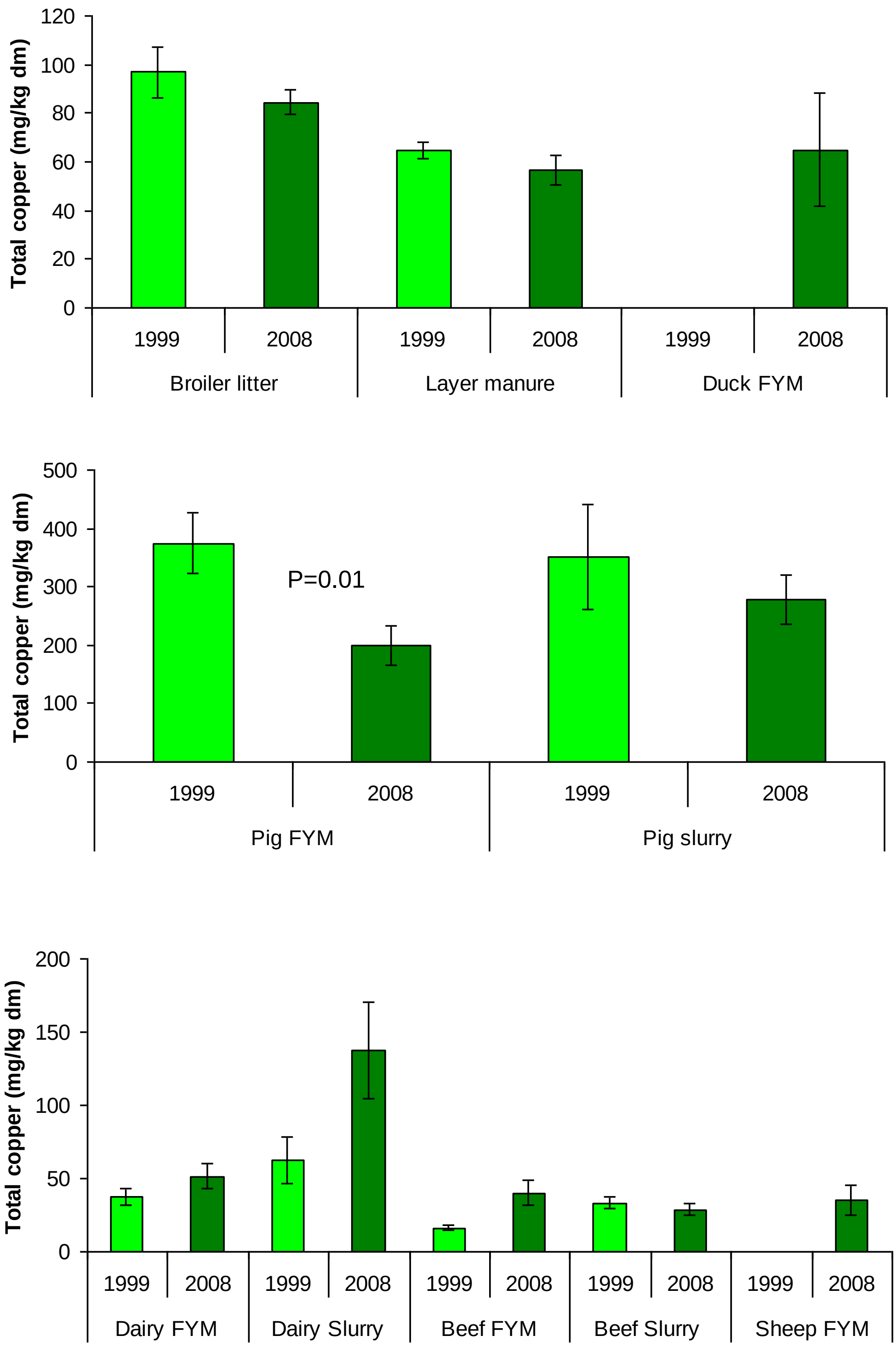






Errors bars represent standard error

Figure 6. Comparison of previous' (Nicholson *et al.*, 1999) and 'current' (2008) manure Cu concentrations



Error bars represent the standard error

Complete diets consist of mixtures of silage/forage and compound feed together, to which farmers add a mineral supplement. Clearly there is potential for the over-supply of minerals, including Cu, if the addition of the mineral supplement is not closely monitored.

Chromium, Ni and Pb concentrations in beef FYM increased between the ‘previous’ and ‘current’ sampling dates (Table 10), although there were no corresponding increases in beef slurry metal concentrations. These data suggest that the increased metal concentrations in beef FYM may originate from a change in metal concentrations in the animal bedding material (for example, through the use of paper crumble in part/full substitution for straw) rather than a change in animal feed composition. However, it was not possible to interrogate the data further to assess potential differences in animal bedding materials from the two sampling dates.

Sheep. Zn and Cu concentrations in sheep FYM (only sampled in 2008/09) were similar to those measured for beef FYM (Figures 5 and 6).

3.3.3 Slurry dry matter content and metal concentrations

The dry matter content of the pig and cattle slurries in the ‘current’ sampling programme ranged from <1% up to 16%; reflecting the effects of different feeding regimes and slurry management systems. The dry matter content of the dairy, beef and pig slurries was shown to be a good predictor of heavy metal concentrations (expressed on a fresh weight basis), indicating that heavy metals were primarily associated with the dry matter rather than being in solution. These relationships (Table 11) can be used to estimate likely slurry heavy metal concentrations based on their dry matter content, where laboratory heavy metal analysis data are not available. For example, cattle slurry with a dry matter content of 10% will typically have a Zn concentration of 16 g/m^3, whereas pig slurry with 6% dry matter content will typically have a Zn concentration of 64 g/m^3.

3.3.4 Total heavy metal inputs to agricultural land from livestock manures

Livestock manure heavy metal inputs to agricultural land in England and Wales were estimated, using manure metal concentrations from the ‘current’ sampling programme. Based on the equations in Table 11, fresh weight metal concentrations at typical dry matter contents for undiluted excreta (10% dm for cattle, 6% dm for pigs, 15% dm for sheep, 35% for laying hens and broilers) were derived (Table 12). These were combined with data on the total quantity of handled manure (as undiluted excreta) produced in England and Wales, based on livestock numbers from the 2008 Agricultural Census and daily excreta volumes (Defra, 2008). Also, the proportions of manure handled as slurry and FYM were estimated using manure management factors collated for Defra project WQ0103 (Manures-GIS; Defra, 2007b).

Table 10. Mean ‘previous’ (Nicholson et al., 1999) and ‘current’ (2008) Cd, Cr, Pb, Ni and As concentrations in livestock manures (standard error given in brackets)

Manure type	Sampling Programme	Total Cd (mg/kg dm)	Total Cr (mg/kg dm)	Total Pb (mg/kg dm)	Total Ni (mg/kg dm)	Total As (mg/kg dm)
Dairy FYM	Previous	0.4 (0.07)	5.3 (3.24)	3.6 (1.5)	3.7 (1.1)	1.6
	Current	0.4 (0.1)	14.8 (4.4)	11.3 (2.7)	6.7 (1.5)	nd
Dairy slurry	Previous	0.3 (0.1)	5.6 (0.6)	5.9 (1.0)	5.4 (0.5)	1.4
	Current	0.1 (0.03)***	3.0 (0.6)***	4.7 (0.8)	3.3 (0.7)**	nd
Beef FYM	Previous	0.1 (0.02)	1.4 (0.1)	2.0 (0.5)	2.0 (0.2)	0.8
	Current	0.3 (0.1)	16.9 (4.1) ***	28.7 (22.6)***	7.7 (1.0)*	nd
Beef slurry	Previous	0.3 (0.05)	4.7 (1.7)	7.1 (1.9)	6.4 (2.3)	2.6
	Current	0.2 (0.1)	7.2 (2.1)	2.8 (0.3)	4.9 (1.0)	nd
Pig FYM	Previous	0.4 (0.04)	2.0 (0.4)	2.9 (0.5)	7.5 (2.9)	0.9
	Current	0.4 (0.06)	22.7 (9.6)***	12 (6.5)	13.9 (5.5)	nd
Pig slurry	Previous	0.3 (0.07)	2.8 (0.7)	2.5 (0.9)	10.4 (4.0)	1.7
	Current	0.3 (0.2)*	2.3 (0.5)	3.5 (0.6)	3.9 (0.6)	nd
Broiler litter	Previous	0.4 (0.07)	17.2 (7.3)	3.6 (0.7)	5.4 (0.8)	9.0 (4.5)
	Current	0.3 (0.04)*	4.6 (0.6)*	5.4 (1.7)	2.9 (0.4)**	0.7 (0.1)
Layer manure	Previous	1.1 (0.2)	4.6 (0.7)	8.4 (1.5)	7.1 (0.9)	0.5 (0.1)
	Current	0.7 (0.09)	4.9 (0.4)	19.9 (10.2)	3.6 (0.4)***	1.3 (0.3)
Sheep FYM	Previous	-	-	-	-	nd
	Current	0.2 (0.05)	4.1 (2.2)	5.4 (2.1)	5.4 (2.3)	nd
Duck FYM	Previous	-	-	-	-	nd
	Current	0.3 (0.1)	4.0 (1.5)	2.5 (0)	2.1 (0.7)	0.6 (0.2)

Asterisks indicate statistical significance of any difference between sampling dates, as determined by the Mann Whitney test: *P<0.05, **P<0.01, ***P<0.001

nd = no data

Table 11. Relationships between dry matter content and metal concentrations for dairy, beef and pig slurries

Slurry type	Equation	Correlation coefficient (r^2) and statistical significance (P)
Dairy cattle (23 samples)	Total Cd (g/m^3 fw) = (0.02 x DM) - 0.001	$r^2 = 33\%$, $P<0.01$
	Total Cr (g/m^3 fw) = (0.05 x DM) - 0.03	$r^2 = 57\%$, $P<0.001$
	Total Cu (g/m^3 fw) = (0.83 x DM) + 1.41	$r^2 = 24\%$, $P<0.05$
	Total Pb (g/m^3 fw) = (0.07 x DM) - 0.02	$r^2 = 48\%$, $P<0.001$
	Total Ni (g/m^3 fw) = (0.05 x DM) - 0.03	$r^2 = 54\%$, $P<0.001$
	Total Zn (g/m^3 fw) = (1.38 x DM) + 2.15	$r^2 = 84\%$, $P<0.001$
Beef cattle (11 samples)	Total Cd (g/m^3 fw)* = (0.02 x DM) - 0.001	$r^2 = 31\%$, $P<0.001$
	Total Cr (g/m^3 fw)* =(0.05 x DM) + 0.02	$r^2 = 40\%$, $P<0.001$
	Total Cu (g/m^3 fw) =(0.25 x DM) + 0.23	$r^2 = 64\%$, $P<0.01$
	Total Pb (g/m^3 fw) =(0.03 x DM) – 0.01	$r^2 = 63\%$, $P<0.01$
	Total Ni (g/m^3 fw) =(0.05 x DM) + 0.03	$r^2 = 56\%$, $P<0.01$
	Total Zn (g/m^3 fw)* =(1.18 x DM) + 2.6	$r^2 = 60\%$, $P<0.001$
Pig (48 samples)	Total Cd (g/m^3 fw) = (0.003 x DM) + 0.0002	$r^2 = 24\%$, $P<0.001$
	Total Cr (g/m^3 fw) =(0.04 x DM) – 0.03	$r^2 = 51\%$, $P<0.001$
	Total Cu (g/m^3 fw) =(4.61 x DM) – 3.43	$r^2 = 32\%$, $P<0.001$
	Total Pb (g/m^3 fw) =(0.03 x DM) – 0.0001	$r^2 = 68\%$, $P<0.001$
	Total Ni (g/m^3 fw) =(0.06 x DM) – 0.03	$r^2 = 52\%$, $P<0.001$
	Total Zn (g/m^3 fw) =(11.73 x DM) - 6.11	$r^2 = 40\%$, $P<0.001$

*regression calculated using data from both dairy and beef slurry samples (34 samples)

Table 12. Typical fresh weight manure dry matter, N and heavy metal concentrations (of undiluted slurry/excreta) and estimated heavy metal addition rates from manures applied at 250 kg/ha total N

