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Management of inputs of heavy metals to agricultural soils and crops

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Summary

- **The soil is a long-term sink for the group of heavy metals often referred to as potentially toxic elements (PTEs). These elements are copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd), lead (Pb), chromium (Cr), mercury (Hg), molybdenum (Mo), selenium (Se), and arsenic (As).**
- **Losses to watercourses and plant offtakes are usually relatively small compared with the total quantities entering the soil from different industrial and agricultural sources.**
- **The wide variation in heavy metal concentrations in Scottish topsoil's reflects the diverse geology of Scotland.**
- **A European Commission regulation specifies the maximum permissible levels of Pb and Cd in cereals, potatoes, and vegetables.**
- **The Sludge (Use in Agriculture) Regulations on agricultural use of sewage sludge currently represent the only statutory based mechanism specifically for controlling heavy metal inputs to agricultural soils in the UK.**
- **Inputs of heavy metals should not be allowed to exceed limit values for PTEs in soil to which sludge is applied and maximum annual quantities of PTEs which may be applied to the soil.**
- **For most organic fertilisers it is their nutrient value that set limits on maximum application rates rather than its PTE levels.**

1. Introduction

Heavy metals in soils may derive from several sources:

i. Geological parent material
ii. Industrial processes – emissions to the atmosphere followed by deposition to soils – solid and liquid wastes applied to land or deposited in landfill – current or abandoned industrial sites – mining
iii. Farming practices – fertilisers and some animal manures and feed wastes

The European Agricultural Fund for Rural Development
Europe investing in rural areas

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Further information on the significance of inputs of these heavy metals for agricultural soils and crops is provided in this technical note.

2. Soils

2.1 Heavy metal concentrations in Scotland

Concentrations of six of the PTEs that are specified in the Code of Practice for Agricultural Use of Sewage Sludge were measured across Scotland as part of the National Soil Inventory of Scotland (NSIS_1) **(The State of Scotland's Soil. March 2011 (sepa.org.uk)** and are shown in Table 1a. Concentrations of the other four PTEs that are specified in the Code of Practice for Agricultural Use of Sewage Sludge are also measured by the SRUC laboratory. The range and mean concentrations of these four PTEs are reported in Table 1b from soil samples taken to a depth of 25cm in Orkney, Caithness, and Aberdeenshire.

Table 1a: Range and mean concentrations of metals in Scottish soils as determined by the National Soil Inventory of Scotland (NSIS_I) (surface horizon).

	NSIS_I (concentration; mg/kg)	
Heavy metal	**Mean**	**Range**
Cadmium (Cd)	0.16	0.02-0.97
Chromium (Cr)	44.7	2.3-215.8
Copper (Cu)	9.4	0.19-63.9
Lead (Pb)	31.8	3.9-238.8
Nickel (Ni)	20.5	0.4-233
Zinc (Zn)	53.8	4.0-223.6

Table 1b: Range and mean concentrations of metals in Orkney, Caithness, and Aberdeenshire soils as determined by the SRUC laboratory.

	SRUC (concentration; mg/kg)	
Heavy metal	**Mean**	**Range**
Arsenic (As)	5.9	0.02-22
Mercury (Hg)	0.075	0.03-0.48
Molybdenum (Mo)	1.1	0.1-7.5
Selenium (Se)	0.45	0.01-1.8

[1] Grading of agricultural land with elevated PTE concentrations under the Agricultural Land Classification system) (htpps://gov.wales/soils-policy-evidence-programme)

The wide range of concentrations reflects the diverse geology of Scotland. In a few areas of Scotland, soil Ni and Cr concentrations are high because the Leslie Association soil has been formed from ultra-basic igneous rocks, mainly serpentine, in Unst and Fetlar, Shetland and in Aberdeenshire. These soils can naturally exceed the Ni and Cr limits set out in the Code of Practice for Agricultural Use of Sewage Sludge. Naturally poorly draining gley soils in Caithness may have Mo levels more than the limit of 4mg/kg set out in the Code of Practice for Agricultural Use of Sewage Sludge. Unlike other metals, this limit is not absolute, but the rules specify that expert advice must be sought.