Manure type	Dry matter content (%)	Total N[3] (kg/t or m^3)	Concentration (g/t or m^3)							Metal addition rate at 250 kg N/ha (kg/ha)						
			Zn	Cu	Ni	Pb	Cr	As	Cd	Zn	Cu	Ni	Pb	Cr	As	Cd
Dairy FYM*	25	6	-	-	-	-	-	-	-	0.5	0.3	0.02	0.02	0.01	0.01	0.001
Beef FYM*	25	6	-	-	-	-	-	-	-	0.5	0.1	0.02	0.01	0.02	0.01	0.001
Pig FYM*	25	7	-	-	-	-	-	-	-	2.0	0.8	0.01	0.01	0.02	0.01	0.007
Sheep FYM[2]	15	7	20	4.0	0.8	0.5	0.8	0.4	0.03	0.6	0.1	0.02	0.01	0.02	0.01	0.001
Dairy slurry	10[1]	3.6	16	9.7	0.5	0.7	0.5	0.2	0.02	1.1	0.7	0.03	0.05	0.03	0.02	0.001
Beef slurry	10[1]	3.6	14	2.7	0.5	0.3	0.5	0.2	0.02	1.0	0.2	0.04	0.02	0.04	0.02	0.001
Pig slurry	6[1]	4.4	64	24.2	0.3	0.2	0.7	0.2	0.2	3.6	1.4	0.02	0.01	0.01	0.01	0.001
Broiler/turkey litter*	60	30	-	-	-	-	-	-	-	0.6	0.1	0.01	0.05	0.01	0.004	0.002
Layer manure	35[1]	19	92	18.5	1.1	7.0	2.0	0.5	0.2	1.2	0.2	0.01	0.09	0.03	0.01	0.003

[1] Dry matter content of undiluted excreta (Smith and Frost, 2000; Smith *et al*., 2000 for cattle, pigs and sheep); Revised “Fertiliser Manual (RB209)” for layer manure (Defra, in press)

[2] Metal concentrations calculated using the regression equations for beef slurry.

[3] Revised “Fertiliser Manual (RB209)”; Defra (in press).

*Metal addition rates were based on the metal concentration in undiluted slurry/excreta and used typical bedding addition rates to calculate the metal added from the excreta portion of the FYM/poultry litter.

Metals in straw were not included in the overall estimates of metal inputs to land with FYM, as the straw was assumed to recycle through the farm system (i.e. metal offtakes in straw were balanced by inputs with FYM containing straw, hence, there was no net change in soil metal content). However, for broiler and turkey litter the quantity and metal concentration estimates included bedding materials (e.g. wood shavings) as these were assumed to be net inputs to the soil system. The quantities of broiler and turkey litter incinerated for energy recovery were excluded from the manure quantity estimates; although the metals contained are recycled to agricultural land as a fertiliser ash (see Section 3.10).

The estimated manure quantities decreased from the 2004 Inventory (which used livestock numbers from the 2004 Census and daily excretion volumes from the 2002 NVZ Action Programme), largely due to changes in livestock numbers and standard daily excretion volumes (Table 13).

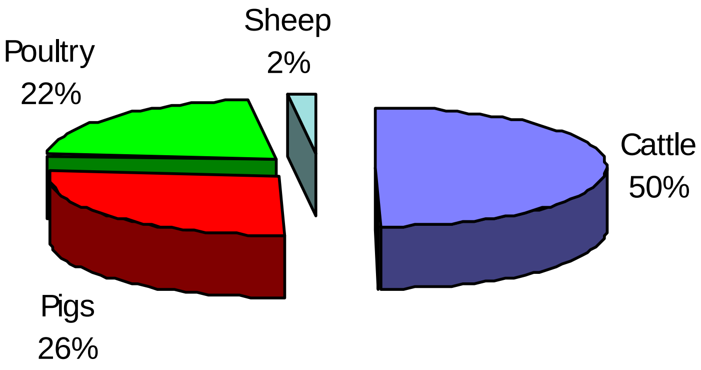
Table 13. Estimated quantities of manure as undiluted excreta (million t/year) applied to land in the 2004 and 2008 inventories.

	2004[1]	**2008[2]**
Cattle slurry	15.2	16.2
Cattle FYM	24.8	16.4
Sheep FYM	nd	1.0
Pig slurry	2.0	2.0
Pig FYM	3.7	2.1
Poultry litter[3]	2.2	2.0
Layer manure	1.0	0.8
Total	*48.9*	*40.5*

[1] Estimated using livestock numbers from 2004 Agricultural census and excretion volumes from Defra (2002). Straw additions included for FYM.
[2] Estimated using livestock numbers from 2008 Agricultural census and excretion volumes from Defra (2008). Straw additions not included for FYM.
[3] Includes bedding materials, but excludes the quantity incinerated (35%).
nd = no data

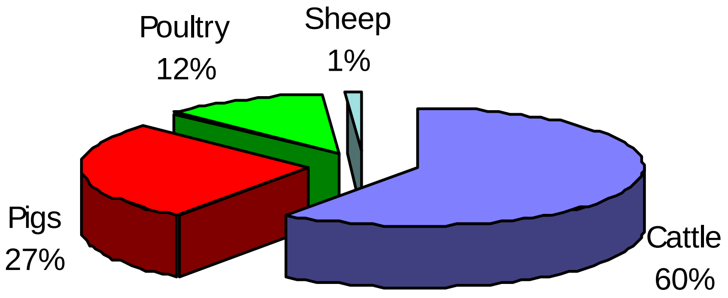
Zinc. The total amount of livestock manure Zn added annually to agricultural land was estimated to be 998 tonnes in 2008; a *c*.40% decrease from the previous estimate of 1666 tonnes, which was mainly due to a decrease in the total quantity of manure applied (Table 13). Cattle accounted for 50% and pigs and poultry each *c*.25% of total Zn inputs (Figure 7), which was broadly similar to the proportions estimated in the previous 2004 inventory.

Figure 7. Proportion of total Zn inputs (998 tonnes) with handled manures from different livestock types



Copper. The total amount of livestock manure Cu added annually to agricultural land was estimated to have decreased from 541 tonnes (in the 2004 Inventory) to 364 tonnes (in 2008), due to a decrease in the total quantity of manure applied (Table 13) and lower Cu concentrations in applied pig and poultry manures. Of this total amount, 60% was from cattle (Figure 8) compared with only *c*.40% in the 2004 Inventory, which was because the amount of Cu added with both pig manure and poultry manure had decreased and Cu concentrations in dairy slurry had increased.

Figure 8. Proportion of total Cu inputs (364 tonnes) with handled manures from different livestock types



Other metals. Figures 9 and 10 show the quantities of livestock manure Ni, Pb, Cd, Cr, As and Hg added annually to agricultural land. Total inputs of all six metals were lower than the 2004 Inventory, with Cd and Ni inputs decreased by over 50%.

Figure 9. Estimated total annual Ni, Pb and Cd, inputs to agricultural land with handled manures

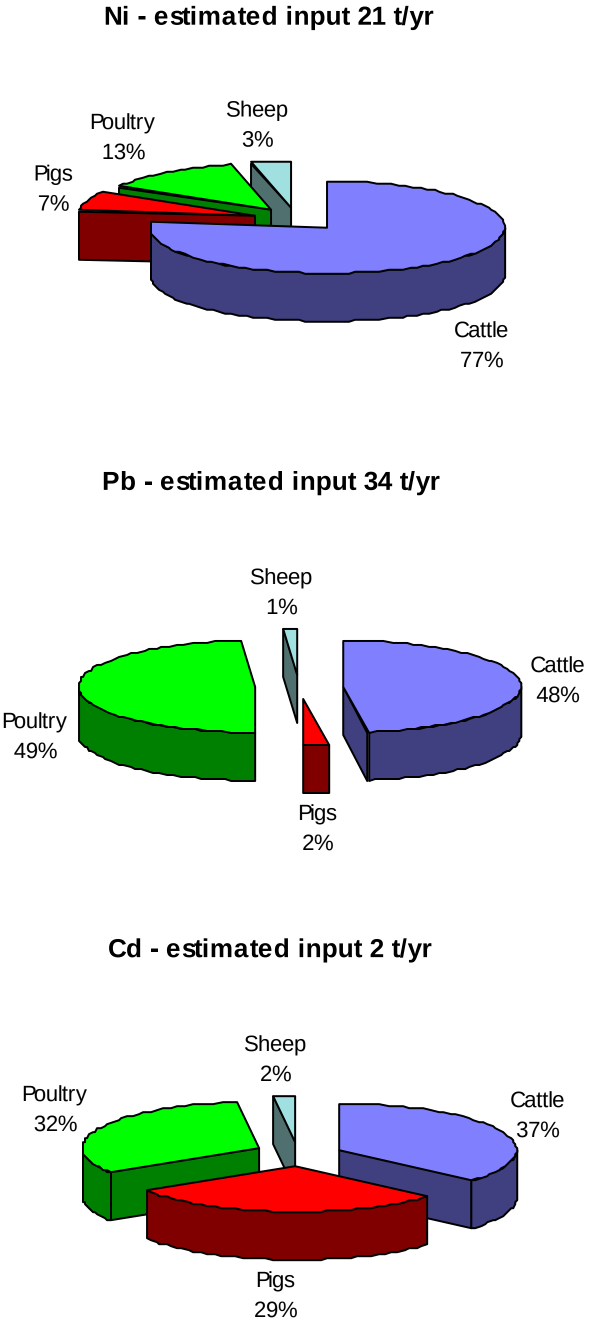
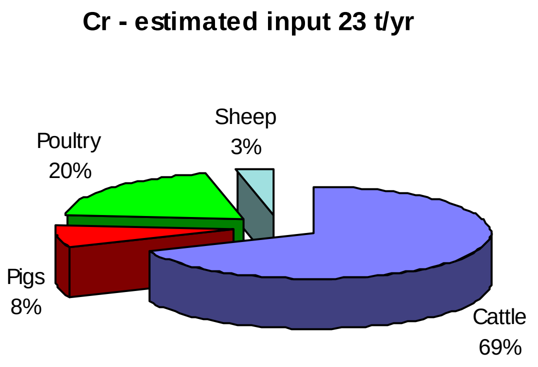
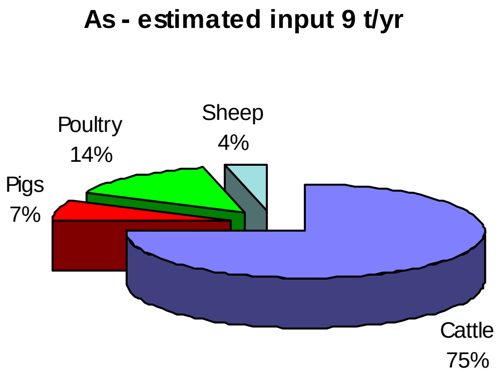
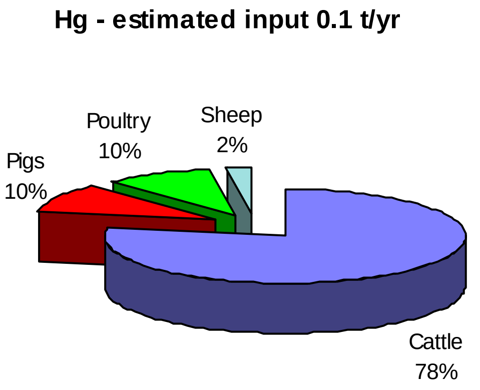


Figure 10. Estimated total annual Cr, As and Hg inputs to agricultural land with handled manures .







3.3.5 Heavy metal addition rates from livestock manures

Metal addition rates from slurry applications were estimated using the manure metal concentration data in Table 12 and for FYM were assumed to be the same as for slurry (i.e. undiluted excreta) at 10% dry matter. All manures were assumed to be applied at a rate equivalent to 250 kg/ha total N, with the quantity applied (in tonnes or m^3 per hectare) calculated by dividing 250 kg N/ha by the typical N content (Table 12).