There are small areas of Scotland where high soil copper concentrations are above the Cu concentrations reported in Table 1a and may impair crop growth. Copper concentrations are generally well below the Code of Practice for Agricultural Use of Sewage Sludge limits across almost all of Scotland but where effluents from distilleries have been spread to land for many years the Cu concentration in soil may be above the sewage sludge limit and new land will be required. Copper is an essential trace element for plants and animals, and low copper concentrations are more likely to adversely affect crop growth (FAS/SRUC TN657, 2014: Management of copper in soils for cereals **(www.fas.scot/publications/technical-notes/)**. Copper deficiency in grazing ruminants may be reported due to low total Cu or due to interaction with a high level of soil Mo. In contrast, sheep are sensitive to Cu toxicity and may experience problems if grazed on pastures with high soil Cu concentrations.

The Selenium Content of Scottish Soil and Food Products was commissioned by the Food Standards Agency Scotland (2009) and reported that Se concentrations tend to be higher in the Central Belt and parts of Fife, because of the geology and soil types, than Dumfries and Aberdeenshire, which are areas that are likely to be low in Se. Soils derived from coarse grained sediments contain less than those derived from clays and shales and leached acid soils and podzols formed on arenaceous parent materials are likely to have the lowest Se concentrations.

2.2 Major sources of heavy metals added to soils

ADAS has estimated heavy metal inputs to agricultural soils in England and Wales from all major sources, including atmospheric deposition, biosolids, livestock manures and footbaths, composts, anaerobic digestates, industrial ‘wastes’ (including paper crumble, food ‘wastes’, water treatment sludges), and ash (from poultry manure incineration). Across the whole agricultural land area, atmospheric deposition was a major source of metals with livestock manures and biosolids also important sources because of the large quantities of these materials applied. Metal addition rates at the individual field level from pig and poultry manures and composts were similar (and sometimes greater) than those from biosolids. The study has provided baseline information upon which to develop and focus future policies limiting heavy metal inputs to and accumulation in topsoil’s (Defra, 2020), The Agricultural Soil Heavy Metal Inventory for 2008 Report 3 Defra Project SP0569.

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

3. Crops

3.1 Heavy metal total concentrations in foodstuffs

The Cd and Pb concentrations of agricultural produce are of particular importance, as the consumption of agricultural foodstuffs is thought to contribute significantly to the dietary intake of these metals that have no known biological function. A European Commission regulation introduced during 2001 specifies the maximum permissible levels of Cd and Pb in foodstuffs (Table 2).

Table 3: Maximum permissible levels of Cd and Pb in foodstuffs.

Heavy metal	Product	Maximum level (mg/kg wet weight)
Cadmium	Cereals excluding wheat grain	0.1
	Wheat grain	0.2
	Leafy vegetables	0.2
	Root vegetables and peeled potatoes	0.1
Lead	Cereals and legumes	0.2
	Peeled potatoes	0.1
	Leafy vegetables	0.3

Surveys in the UK indicate that in general, wheat takes up higher concentrations of Cd than barley, although both species take up similarly low amounts of Pb. Concentrations of Cd and Pb in most samples were below the European Commission limits and most growers will not need to take any specific action to ensure crops comply with these limits. Lead poisoning, especially in young children, has led to the prohibition of Pb additives in petrol and paint in many countries. Lead is less labile in soils than Cd, and even at high concentrations uptake by plants is usually small.

3.2 Crop nutrient analysis after harvest

Yield Enhancement Network (YEN) grain nutrient analysis and benchmarking measures 12 nutrients after harvest, including Cu, Zn and Mo, but critical thresholds are not known in cereals or other crops for these metals. At harvest grain contains most of crop's uptake of Cu and Zn whereas straw contains most of the Mo. Benchmarking is best done each season because most nutrient concentrations show variation between seasons due to different nutrient uptake and grain-filling conditions.

Although Se is not considered essential for the healthy growth of plants, it is an essential micronutrient for both humans and animals. There is evidence from surveys that the Se concentration of Scottish wheat is lower than other parts of the UK.

3.3 Visual symptoms of heavy metal toxicity in barley

As part of reviewing the rules for sewage sludge application to agricultural land Smith (1996) reported symptoms of heavy metal toxicity in barley (Table 4).