The highest Zn and Cu addition rates were from pig slurry (3.6 kg Zn/ha and 1.4 kg Cu/ha) and pig FYM (2.0 kg Zn/ha and 0.8 kg Cu/ha), Table 12. Zinc addition rates from pig slurry were higher than in the 2004 Inventory (2.3 kg Zn/ha), whilst Cu addition rates were lower than in the 2004 Inventory (1.7 kg Cu/ha), reflecting the changes in manure metal concentrations discussed in Section 3.3.2. Metal addition rates from cattle and poultry manures (0.5-1.2 kg Zn/ha and 0.1-0.7 kg Cu/ha) were lower than from pig manures. However, Cu addition rates from dairy slurry had increased from 0.3 (in the 2004 Inventory) to 0.7 kg Cu/ha, reflecting increased manure concentrations probably as a result of increased feed supplementation discussed in Section 3.3.2.

3.4 Fertilisers and lime

Inorganic or mineral fertilisers (nitrogen, phosphate, potash and gypsum) and lime are a source of heavy metals, and their long-term application can increase soil metal concentrations and lead to accumulation in the food chain (e.g. Nicholson *et al*., 1994). Cadmium is of particular concern and is present in the rock phosphate used to produce all inorganic phosphate fertilisers (Nziguheba and Smolders, 2008).

Data on inorganic fertiliser (nitrogen, phosphate, potash and gypsum) and lime use on farms in England and Wales was obtained from “The British Survey of Fertiliser Practice” (Benford, 2009). Heavy metal concentrations in phosphate and other fertilisers used in the UK were obtained from Marks (1996). However, there was only limited and historical information on metal concentrations in liming materials (Chater and Williams, 1974). Data on the metal content (Zn and Cu only) of agricultural gypsum was taken from WRAP (2007).

The “British Survey of Fertiliser Practice” showed continuing decreases in overall application rates of nitrogen, phosphate and potash on all crops and grass over the 2004 to 2008 period, due to poor economic returns from farming, the volatile fertiliser market and price increases over the period leading up to the 2008 cropping season (Benford, 2009). As a result, total metal inputs from fertilisers decreased (e.g. total Cd inputs with phosphate fertilisers decreased from *c.*7 t/yr in the 2004 Inventory to *c*.5 t/yr in the current version). Nevertheless, phosphate fertilisers continued to contribute a large proportion (>70%) of the inorganic fertiliser and lime category derived Zn, Cd, Cr and As inputs to agricultural land. Nickel and Pb inputs from lime were also relatively high (*c.*50% of total inputs from inorganic fertilisers and lime), but this was mainly due to the large quantities applied (2.6 million tonnes in 2008) rather than elevated metal concentrations. Notably, Cd addition rates from lime were similar to those from phosphate fertilisers (*c.*1.3 g/ha/yr), although the accompanying increase in soil pH following lime application would tend to decrease the bio-availability of Cd for plant uptake and leaching.

Copper deficiency in crops is associated with sandy soils, 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 Cu (Chalmers *et al.,* 1999). Of the trace element fertilisers applied in England and Wales, only Cu (as copper sulphate or copper oxide) is regularly used, with *c*.2% of the total cropping area reported to receive a foliar Cu spray 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, adding *c*.28 tonnes of Cu each year to soils in England and Wales.

3.5 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 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 estimated from published data on pesticide usage (Garthwaite and Thomas, 2004; Garthwaite *et a*l., 2006a, 2006b) and information on the heavy metal content of the active ingredients (Whitehead, 2001).

A total of 16 tonnes of Zn and 2 tonnes of Cu were estimated to be applied annually with agrochemical products in England and Wales. Metal input rates were based on the effective area receiving fungicides (i.e. the total spray hectares divided by the average number of spray passes). Zn and Cu addition rates to land growing hops were elevated because the crop receives an average of 6 spray passes, although the area receiving these elevated rates is small (*c.*1,200ha). Top fruit can also receive relatively high Cu addition rates, but again the land area affected is small (*c*.1,500 ha). Nevertheless, addition rates with agrochemicals applied to top fruit have reduced from 125 to *c*.70 g Zn/ha/yr, and from 1,260 to *c*.610 g Cu/ha/yr. For hops, addition rates were estimated to have fallen from *c*.12,900 to *c*.3,600 g Zn/ha/yr, and from *c*.2,700 to *c*.1,400 g Cu/ha/yr.

The quantities of heavy metals estimated to be entering soils in England and Wales with agrochemical additions 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 tonnes of Cu are applied annually in Italy and around 3,500 tonnes annually in France (Eckel *et al*., 2005). Other products used to control diseases in vineyards may also contain As with, for example, 800-900 tonnes of As estimated to be applied annually in France (Eckel *et al*., 2005). One possible effect of climate change would be to encourage UK wine production and would probably lead to an increased use of metal-containing products. Careful monitoring would be required to avoid the build up of undesirable Cu levels in these soils.

3.6 Irrigation water

In England and Wales, irrigation is only widely practised in certain regions (e.g. central, eastern and south-east England) and mainly on light soils for high value crops (e.g. salads, vegetables, potatoes, sugar beet). The amount of irrigation water used varies greatly depending on the season, with greater amounts applied under dry conditions. Information on annual use is reported every two to three years through the “Survey of Irrigation of Outdoor Crops”, which provides data on the irrigated area, volumes used and practices etc. The most recent survey was in 2005, following changes to the water abstraction licensing system and implementation of the Water Act 2003 (Weatherhead and Rivas-Casado, 2007).

To remove anomalies created by using a single year’s survey data, we calculated average irrigation areas/volumes using data from the 1995, 2001 and 2005 irrigation surveys, which better reflected the long-term increase in irrigation areas and volumes reported over time. As more than half (54%) of irrigation water is sourced from surface waters, irrigation water metal concentrations were derived from the 2007 “e-Digest of Environmental Statistics” (Defra, 2007c) data for river waters (median of >200 sites).

Irrigation water was shown to be a relatively minor source of heavy metals to agricultural land, both in terms of total inputs (Table 15) and at an individual field-level. Although climate change could greatly increase the area of UK crops requiring irrigation, 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 metal inputs to agricultural land in the future.

3.7 Industrial ‘wastes’

The recycling of industrial ‘wastes’ to agricultural land is expanding as measures to reduce landfill disposal are introduced (CEU, 1999). In England and Wales, the landspreading of industrial ‘wastes’ is normally carried out under a Paragraph 7 exemption from the Environmental Permitting Regulations (SI, 2010) or under a Standard Rules Mobile Plant Permit for landspreading (EA, 2010). 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 etc.), abattoirs, paper and textile production, tanneries and pharmaceutical/chemical processing.

The quantities, composition and application rates of industrial ‘waste’ materials applied to agricultural land in England and Wales were recently complied as part of Defra Project WR1103 (The Environmental Impacts of the Activity of Spreading Waste to Land; Peacock and Turrell, 2009). This project used data from the Environment Agency Electronic Data Records Management (eDRM) system, which stores scanned copies of all applications for Paragraph 7 exemptions. The authors used The European Waste Catalogue (EWC) 2002 codes to classify the different types of waste materials; the EWC is split in to twenty chapters based on the source from which the waste was generated (making up the first two digits of the code). We used these data to estimate total metal inputs from the following broad classes of wastes: food preparation and processing (EWC02); construction and demolition (EWC17); water treatment sludge (EWC19) and mixed sludge (no EWC code assigned). Some anaerobic digestates (of unknown origin) were also included in the EWC19 category. However, we excluded these and used data supplied directly to ADAS by digestion plant operators (see Section 3.8). Similarly, data on composts included in the EWC20 category were also excluded, as these are considered separately in the Inventory (see Section 3.10).

In this project, data from the broad EWC categories (as reported in Defra project WR1103) was used to calculate total metal additions to agricultural land. More detailed data from WR1103 (provided to ADAS separately and used to derive the data in Table 14) was used to look at metal application rates at the field-level for certain types of ‘wastes’.

Unprocessed food ‘wastes’. Data from Peacock and Turrell (2009) (Defra project WR1103) on ‘wastes’ from food processing and preparation (EWC02) indicated that almost 4 million m^3 (tonnes) are applied to agricultural land. As these are generally low dry matter products, they tend to be applied at high application rates (*c.*180 t/ha). In the 2004 Inventory, there was no information on unprocessed food ‘waste’ application rates and hence it was not possible to estimate metal addition rates. Unprocessed food ‘wastes’ input important quantities of metals at the field-level (see later Figures 12 and 13), and in particular, Cd addition rates from unprocessed food ‘wastes’ were estimated to be typically >25 g/ha) which is considerably higher than inputs from phosphate fertilisers and lime (*c*.1.3 g/ha). Using more detailed data from Defra project WR1103, it was estimated that the highest rates of Zn, Ni and Cr additions were from the application of liquids from meat production; in contrast there were generally low metal addition rates from dairy processing ‘wastes’ (Table 14). Cadmium addition rates ranged from 30 to 80 g/ha from all unprocessed food ‘wastes’ (except dairy ‘wastes’), which is much higher than the addition rate from biosolids (12 g/ha).

Table 14. Typical application rates and metal addition rates (g/ha) for different unprocessed food 'wastes'.

	Sludge from meat production	Liquid from meat production	Dairy processing	Egg processing	Vegetable processing	Bakeries	Beverage production*
Application rate (m^3/ha)	143	215	132	193	158	128	150
Zn	878	2707	143	1477	734	696	1279
Cu	1173	1888	43	2503	975	494	226
Ni	946	1937	4	1781	569	338	81
Pb	53	82	6	89	78	42	45
Cd	44	29	<1	79	39	36	32
Cr	201	601	8	267	200	63	69
Hg	5	3	2	10	5	5	6

*excludes tea and coffee production

'Waste' soil. Around 96 kt of 'waste' soil from construction sites (EWC17) were estimated to be applied annually to agricultural land (Peacock and Turrell, 2009) and represent only a minor source of total heavy metals inputs**.**

Water treatment cake. Around 1.2 million tonnes of water treatment cake (EWC19-09) were estimated to be applied annually to agricultural land in England and Wales (Peacock and Turrell, 2009). Metal addition rates of Zn, Ni and Cd were similar to or greater than those from biosolids (see later Figures 12 and 13).

Paper crumble. The organic matter content and liming properties of paper crumble make it a valuable soil conditioner, particularly on acidic soils. A recent study on the production and land spreading of paper crumble (Gibbs *et al*., 2005) provided comprehensive information on their heavy metal content and quantities applied to agricultural land, which was used in the 2004 Inventory and has been used here.

'Waste' gypsum. Gypsum from power station flue gas desulphurisation (FGD) plants is applied to agricultural land, although it was not possible to obtain any data on the quantities applied. Gypsum recovered from waste plasterboard can be applied to agricultural land under a Paragraph 7 exemption and under a standard permit. A Quality Protocol has been developed to facilitate application to land for agricultural benefit whilst protecting the soil (WRAP/EA, 2010). Data from the Technical Report produced to support the Quality Protocol (WRAP/EA, 2008a) were used to estimate potential metal addition rates from this source, although no estimate of the total quantities that might be applied could be made at this stage.

3.8 Dredgings

Although some data on the quantities and application rates of dredgings were reported by Peacock and Turrell (2009) (under code EWC17), in the research undertaken here mean composition data supplied directly to ADAS by British Waterways for over 1000 canal dredging samples from 1992 was used. Dredging metal concentrations were 2 to 4-fold higher than those used in the 2004 Inventory (which were based on *c.*100 canal dredging samples).

The total quantity of dredgings applied to agricultural land reported in Defra project WR1103 was *c.*240,000 tonnes, which was much less than the 5,000,000 tonnes used in the 2004 Inventory (J. Lees, Environment Agency, pers. comm.). As a result, dredging metal inputs were much lower than in the 2004 Inventory (e.g. total Zn inputs were reduced from *c.*600 to *c.*60 tonnes), although there is still a high degree of uncertainty associated with both of these estimates.

The maximum permitted application rate to agricultural land for dredgings from inland waters applied under an exemption from the Environmental Permitting Regulations (SI, 2007) is 5000 t/ha/yr, although the mean application rate reported in Defra Project WR1103 was much less at 602 t/ha. Nevertheless, addition rates of all metals were high, although repeat applications of dredgings are unlikely in the short-term (dredgings are not generally transported long distances for economic reasons and inland waterways are not frequently dredged) and would not be allowed once topsoils had reached maximum permitted heavy metal concentrations for biosolids amended soils.

3.9 Digestate

Anaerobic digestion (AD) is a treatment process which harnesses natural decomposition processes to produce biogas and a residue known as digestate, from biodegradable materials, such as animal slurry, food ‘waste’ and sewage sludge. Although there are currently very few AD plants, other than those treating sewage sludge, significant growth in use of this technology is expected over the next few years.