Table 4: Visual symptoms of heavy metal toxicity in barley

Element	Symptom
Zinc	yellow leaves, brown patches, and pale green stripes on leaves
Copper	bluish leaves
Nickel	longitudinal white stripes and brown patches on leaves
Cadmium	red-brown patches on leaves, stunted stems
Mercury	yellow leaves, red stems
Chromium	yellow leaves, pale green longitudinal stripes on leaves

Source: Smith (1996) Agricultural recycling of sewage sludge and the environment, CAB International

3.4 Heavy metal concentrations in herbage

3.4.1 Molybdenum. Deficiency of Mo is considered relatively rare in agricultural plants, but very high Mo can cause livestock health issues by depressing the availability and absorption of Cu. SAC Consultancy has a classification and interpretation of available soil Mo levels for crops and animal nutrition. The Mo soil extractant used is 1M neutral ammonium acetate with a soil: solution ratio of 1:16 (w/v). The Mo data for soils of all drainage classes maintained at about pH 6 and containing up to 12% organic matter are classified in one of the 5 categories in Table 5.

Table 5: Classification and interpretation of soil Mo levels for brassica crops and leafy herbage.

Soil status	Extractable Mo	Probability of Mo deficiency in brassica crops	Probable Mo concentration in leafy herbage in Aug-Oct
	mg/kg soil		mg/kg DM
VL (very low)	<0.01	Probability of deficiency in some crops	<1.5
L (low)	0.01-0.04	No deficiency expected	<2.0
M (moderate)	0.05-0.08	No deficiency	1.5-3.5
H (high)	0.08-0.20	No deficiency	3-8
VH (very high)	>0.20	No deficiency	>5

Applying lime to acid soils substantially increases the availability of Mo and is greater on soils with poor than free natural pedological drainage conditions. Molybdenum is more readily taken up by plants than Cu, irrespective of the amount of available Cu. Where soil pH is clearly lower or higher than 6.0, herbage Mo should be determined as well as soil Mo. Where soil organic matter contents are greater than 12% both soil and herbage Mo should be determined. Herbage in May, June and July are expected to have lower concentrations of Mo.

Normal liming of grassland ensures that Mo supply is not limiting herbage production and, therefore, Mo should not be applied because even a small increase in concentration of Mo in herbage can adversely affect Cu metabolism in ruminants. Clover takes up soil Mo more readily than grasses, so that applications of nitrogen tend to decrease the Mo concentration of mixed swards by decreasing the proportion of clover. Where herbage Mo concentration is high there is a large increase from June to October.

3.4.2 Selenium. Although Se is not considered essential for the healthy growth of plants, it is an essential micro-nutrient for both humans and animals. Selenium has a very narrow range between dietary deficiency and excess. The Se concentrations of Scottish soils are generally below the 0.6 mg/kg recommended threshold for grazing livestock. The most realistic choice of controlling the Se supply of livestock through the fodder plants is to add Se to the fertiliser. The uptake of Se in herbage is influenced by the form of Se added. Trials have shown that selenate, salt or prill form, is more potent than selenite in its ability to increase Se concentrations in herbage, at least during the year of treatment. In contrast, application of selenite at 300 g/ha Se produced herbage with Se concentrations above background in most cuts over the 3-year period of a trial. In addition, selenite application, even at 300 g/ha, did not produce toxic levels of Se in herbage. The amount of Se taken up by the herbage above background, expressed as a percentage of the amount added, ranged from 1.4 to 2.2% for selenite treatments to 16 to 37% for the selenate and prill treatments. However, there is a greater potential risk of pollution of surface and ground waters from the more mobile selenate form, as well as a greater risk of producing herbage levels of Se that are potentially toxic to grazing animals, immediately following selenate treatment. Selenite is known to become rapidly fixed in soils particularly by organic matter and by iron oxides.

The use of selenite as a grassland fertiliser appears more attractive than selenate, because of the lower risk of it poisoning livestock and of entering watercourses. It should be feasible to spray-impregnate a grassland fertiliser with sufficient sodium selenite to supply annually 100 g/ha of Se for use on grassland where Se deficiency in livestock has been confirmed by veterinary tests. The unknown factor in this approach is the possibility of a build-up of a fraction of Se in the soil which might be released into a plant-available form over a long period of time. Interestingly, the maximum allowable concentration of total Se in soil under grass after application of sewage sludge, when samples are taken to a depth of 7.5 cm, is 5 mg/kg dry soil, which is higher than the total Se that has been recorded in soil in Scotland.

3.4.3 Nickel. Nickel plays an essential role in the metabolism of urea nitrogen by rumen micro-organisms ruminants. Ruminants maintained on low intakes of N may be particularly susceptible to the effects of Ni deficiency. Nitrogen application is known to decrease the Ni content of grasses and liming strongly depresses the Ni content of grasses and clovers.

3.4.4 Cadmium. The most widely recognised contamination of inorganic fertilisers is associated with Cd present in the rock phosphate feedstock of all phosphate fertiliser materials. Concerns over the potential consequences for human health from the accumulation of Cd in the environment have led to fertiliser manufacturers voluntarily changing the source of raw materials to reduce inputs. Cadmium has been shown to accumulate in the organs of livestock grazing on land where phosphate fertilisers or historic sewage sludges have been applied over several years. Cadmium has also been demonstrated to have an adverse effect on soil organisms and microbial processes. Cadmium is highly labile in soils at low soil pH, and the application of sludge to soils with a pH less than 5.0 is prohibited by The Sludge (Use in Agriculture) Regulations 1989, as amended.

3.4.5 Lead. Lead has no nutritional function. Even at high Pb concentrations uptake by plants is usually small. Historically Pb in herbage has been associated with Pb depositions on to leaves near busy roads. Lead poisoning has led to the prohibition of Pb additives to petrol and surface contamination of Pb is expected to decline.

3.4.6 Essential trace elements. Zinc and Cu are trace elements essential to the functioning of biological systems, although at elevated concentrations they can become phytotoxic, and Zn has been shown to have adverse effects on soil microorganisms & microbial processes. Copper deficiency in grazing ruminants is widely reported and may be due to low soil Cu or due to interaction with a high level of soil Mo. In contrast, sheep are sensitive to Cu toxicity and may experience problems if grazed on pastures with high soil Cu concentrations.

4. Organic fertilisers

4.1 Heavy metal concentrations in livestock manures

The heavy metal content of livestock manures largely reflects concentrations in the feed and the efficiency of feed conversion by the animal, although for some livestock there may be significant inputs of metals given on veterinary prescription (pigs) or used in footbaths (sheep and cattle). For all livestock, most heavy metals consumed in feed are excreted in the faeces or urine and will thus be present in livestock manure that is subsequently applied to land. Typical heavy metals concentrations in livestock manures from a survey of 85 samples collected from commercial farms in England and Wales in the mid-1990s (Nicholson et al., 1999. Heavy metal contents of livestock feeds and animal manures in England and Wales. Bioresource Technology 70, 23-31) have been adapted and are shown in Table 6. The highest concentrations of Zn and Cu were in pig slurry and laying hen manure, reflecting the levels of dietary supplementation. A reduction in the heavy metal content of livestock feeds would lead to an associated reduction in excretal outputs and hence metal inputs to soils. Zinc and Cu are permitted additives to livestock feeds and concentrations in complete feeding stuffs for different livestock classes are currently controlled under the EU Feeding Stuffs Directive and implemented in the UK by the Feeding Stuffs Regulations (SI, 2000).

Table 6: Typical dry matter and heavy metal contents of livestock manures: kg/t (solid manures) or kg/m^3 (slurries)

	Dry matter (%)	Zn	Cu	Ni	Pb	Cd	Cr	As
kg/t (solid manures) or kg/m^3 (slurries)								
Dairy FYM	18	28	6.9	0.68	0.66	0.07	0.98	0.30
Dairy slurry	8	15	4.7	0.41	0.45	0.03	0.43	0.11
Beef FYM	21	17	3.4	0.42	0.41	0.03	0.30	0.17
Beef slurry	12	16	4.0	0.77	0.85	0.03	0.56	0.31
Pig FYM	22	93	81	1.63	0.64	0.08	0.43	0.19
Pig slurry	4.4	25	15	0.46	0.11	0.01	0.12	0.07
Broiler/Turkey litter	60	224	57	3.20	2.15	0.25	10.2	5.34
Layer manure	41	187	26	2.89	3.41	0.43	1.86	0.19

4.2 Heavy metal concentrations in bulky organic fertilisers

Heavy metals are present in sewage sludge because of domestic, road run-off and industrial inputs to the urban wastewater collection system and are referred to as potentially toxic elements (PTEs). The Sludge (Use in Agriculture) Regulations 1989 (SI, 1989), as amended in 1990, and supported by a Code of Practice for Agriculture Use of Sewage Sludge (DoE, 1996) on the protection of soil where sewage sludge is used in agriculture defines quality standards including limit values for PTEs in soil to which sludge is applied and maximum annual quantities of PTEs which may be applied to the soil (see Table 7). Responsibility rests with the producer for compliance with The Sludge Regulations regarding the analytical testing of the sewage sludge and farmers should not allow spreading without this having been done.