Digestate can be beneficially applied to farmland as a fertiliser and soil conditioner, under an exemption from the Environmental Permitting Regulations (SI, 2007) or in accordance with the Anaerobic Digestate Quality Protocol (EA, 2009). Data on the quantities of digestate applied to agricultural land (the food ‘waste’ component only, to avoid ‘double counting’ of co-digested slurry) and their metal and nutrient contents, were supplied directly to ADAS by existing AD plant operators.

Around 100 kt (fresh weight) of digestate were applied to agricultural land in 2008, making a very small contribution to total metal inputs.

3.10 Ash

The incineration of wastes for energy recovery is an increasingly common practice. Paper crumble can be incinerated and the resulting ash (paper sludge ash – PSA) applied to agricultural land, for its liming properties. The Environment Agency in partnership with WRAP have produced a Technical Report to support the development of a Quality Protocol for PSA (WRAP/EA, 2008b), which contains data on metal contents and suggested application rates, which we used in this study to estimate metal loading rates from this source. The Technical Report estimates that around 88,000 tonnes of PSA was sold for various ‘end uses’; in the absence of other data, we assumed that 25% of this was applied to agricultural land, although this may not be a robust estimate.

Poultry litter is burnt for energy recovery in power stations in the UK and Europe, and the resulting ash is marketed as a PK-rich fertiliser. Data on the metal content of these products published by the producers (Fibrophos, 2009; Cropkare, 2009) and quantities applied (*c*.90 kt/annum) were supplied to ADAS, and were used to calculate metal inputs from this source.

At present, PSA and poultry litter ash are a relatively minor source of total metal inputs to agricultural soils in England and Wales (<5% of total Zn and Cu inputs). However, metal (in particular Cu, Cr and As) addition rates from PSA can be elevated compared with other sources (see later Figures 12 and 13).

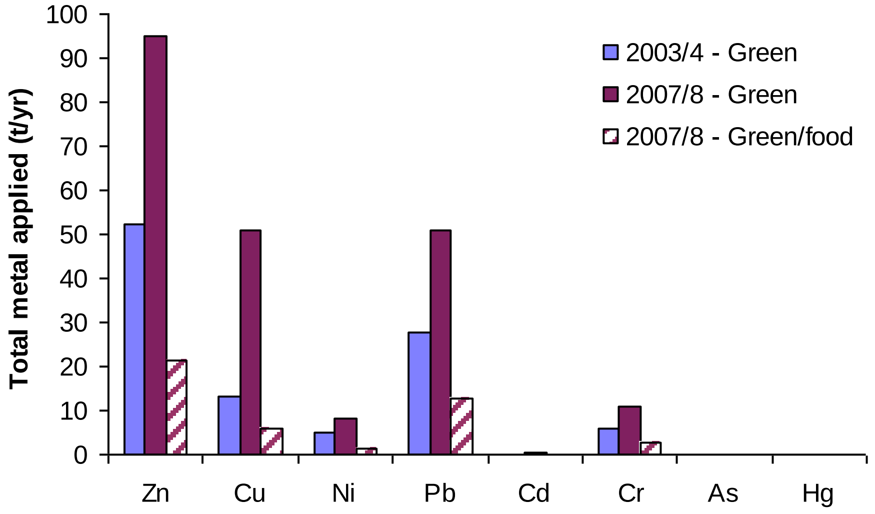
3.11 Compost

Source separated compost may be applied to agricultural land under a Paragraph 7 exemption or under the Compost Quality Protocol (WRAP/EA, 2008c).

Statistics on the quantity of composted materials produced in the UK are reported annually by the Association for Organics Recycling (AFOR), with the most recent report for the period 2007/08 (AFOR, 2009). The total quantity of compost produced in the UK increased from 2.5 Mt in 2006/07 to 2.69 Mt in 2007/08. During 2007/08 the agricultural sector remained the largest market, accounting for 1.25 Mt of compost (46% of the total), mostly for use on arable/cereal crops. It has been assumed for the purposes of this research that 82% (2.2 Mt) of the total compost produced was generated in England and Wales, of which 1 Mt was used in the agricultural sector. Typical compost application rates were assumed to apply the equivalent of 250 kg total N/ha, assuming a total N content of 7.5 kg/t and 60% dry matter for green compost (i.e. 33 t/ha), and 11 kg/t and 60% dry matter for green/food compost (i.e. 23 t/ha).

Total metal inputs from compost approximately doubled between the 2004 Inventory (which used compost data for 2003/04) and the 2008 Inventory (which used data for 2007/8), largely due to the increased quantities applied (Figure 11).

Figure 11. Total metal inputs to agricultural land in England and Wales with compost in the 2004 (2003/4 data) and 2008 (2007/8 data) Inventories



Currently, compost inputs are a relatively small (but growing) source of heavy metals to agricultural land on a national basis, although metal addition rates at the field-level can be relatively high compared with other sources. Compost regulations, both statutory and voluntary, will continue to control 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 (e.g. the Landfill Directive; the UK Waste Strategy) will further increase the recycling of composted materials (and heavy metal inputs) to agricultural land in the future.

3.12 Corrosion

To make an assessment of Zn inputs to soils from the corrosion of galvanised structures, it was first necessary to distinguish between corrosion and runoff. “Runoff is the amount of metal being released from the corrosion-product layer during precipitation, and corrosion is the total amount of metal that has been oxidized. It includes both metal runoff and metal incorporated in corrosion products“ (Karlen *et al*., 2001). These authors measured annual run-off rates for general galvanised materials of 2.7 g Zn/m^2. This value was combined with information on the amount of galvanised product used in the agricultural sector, provided by the Galvanisers Association (W. Piatkiewicz, pers. comm.), to estimate Zn inputs to agricultural land.

Corrosion was estimated to be a minor contributor (*c*.1%) of total Zn inputs to agricultural soils. Zinc inputs from galvanised materials were estimated to decrease from *c*.60 t/year in the 2004 Inventory to *c*.30 t/yr in the 2008 Inventory, primarily because of the use of run-off rates as opposed to corrosion rates. However, it is known that Zn inputs local to these sources can be very high, with some researchers even using soils collected around galvanised electricity transmission towers in experiments where contaminated soils were required (e.g. Smolders *et al*., 2004).

3.13 Livestock footbaths

The use of cattle footbaths can help to reduce the incidence of foot lameness. Published advice recommends that 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 (Defra, 2005). The main types of cattle footbath solutions in use are formalin and Zn/Cu sulphate. On sheep farms, it is recommended that footbathing should be routinely carried out about 5 times a year and more frequently if foot rot is a serious problem (Defra, 2003). Formalin and Zn sulphate are the most commonly used products (Cu sulphate is not used due to the sensitivity of sheep to Cu). Defra advice 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 (and Cu) concentrations could build-up.

An estimate of Zn/Cu sulphate footbath use in England and Wales was made, using data on livestock numbers from the 2008 Agricultural Census and information on footbath use and disposal from the Farm Practices Survey (Defra, 2006; 2007d). Annual use on dairy farms was estimated to be 90 tonnes of Zn and 45 tonnes of Cu, with use on beef farms lower at 8 tonnes of Zn and 20 tonnes of Cu. On dairy farms, 85% of footbaths were reported to be emptied into a slurry store, whereas on beef farms only 50% were emptied into a slurry store, with the remainder spread directly on land. Around 70% of sheep farms disposed of footbaths directly to land, adding around 11 tonnes of Zn to soils each year.

Footbaths which are disposed directly to land were only estimated to contribute *c*.1% of total Zn and Cu inputs to agricultural soils. However, the metals in footbaths emptied into slurry stores will contribute to metal concentrations in the slurries when they are spread to land. In this research, the theoretical contribution of footbath metal additions to overall slurry metal concentrations was calculated, assuming that the total quantity of metals in footbaths emptied to slurry stores were equally mixed with the total volume of dairy and beef slurry generated. For dairy slurry, it was estimated that footbaths contributed *c*.35% of Zn and Cu concentrations, whereas for beef slurry footbaths were estimated to contribute *c*.7% of the Zn (and 99% of the total Cu concentrations, which should be treated with caution).

3.14 Lead shot

The use of lead shot in shotgun cartridges at clay pigeon shoots and other shooting activities was estimated in the 2004 Inventory, using data published by Mellor and McCartney (1994). This was updated using information from Penn (2008), who gave an estimated figure of 250 million cartridges per year, of which half were assumed in this research to be used for clay pigeon shooting on agricultural land, and the remainder on moorland (i.e. non-agricultural land).

These estimates show that lead shot is still the single most important source of Pb inputs to soils in England and Wales, with over 3,000 tonnes deposited annually (reduced from 15,000 tonnes in the 2004 Inventory). The Clay Pigeon Association currently lists *c.*400 shooting grounds in England and Wales (CPSA, 2009). Theoretical Pb input rates at these sites were calculated by assuming that each ground was 15 ha in size. Estimated addition rates were extremely high (*c*.500 kg/ha) on these relatively small areas of land, which was consistent with the data reported by Mellor and McCartney (1994) who found that topsoil total Pb concentrations at a clay pigeon shooting site in northern England commonly exceeded 5,000 mg/kg.

3.15 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 2008 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 re-deposited on flooded land further downstream. In addition, highway run-off or spray may contribute to the heavy metal burden of agricultural soils close to major roads. Machinery abrasion (e.g. ploughs, discs, tines etc.) used to cultivate agricultural land has also been suggested as a potential (if minor) source of heavy metals (Nicholson *et al*., 2008).

3.16 Data summary

A summary of all data sources used in the 2008 Inventory, including details of the age and provenance of the data, is given in Appendix I (Table A1).

4. THE IMPORTANCE OF DIFFERENT HEAVY METAL SOURCES

Estimated total annual heavy metal inputs to agricultural land in England and Wales (Table 15) were considerably lower than previously reported in the 2004 Inventory (Nicholson *et al.*, 2008). This was mainly due to lower estimated atmospheric deposition inputs, which *alone* accounted for >90% of the total reductions in Pb and Hg inputs, and for 48-76% of reductions in other metal inputs (Table 15). Nevertheless, atmospheric deposition still accounted for 24-35% of the total annual heavy metal inputs to agricultural land for Zn, Cu, Ni, Cd, Pb and As, and *c.*80% for Hg (Figure 12), compared with 20-60 % of total inputs in the 2004 Inventory (*c.*80% for Hg).

Table 15. Estimated total annual metal inputs (t/yr) to agricultural soils in England and Wales from different sources.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	1009	333	72	99	6.3	20	8.1	9.0
Livestock manures	998	364	21	34	1.7	23	9.5	0.1
Biosolids	701	364	42	167	1.9	101	6.6	1.5
Industrial ‘wastes’[1]	80	41	32	10	1.2	10	0.2	0.2
Dredgings	63	17	8	19	0.3	9	2	0.2
Compost[2]	116	34	9	64	0.4	14	<0.1	0.1
Digestate	1	<1	<1	<1	<0.1	<1	nd	nd
Footbaths[3]	28	17	-	-	-	-	-	-
Fertilisers and lime	150	32	25	12	6.7	71	4.5	<0.1
Ash[4]	145	43	<1	<1	<0.1	<1	<0.1	<0.1
Plant protection products	16	2	nd	nd	nd	nd	nd	nd
Irrigation water	1	<1	<1	<1	<0.1	<1	0.1	<0.1
Corrosion	28	nd	nd	nd	nd	nd	nd	nd
Lead shot	nd	nd	nd	3250[5]	nd	nd	nd	nd
Total (2008)	***3336***	***1248***	***210***	***406***	***18.5***	***248***	***31***	***11***
Total (2004 Inventory)	*5934*	*1648*	*371*	*960*	*39.2*	*383*	*80*	*13*
Proportion of reduction in total inputs due to revised deposition estimates (%)[6]	*57*	*76*	*67*	*92*	*74*	*48*	*54*	*100*

nd: no data

[1] Including paper crumble, food ‘wastes’, water treatment cake

[2] Including green compost and green/food compost

[3] Only includes the proportion of footbaths disposed directly to land. Metals in footbaths emptied to slurry/manure stores are assumed to be included in the contribution from livestock manures

[4] Ash from the incineration of poultry litter (not including paper sludge ash)

[5] Not included in total due to the uncertainty of the estimate

[6] Calculated from the change in metal inputs from atmospheric deposition since 2004 and the change in total metal inputs from all sources since 2004.

Livestock manures were estimated to account for *c*.30% of Zn, Cu and As inputs, but were a less important source of the other metals. This was similar to the 2004 Inventory, where manures were also estimated to contribute *c*.30% of total Zn and Cu inputs.

Biosolids were estimated to contribute between 10% (Cd) and 41% (Cr) of total metal inputs. In general, the proportion of total metal inputs from biosolids increased from the 2004 Inventory (e.g. 7% of Zn inputs in 2004 compared with 21% in 2008), because of the increased quantities of biosolids applied to agricultural land (see Section 3.2) and the decrease in total metal inputs (Table 15).

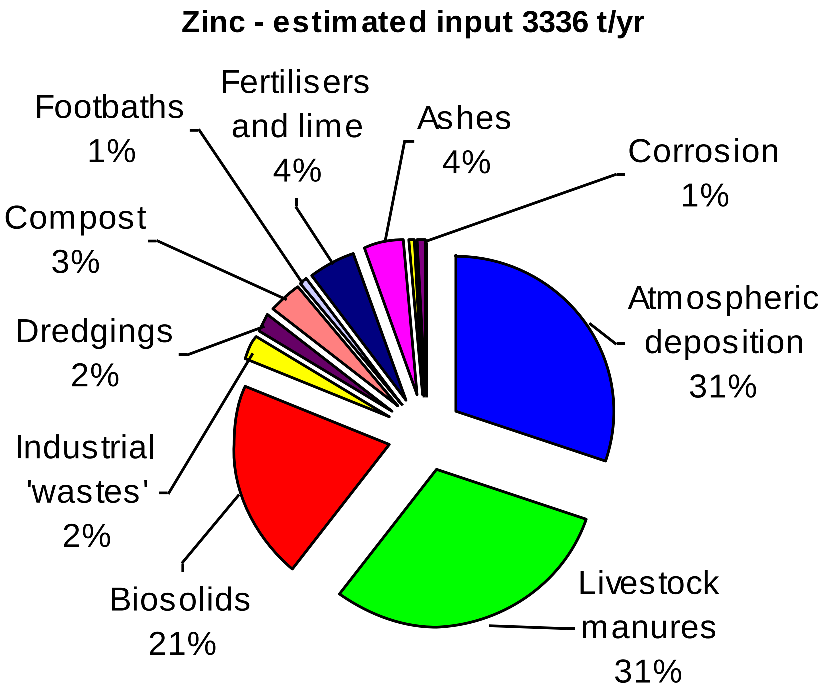
Industrial 'wastes' (including paper crumble, food 'wastes' and water treatment cake) were an important source of Ni (15%) and Cd (7%), whilst inorganic fertilisers (mainly phosphate fertilisers) and lime contributed *c.*30% of Cd and Cr inputs. Green and green/food composts were estimated to contribute 16% of Pb inputs to agricultural soils, but accounted for no more than 5% of other metal inputs, despite an approximate doubling in the quantities applied to land since the 2004 Inventory (Section 3.11).

Although atmospheric deposition was generally an important source of total heavy metal inputs to agricultural land on a national scale, metal addition rates at an *individual field-level* were small compared with other sources. For Zn, Cu, Cr and As the highest addition rates at a field-level were from biosolids (applied at 250 kg total N/ha/yr; *c.*6.5 t dry solids/ha/yr), although Zn and Cu addition rates from some pig and poultry manures (applied at 250 kg total N/ha/yr) were of a similar magnitude (Figures 13 and 14). Metal addition rates from green and green/food composts (applied at 250 kg total N/ha/yr; 23-33 tonnes fresh weight/ha) were similar to (and sometimes greater than) those from biosolids.

'Wastes' from food production (e.g. dairies, soft drinks manufacture etc.) are generally low dry matter liquids and as a result are commonly applied at elevated rates to agricultural land (*c*.180 m^3/ha) to achieve benefits from the crop nutrients they contain. Consequently, Ni and Cd addition rates with these materials were estimated to be higher than from biosolids (Figures 13 and 14). Similarly, water treatment cake was also estimated to add elevated rates of metals, in particular Ni and Zn. Digestate (applied at 250 kg total N/ha/yr; *c.*30 t fresh weight/ha) did not add significant quantities of metals at the field-level compared with other organic materials. Notably, annual metal addition rates from all the sources discussed above were below the current maxima (expressed as an average annual rate over 10 years) for biosolids application to agricultural soils (DoE, 1996).

Figure 12. Estimates of the proportion (%) of total annual a) Zn; b) Cu; c) Ni, d) Pb; e) Cd; f) Cr; g) As and h) Hg inputs to agricultural soils in England and Wales from different sources.

a)



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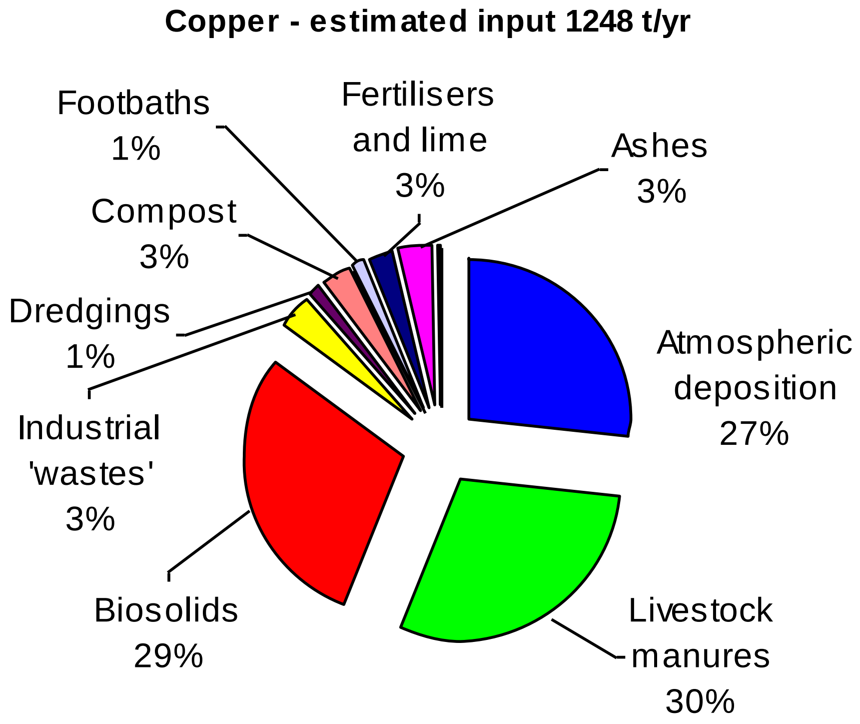
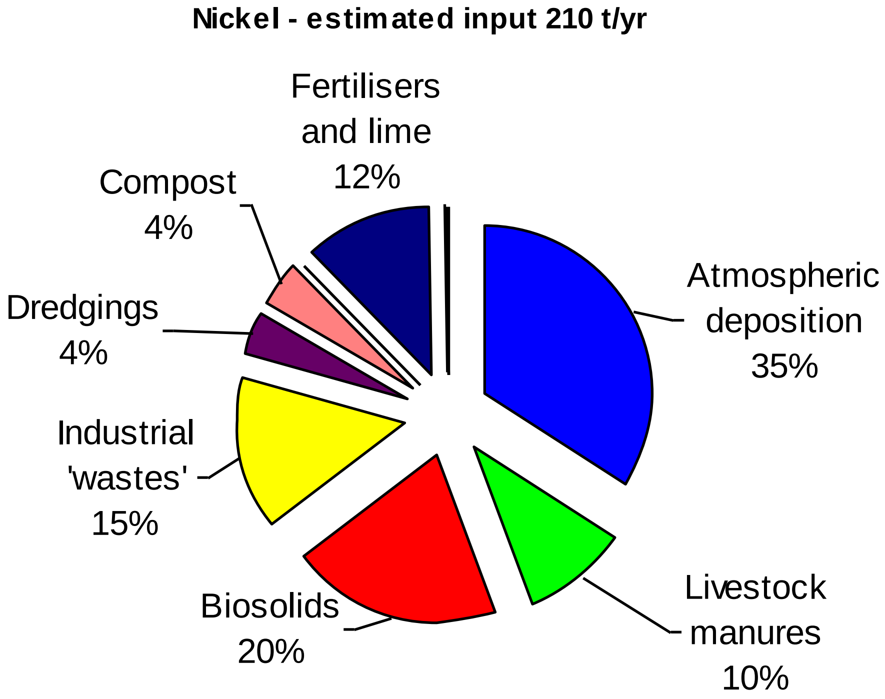


Figure 12. Estimates of the proportion (%) of total annual a) Zn; b) Cu; c) Ni, d) Pb; e) Cd; f) Cr; g) As and h) Hg inputs to agricultural soils in England and Wales from different sources (cont.)

c)



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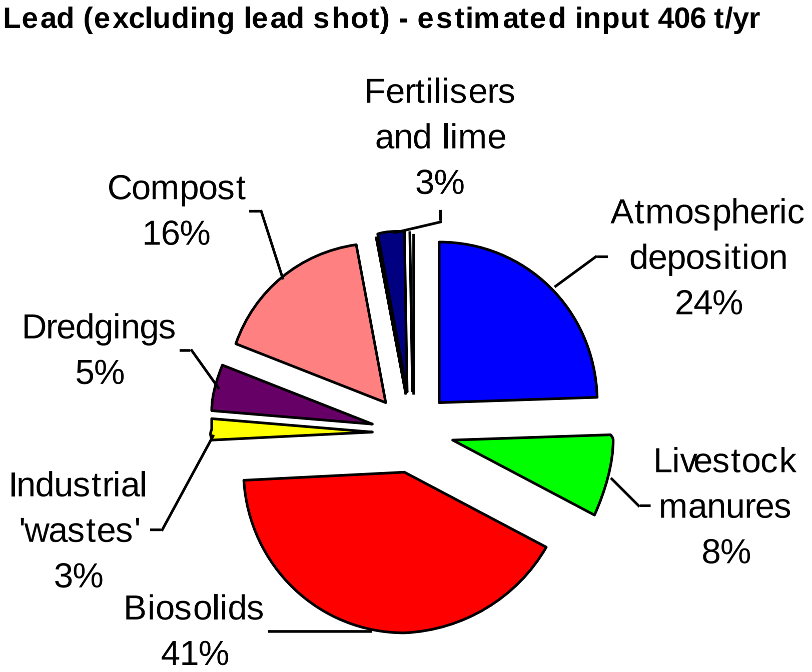
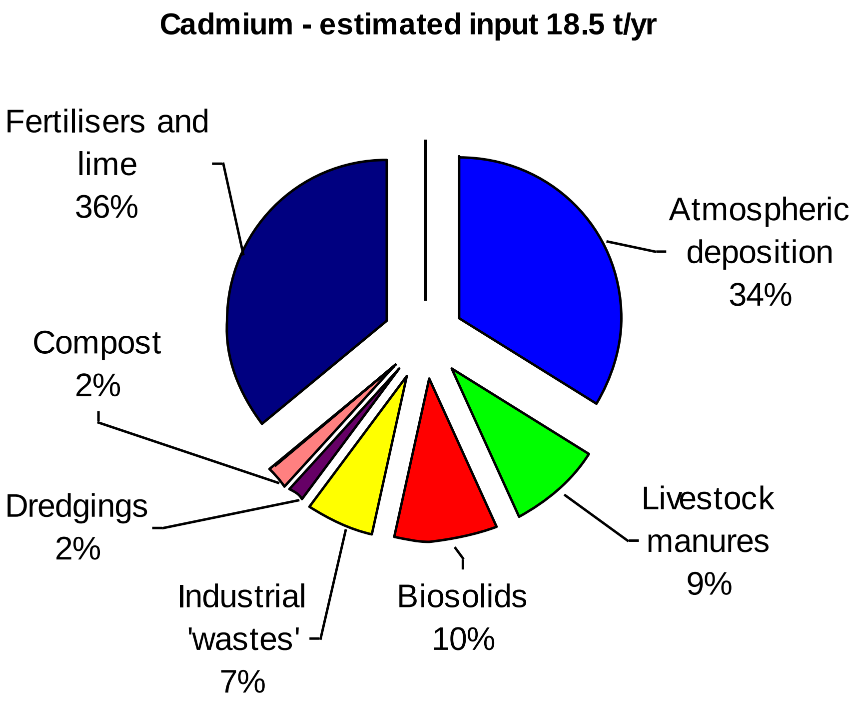


Figure 12. Estimates of the proportion (%) of total annual a) Zn; b) Cu; c) Ni, d) Pb; e) Cd; f) Cr; g) As and h) Hg inputs to agricultural soils in England and Wales from different sources (cont.).

e)



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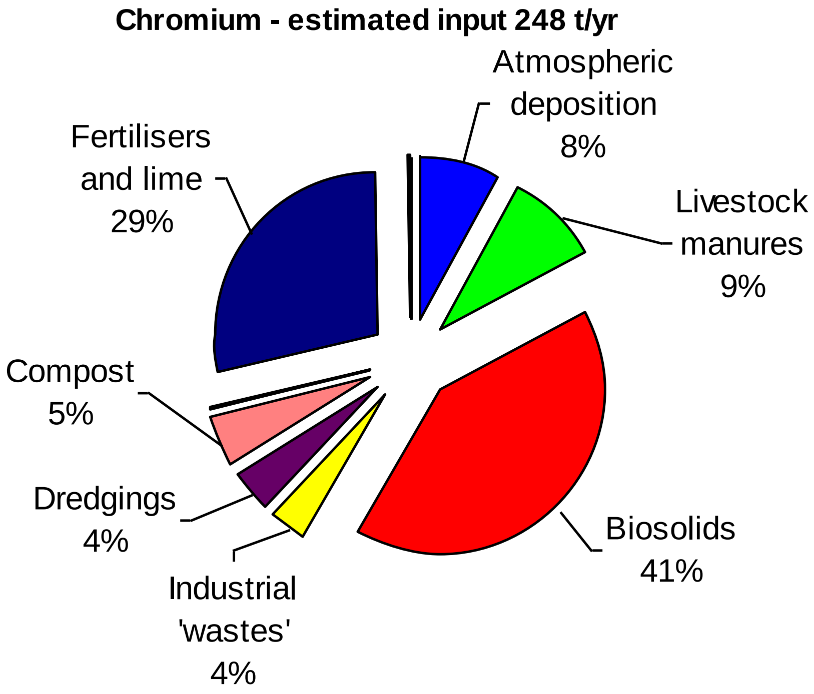
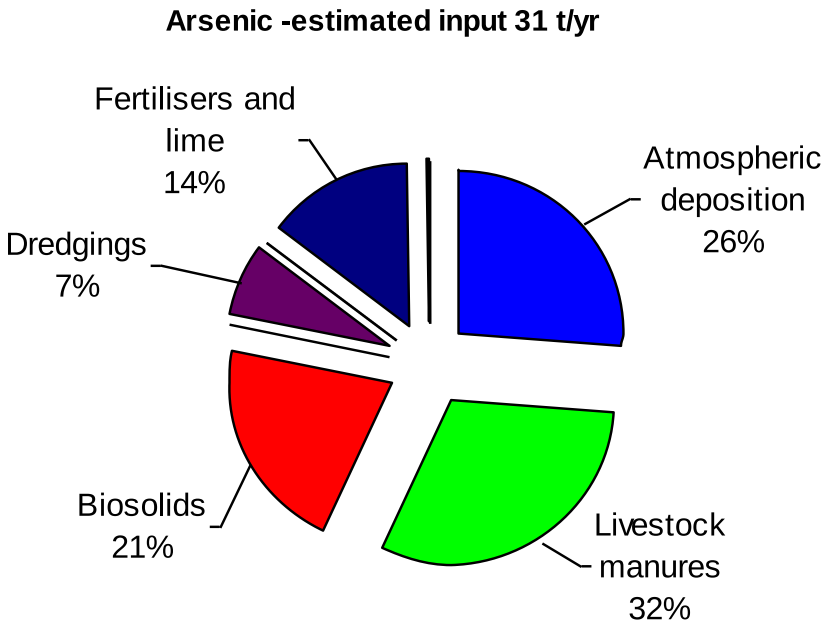


Figure 12. Estimates of the proportion (%) of total annual a) Zn; b) Cu; c) Ni, d) Pb; e) Cd; f) Cr; g) As and h) Hg inputs to agricultural soils in England and Wales from different sources (cont.).

g)



h)

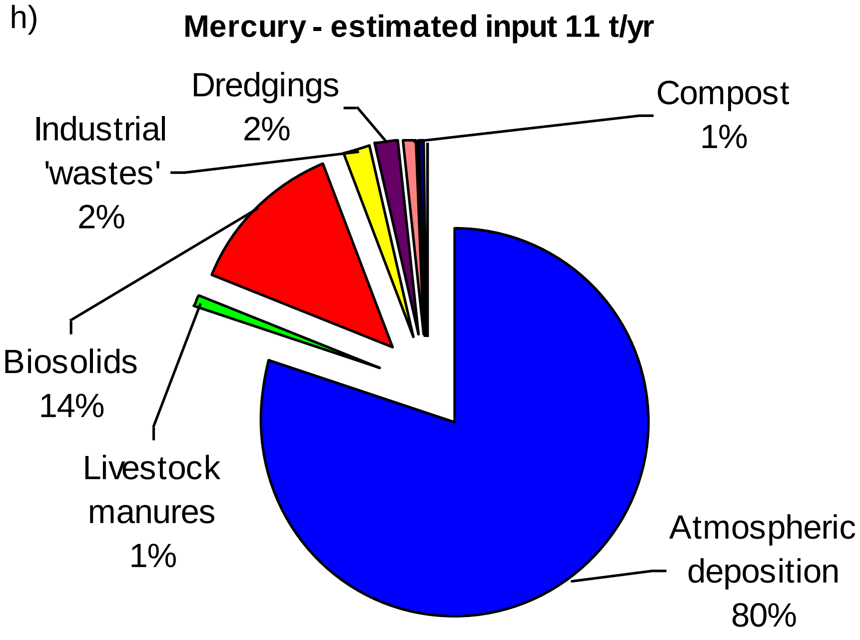
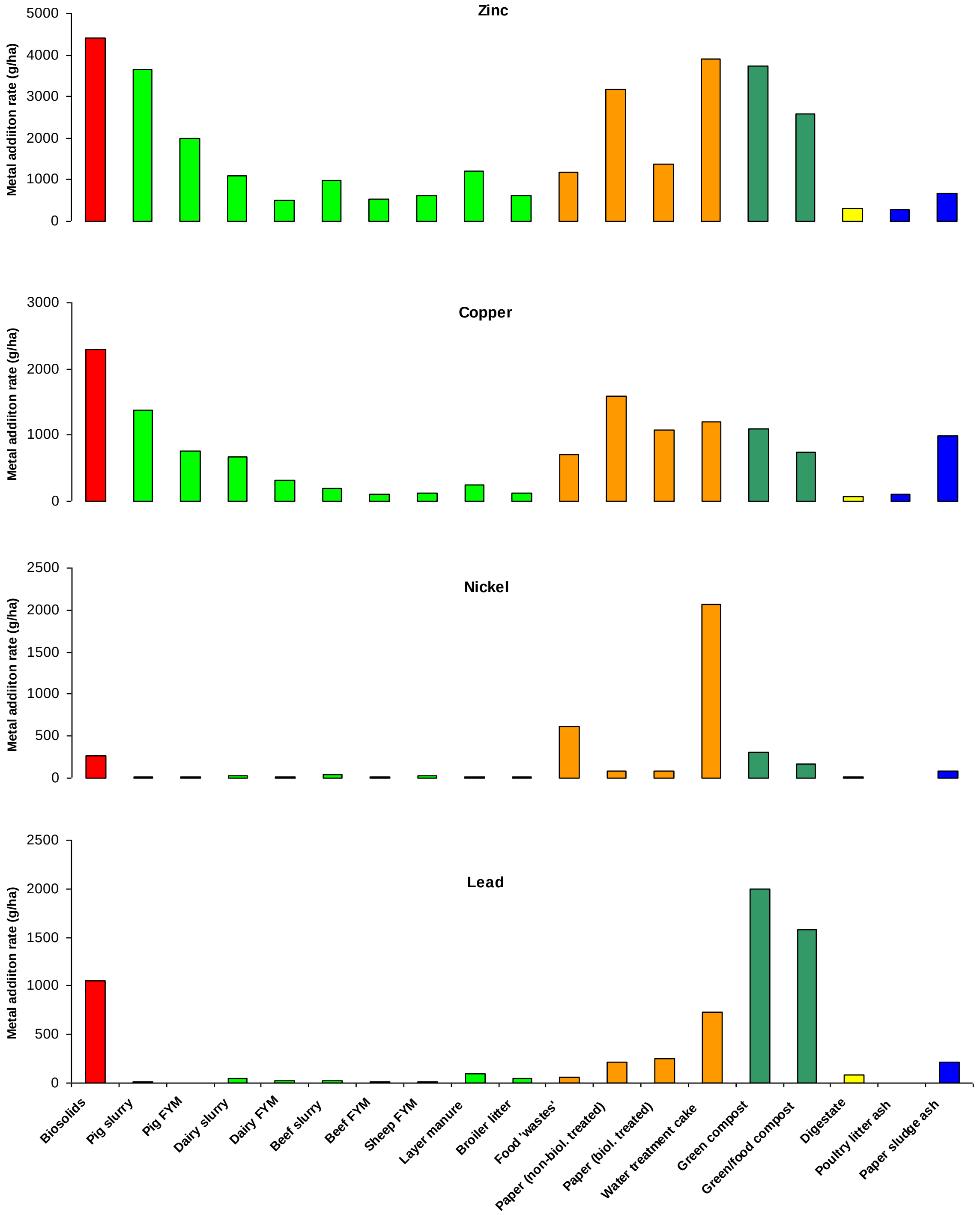


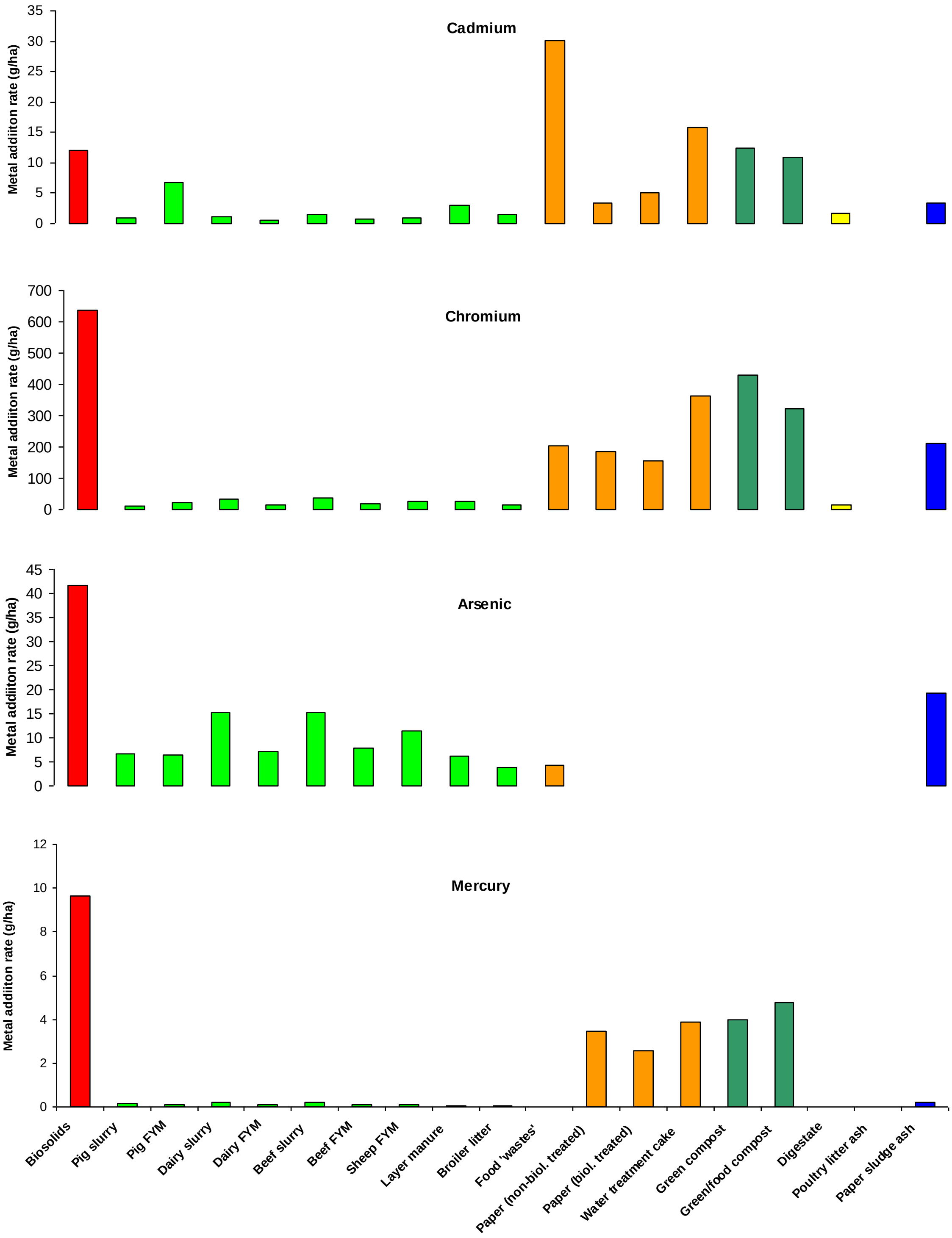
Figure 13. Zn, Cu, Ni and Pb addition rates from selected sources



Materials applied at the following annual rates:

Biosolids/livestock manures: *c*.250 kg N/ha	Green compost: 23 t/ha (*c*.250 kg N/ha)
Food 'wastes': *c*.180 m^3/ha (96 kg N/ha)	Green/food compost: 33 t/ha (*c*.250 kg N/ha)
Paper (phys/chem. treated): 69 t/ha	Poultry litter ash: 250 kg/ha
Paper (biol. treated): 33 t/ha	Paper sludge ash: 10 t/ha
Digestate: 30 t/ha (*c*.250 kg N/ha)	Water treatment cake: 96 t/ha

Figure 14. Cd, Cr, As and Hg addition rates from selected sources



Materials applied at the following annual rates:
Biosolids/livestock manures: 250 kg N/ha
Food ‘wastes’: *c*.180 m^3/ha (96 kg N/ha)
Paper (phys/chem.): 69 t/ha
Paper (biol.): 33 t/ha
Digestate: 30 t/ha (*c*.250 kg N/ha)

Green compost: 23 t/ha (*c*.250 kg N/ha)
Green/food compost: 33 t/ha (*c*.250 kg N/ha)
Poultry litter ash: 250 kg/ha
Paper sludge ash: 10 t/ha
Water treatment cake: 96 t/ha

A comparison of heavy metal loadings assuming the selected organic materials were applied on an equivalent N rate basis is shown in Table 16. For example, if biosolids and water treatment cake were both applied at a rate to supply 250 kg total N/ha (the legal maximum in NVZs and the recommended upper rate in the Code of Good Agricultural Practice), then the water treatment cake would add *c*.60% more Zn than biosolids and a similar quantity of Cu. Also, green compost would supply similar amounts of Zn to biosolids/pig slurry/paper crumble (non-biologically treated)/food 'wastes', and biosolids similar amounts of Cu to paper crumble (non-biologically treated)/food 'wastes'.

Table 16. Metal content of selected organic materials expressed as g of metal per kg of total nitrogen (N)

	N (g/kg fresh weight)	Dry matter	Metal concentration (g metal/kg N)						
Organic material		(%)	Zn	Cu	Ni	Cd	Pb	Cr	Hg
Dairy cattle slurry	3.6[1]	10	4.4	2.7	0.1	0.01	0.2	0.1	<0.1
Beef cattle slurry	3.6[1]	10	4.0	0.8	0.1	0.01	0.1	0.2	<0.1
Pig slurry	4.4[1]	6	14.6	5.5	0.1	<0.01	<0.1	0.1	<0.1
Layer manure	19[1]	35	4.8	1.0	0.1	0.01	0.4	0.1	<0.1
Biosolids	36[2]	-	17.7	9.2	1.1	0.05	4.2	2.6	<0.1
Green compost	7.5[1]	60	14.9	4.4	1.3	0.05	8.0	1.7	<0.1
Green/food compost	11[1]	60	10.3	3.0	0.7	0.04	6.3	1.3	<0.1
Paper crumble (bio-treated)	7.5[3]	28	5.1	4.0	0.4	0.03	1.1	0.7	<0.1
Paper crumble (non bio-treated)	2.2[3]	41	18.6	9.9	0.6	0.02	1.5	1.2	<0.1
Digestate	8.2[4]	4	1.2	0.2	<0.1	0.01	0.2	0.1	nd
Food 'wastes'	0.5[5]	5	15.2	9.2	8.6	0.34	0.7	2.6	<0.1
Water treatment cake	1.4[5]	21	28.8	8.9	15.5	0.14	5.4	2.6	<0.1

[1] Revised "Fertiliser Manual (RB209)"; Defra (in press).

[2] N concentration in the dry solids. Environment Agency "Sewage Sludge Survey 2001 to 2007" (Mat Davis, EA; pers. comm.)

[3] Gibbs *et al*. (2005)

[4] Data supplied directly to ADAS by existing AD plant operators

[5] Peacock and Turrell (2009)

nd = no data

Similarly, Table 17 shows a comparison of heavy metal loadings if the selected organic materials were applied on an equivalent phosphate (P_2O_5) rate basis. For example, if biosolids and green compost were applied at a rate to supply the same amount of P_2O_5, then green compost would add *c*.4-fold more Zn than biosolids and *c*.2-fold more Cu. Also, biosolids were shown to supply similar amounts of Zn to cattle slurry, paper crumble (biologically treated) and digestate.

Table 17. Metal content of selected organic materials expressed as g of metal per kg of total phosphate (P_2O_5)

Organic material	P_2O_5 (g/kg fresh weight)	Dry matter (%)	Metal concentration (g metal/kg P_2O_5) Zn	Cu	Ni	Cd	Pb	Cr	Hg
Dairy cattle slurry	1.8[1]	10	8.9	5.4	0.3	0.02	0.4	0.3	<0.1
Beef cattle slurry	1.8[1]	10	8.0	1.5	0.3	0.02	0.2	0.3	<0.1
Pig slurry	2.6[1]	6	24.7	9.3	0.1	<0.01	0.1	0.1	<0.1
Layer manure	14[1]	35	6.6	1.3	0.1	0.01	0.5	0.1	<0.1
Biosolids	71[2]	-	9.0	4.7	0.5	0.03	2.1	1.3	<0.1
Green compost	3.0[1]	60	37.5	11.0	3.1	0.1	20.1	4.3	<0.1
Green/food compost	3.8[1]	60	29.8	8.6	2.0	0.1	18.2	3.7	0.1
Paper crumble (bio-treated)	3.8[3]	28	10.0	8.0	0.8	0.1	2.1	1.3	<0.1
Paper crumble (non bio-treated)	0.5[3]	41	82.9	44.3	2.6	0.1	6.7	5.3	0.1
Digestate	1.1[4]	4	9.0	1.8	0.3	0.07	1.4	0.5	nd
Food ‘wastes’	0.4[5]	5	20.5	12.3	11.6	0.5	1.0	3.6	0.1
Water treatment cake	0.4[5]	21	106	32.9	57.1	0.5	19.7	9.7	<0.1

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[1] Revised “Fertiliser Manual (RB209)”; Defra (in press).

[2] P_2O_5 concentration in the dry solids. Environment Agency “Sewage Sludge Survey 2001 to 2007” (Mat Davis, EA; pers. comm.)

[3] Gibbs *et al*. (2005)

[4] Data supplied directly to ADAS by existing AD plant operators

[5] Peacock and Turrell (2009)

nd = no data

5. EFFECTS ON AGRICULTURAL SOIL QUALITY

5.1 Time to reach current soil metal limits

Field-level heavy metal addition rates were used to estimate the time (number of years) required to raise topsoil metal concentrations from ‘typical’ background values (i.e. mean topsoil concentrations in England and Wales; McGrath and Loveland, 1992) to the maximum permissible concentrations of heavy metals (at soil pH 6-7) stipulated in the Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996; Table 6). This estimate assumed that all fields received annual inputs from atmospheric deposition and had the same rate of metal loss, via crop offtake and leaching. Losses of metals via crop offtake were based on typical yields and metal concentrations in cereal grain (Alloway *et al*., 2000), but offtakes with straw were not considered as straw was assumed to be recycled through the system in FYM (see Section 3.3.4) or to be incorporated directly back into the soil. Leaching losses were based on data from Keller *et al*. (2002) from lysimeter experiments using a loamy sand soil where sewage sludge had been applied (data from the untreated controls was used). Note: it was assumed that the leaching losses reported by Keller *et al*. (2002) related to metals lost from the top 30cm of the soil profile.

The limiting metal for most organic and inorganic material additions was Zn, with the soil limit value of 200 mg/kg reached after less than 200 years of annual biosolids, pig slurry, compost and water treatment cake additions. Clearly, these times would decrease if soil Zn concentrations were already above ‘background’ values, if more than one material was applied to a field in a year, or if application rates or input material Zn concentrations were higher than those assumed here. In comparison, it was estimated to take >1,000 years for cattle FYM applications to raise topsoil Zn concentrations to the 200 mg/kg limit value. For food ‘wastes’, the limiting metal was generally Cd, where the maximum permitted soil concentration of 3 mg/kg was estimated to be reached after *c.*300 years. Similar estimates for the other metals (Cu, Ni, Pb, Cd, Cr, As and Hg) are provided in Table 18.

5.2 Time to reach possible alternative soil metal limits

Using the methodology described above, estimates were made of the time (number of years) required to raise topsoil metal concentrations from ‘background values’ to possible alternative maximum permissible concentrations, which were assumed to be 75% and 50% of the current limits values (Tables 19 and 20). This showed that the soil metal limit concentrations would be met more rapidly if they were set at lower levels than at present, and in many cases for Zn were <50 years of annual application.

It is important to note that the estimates in Tables 18-20 should be treated as ‘worst-case’ scenarios, as they assume that the materials are applied every year to the same field. In practice, most materials are not applied this often; ‘typical’ application frequencies for livestock manures/digestate/composts would be every 1-2 years, for biosolids every 2-5 years and paper crumble/water treatment cake/lime every 4-5 years.

Table 18. Estimated time (years) required to raise soil metal concentrations from 'background'[a] to current limit[b] concentrations, assuming annual applications of each material.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Biosolids	111	199	765	961	721	>1000	>1000	329
Pig slurry	136	333	>1000	>1000	>1000	>1000	>1000	>1000
Pig FYM	265	612	>1000	>1000	>1000	>1000	>1000	>1000
Dairy slurry	541	683	>1000	>1000	>1000	>1000	>1000	>1000
Dairy FYM	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Beef slurry	621	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Beef FYM	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Sheep FYM	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Layer manure	484	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Broiler litter	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Food 'wastes'	501	648	332	>1000	293	>1000	>1000	>1000
Paper (phys/chem treated)	158	290	>1000	>1000	<1000	>1000	>1000	789
Paper (biol. treated)	408	429	>1000	>1000	>1000	>1000	>1000	989
Water treatment cake	126	385	99	>1000	552	>1000	>1000	716
Green compost	133	421	649	508	698	>1000	>1000	702
Green/food compost	198	620	>1000	642	789	>1000	>1000	608
Anaerobic digestate	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Phosphate fertiliser	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Lime	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Poultry litter ash	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Paper sludge ash	>1000	469	>1000	>1000	>1000	>1000	>1000	>1000
Plant protection (hops)	136	334	>1000	>1000	>1000	>1000	>1000	>1000
Atmospheric deposition	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000

🟥	🟧	🟨	🟩
<200 years	200-400 years	400-600 years	>600 years

[a] Median soil concentration in England and Wales (McGrath and Loveland, 1992; ADAS, 1996)

[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 30cm.

Table 19. Time (years) required to raise soil metals concentrations from 'background'[a] to possible alternative limit[b] concentrations (75% of current values), assuming annual applications of each material.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Biosolids	64	142	491	684	486	>1000	>1000	238
Pig slurry	78	237	>1000	>1000	4360	>1000	>1000	>1000
Pig FYM	152	435	>1000	>1000	832	>1000	>1000	>1000
Dairy slurry	312	486	>1000	>1000	>1000	>1000	>1000	>1000
Dairy FYM	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Beef slurry	358	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Beef FYM	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Sheep FYM	712	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Layer manure	279	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Broiler litter	754	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Food 'wastes'	289	461	213	>1000	198	>1000	>1000	>1000
Paper (phys/chem treated)	91	206	>1000	>1000	>1000	>1000	>1000	570
Paper (biol. treated)	235	305	>1000	>1000	>1000	>1000	>1000	714
Water treatment cake	73	274	63	987	372	>1000	>1000	517
Green compost	77	300	417	361	470	>1000	>1000	507
Green/food compost	114	441	752	457	532	>1000	>1000	439
Digestate	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Phosphate fertiliser	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Lime	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Poultry litter ash	933	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Paper sludge ash	626	333	>1000	>1000	>1000	>1000	>1000	>1000
Plant protection (hops)	78	238	>1000	>1000	>1000	>1000	>1000	>1000
Atmospheric deposition	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000

🟥	🟧	🟨	🟩
<200 years	200-400 years	400-600 years	>600 years

[a] Median soil concentration in England and Wales (McGrath and Loveland, 1992; ADAS, 1996)

[b] Three-quarters of the current 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 30 cm.

Table 20. Time (years) required to raise soil metals concentrations from 'background'[a] to possible alternative limit[b] concentrations (50% of current values), assuming annual applications of each material.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Biosolids	17	84	218	407	251	988	>1000	146
Pig slurry	21	141	>1000	>1000	>1000	>1000	>1000	>1000
Pig FYM	40	259	>1000	>1000	429	>1000	>1000	>1000
Dairy slurry	83	288	>1000	>1000	>1000	>1000	>1000	>1000
Dairy FYM	275	633	>1000	>1000	>1000	>1000	>1000	>1000
Beef slurry	95	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Beef FYM	266	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Sheep FYM	189	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Layer manure	74	819	>1000	>1000	925	>1000	>1000	>1000
Broiler litter	200	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Food 'wastes'	76	274	94	>1000	102	>1000	>1000	>1000
Paper (phys/chem treated)	24	123	629	>1000	799	>1000	>1000	351
Paper (biol. treated)	62	181	632	>1000	569	>1000	>1000	439
Water treatment cake	19	163	28	587	192	>1000	>1000	318
Green compost	20	178	185	215	243	>1000	>1000	312
Green/food compost	30	262	333	272	275	>1000	>1000	270
Digestate	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Phosphate fertiliser	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Lime	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Poultry litter ash	247	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Paper sludge ash	166	198	>1000	>1000	809	>1000	>1000	>1000
Plant protection (hops)	21	141	>1000	>1000	>1000	>1000	>1000	>1000
Atmospheric deposition	>1000	>1000	>1000	>1000	>1000	>1000	>1000	780

🟥 <200 years 🟧 200-400 years 🟨 400-600 years 🟩 >600 years

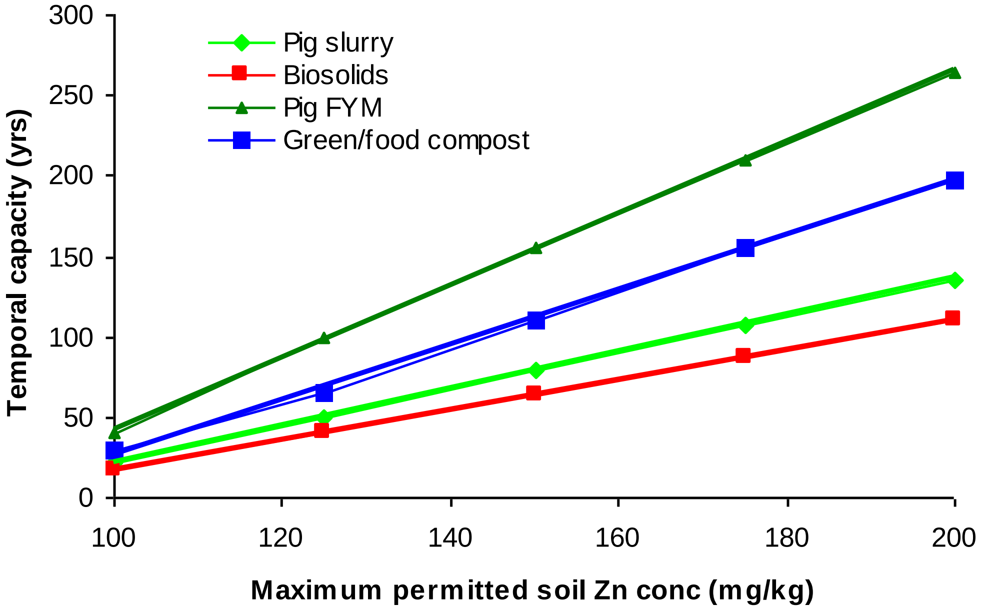
[a] Median soil concentration in England and Wales (McGrath and Loveland, 1992; ADAS, 1996)

[b] Half of the current 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 30cm.

As Zn was the limiting metal for most input sources, a graphic illustration was produced to demonstrate how changing the soil Zn limit values (from 200 mg/kg to 100 mg/kg) would affect the temporal capacity of a 'typical' soil to accept selected organic material additions (Figure 15). The linear relationship between the soil Zn limit values and temporal capacity to accept organic materials depended on the material applied, and was shorter for biosolids/pig slurry than pig FYM. Notably, reducing the soil Zn limit value to 150 mg/kg reduced the temporal capacity of the soil to accept biosolids to *c*.60 years, pig slurry to *c*.80 years and green/food compost to *c.*110 years.

Figure 15. Effect on the soil temporal capacity for Zn of changing maximum permissible soil Zn concentrations for selected organic materials.



6. SUMMARY AND CONCLUSIONS

In response to concerns over the impact of heavy metal inputs on long-term soil fertility and the potential transfer of certain metals to human diets, an updated inventory of heavy metal inputs to agricultural soils (for 2008) was compiled for England and Wales.

Whilst atmospheric deposition was shown to be a major source of total heavy metal inputs to agricultural land at the *national level* (24-35% of total inputs of Zn, Cu, Ni, Cd, Pb and As, and 80% for Hg), livestock manures (*c*.30% of Zn, Cu and As inputs) and biosolids (10-41% of metal inputs) were also important sources because of the large quantities applied. Also, the results showed that metal addition rates at the *field-level* from some pig and poultry manures and green compost were similar to (and sometimes greater than) those from biosolids. Moreover, metal inputs from ‘food waste’ materials, which are increasingly being applied to agricultural land, sometimes exceeded those from biosolids.

The soil temporal capacity for Zn (based on current maximum permitted soil Zn concentrations where biosolids are applied and for a topsoil at current background Zn concentrations) was estimated to be reached after less than 200 years of annual biosolids, pig slurry, compost or water treatment cake additions. In comparison, it was estimated to take >1,000 years for cattle FYM applications to raise topsoil Zn concentrations to the maximum permitted limits. For food ‘wastes’, the limiting metal was generally Cd, with the maximum permitted concentration estimated to be reached after *c.*300 years. It is important to note that these estimates represent a ‘worst-case’ scenario, as they assume that the materials are applied every year to the same field, which is not always the usual practice. Notably, where metal loading rates are calculated on an N equivalent basis, water treatment cake was shown to supply *c*.60% more Zn and similar amounts of Cu to biosolids. Also, green compost would supply similar amounts of Zn to biosolids/pig slurry/paper crumble (non biologically treated)/food ‘wastes’, and biosolids similar amounts of Cu to paper crumble (non biologically treated)/food ‘wastes’. Furthermore, where metal loading rates are calculated on a phosphate equivalent basis, green compost would add *c*.4-fold more Zn than biosolids and *c.*2-fold more Cu. Also, biosolids were shown to supply similar amounts of Zn to cattle slurry, paper crumble (biologically treated) and digestate.

This study has provided baseline information for the development of strategies to reduce heavy metal inputs to agricultural land and to effectively target any future policies for minimising long-term metal accumulation in soils.

7. FURTHER WORK

- There would be benefit in producing regular updates (e.g. every 2-3 years) to the inventory of metal inputs to agricultural soils (particularly in light of the short-term changes noted in this study in livestock manure, compost and food ‘waste’ additions), which could act as an indicator of soil quality/protection.
- There would be merit in initiating work to quantify *atmospheric heavy metal deposition* to lowland agricultural soils and as part of such a study to robustly compare deposition rates measured by different techniques.
- There is a need to collect *more robust data* on the contribution of footbaths, digestate, food ‘wastes’, paper sludge ash, gypsum, lead shot etc. to metal loading rates to agricultural soils.

8. KNOWLEDGE TRANSFER

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APPENDIX I

Table A1. Data age and provenance

	Age of data	Source	Notes
Atmospheric deposition			
• Metal deposition rates	1995-98	Alloway *et al*. (2000)	Deposition rates adjusted based on proportions of dry deposition collected by the CEH 'Rural Heavy Metal Monitoring Network' and observed temporal trends (see Section 3.1)
Biosolids			
• Quantity	2007	Environment Agency, UK Sewage Sludge Survey	
• Metal concentrations	2001-07		
Compost			
• Quantity to land	2007/8	AFOR (2009)	
• Metal concentrations	Supplied in 2008	Composting Association, Compost Certification Scheme summary statistics, 20 March 2008	Data for *c.*100 composts certified for PAS100 compliance
Corrosion			
• Corrosion rate	2008	SO_2 data from the UK National Air Quality Archive, 2008 (England and Wales data only)	
• Galvanised products market	1998	WS Atkins (2000)	Estimates uncertain
• Use in agricultural products	2004	Zinc Galvanisers Association (pers. comm..)	Estimates uncertain
Digestate			
• Quantity to land and metal concentrations	2008	Existing producers	Likely to increase in future

	Age of data	Source	Notes
Fertiliser and lime			
• Fertiliser and lime use	2008	British Survey of Fertiliser Practice. Benford (2009)	
• Metal concentrations- fertilisers	1996	Marks (1996)	Data is old
• Metals concentrations - lime	Early 1970s	Chater & Williams (1974)	Data is old.
Footbaths			
• Footbath use	2007	Farm Practice Survey 2007. Defra (2007d).	
• Volume and type	2006	Farm Practice Survey 2006. Defra (2006)	
• Disposal route	2006	Farm Practice Survey 2006. Defra (2006)	
Industrial 'wastes'			
• Quantities and metal concentrations	2007/8	Defra project WR1103.	Wastes spread under Paragraph 7 exemptions between 30 April 2007 and 1 May 2008
• Metal addition rates	2007/8	Defra project SP0578	As above
• Metal concentrations in dredgings	1992	British Waterways (pers. comm.)	Mean analysis of 1000 British Waterways canal dredgings samples
• Paper crumble (quantity and metal concentrations)	2003	Gibbs *et al.* (2005).	
Irrigation water			
• Irrigated area	2005	Weatherhead & Rivas-Casado (2007).	
• Metal concentrations	2005	Defra (2007c)	

	Age of data	Source	Notes
Lead shot			
• Quantities of shot used and area of ranges	2008	CPSA (2009); Penn (2008)	Estimate is very uncertain
Livestock manures			
• Metal concentrations	2008/9	Defra project SP0569 and LINK project LK0988	
• Quantities	2008	Livestock numbers from the 2008 Agricultural Census; daily excretion values from 2009 NVZ Action Programme (Defra, 2008);	Apportionment to housing/grazing and slurry/FYM from Defra project WQ0103 (Manures-GIS; Defra, 2007b).
Plant protection			
• Pesticide use	2004-2006	Garthwaite & Thomas (2004); Garthwaite *et al*. (2006a); Garthwaite *et a*l. (2006b).	
• Metals in pesticides	Mid 1990s	Whitehead (2001)	
Poultry litter ash			
• Quantity and metal concentration	Mid 2000's	http://www.fibrophos.co.uk; http://cropkare.com/traceelem.html	
Other data			
• Agricultural land area	2008	2008 Agricultural Census.	Excluding rough grazing, set-aside and woodland.