The regulations on agricultural use of sewage sludge currently represent the only statutory based mechanism specifically for controlling heavy metal inputs to agricultural soils in the UK. Further information on legislation relating to the use of organic fertilisers on agricultural land is found in FAS/SRUC TN699, 2019: Agricultural use of biosolids, composts, anaerobic digestates and other industrial organic fertilisers **(www.fas.scot/publications/technical-notes/)**.

Table 7: Maximum permissible concentrations of potentially toxic elements (PTEs) in soil (0-25 cm)[1] after application of sewage sludge waste and maximum annual rates of addition

Potentially Toxic Element (PTE)	Maximum permissible concentration of PTE in soil (mg/kg dry solids)				Maximum permissible average annual rate of PTE addition over a 10-year period (kg/ha)
	pH[3] 5.0 - 5.5	pH 5.5 - 6.0	pH 6.0 – 7.0	pH[4] >7.0	
Zinc (Zn)	200	200	200	200	15
Copper (Cu)	80 (130)	100 (170)	135 (225)	200	7.5
Nickel (Ni)	50 (80)	60 (100)	75 (125)	100	3
	for pH 5.0 and above				
Cadmium (Cd)	3				0.15
Lead (Pb)	300				15
Mercury (Hg)	1 (1.5)				0.1
Chromium[2] (Cr)	400 (600)				15
Molybdenum[2] (Mo)	4				0.2
Selenium[2] (Se)	3 (5)				0.15
Arsenic[2] (As)	50				0.7

1. The maximum permissible concentration for grassland soils sampled to a depth of 7.5 cm is the same except given in brackets.
2. These are recommended, not regulatory limits.
3. Application of sludge to soils with a pH less than 5.0 is prohibited.
4. The increased permissible PTE concentrations in soils of pH greater than 7.0 apply only to soils containing more than 5% calcium carbonate.

Additional safeguards to protect soils, the wider environment and human and animal health are set out in a voluntary industry standard, the Biosolids Assurance Scheme – The Scheme Standard, Issue 4, 13th November 2017 **(https://assuredbiosolids.co.uk/wp-content/uploads/2018/04/BAS-STANDARD-Issue-4-Online-version.pdf)**. All sludge producers in Scotland have signed up to this Scheme.

Due to the successful controls that have been placed on the use of heavy metals in the industrial and food production sectors the levels of heavy metal PTEs are now rarely the limiting factor determining an appropriate spreading rate. The exception is Cu from distillation using some of the copper stills. The fertiliser value is now the most common limiting factor on potential spreading rates.

Changes in biosolids production technologies and advanced chemical and thermal digestion processes may impact on the PTE content of biosolids. The continued growth in the bio-energy sector has resulted in a significant increase in both digestate volumes and types as the range of feedstocks available increases. It is always advisable to request an analysis report on a regular basis when receiving any type of organic material for on farm use. Care should be taken with dredgings from urban rivers, as these may contain high levels of heavy metals.

Analysis is particularly important where the properties of the organic materials concerned are likely to vary widely from typical values in Table 8. Regular testing is recommended, particularly when feedstocks change. Several Scottish AD plants separate their digestate into liquor and fibre fractions. The variability between these digestate fractions can be considerable (due to differences in feedstock, process, and post-processing technologies) and we recommend that such products should be tested individually. Producers of PAS100 compost and PAS110 digestate should be able to supply a typical analysis of their product. Testing for Zn, Cu, Ni, Cd, Pb, Cr, and Hg is mandatory for PAS 100 and PAS 110 when they are produced from waste products.

When organic materials classified as wastes are imported on to the farm, then their application to land is regulated by SEPA. To spread organic wastes on land you must register for a Paragraph 7 – waste management licence exemption (land treatment for benefit to agriculture or ecological improvement). All applications to SEPA must include a "Certificate of Agricultural Benefit" (prepared by a suitably qualified individual), which demonstrates that the material will result in agricultural benefit or ecological improvement when used as described in the completed Paragraph 7 form. Paragraph 7 exemptions are normally required for paper crumble, distillery pot ale, spent lees and other distillery effluents, brewery wastewater, abattoir wastewater, off-specification, or waste composts and digestates, and SEPA often requests analysis of Zn, Cu, Ni, Cd, Pb, Cr, and Hg contents.

Table 8: Typical dry matter and heavy metal contents of bulky organic fertilisers as received (fresh)

	Biosolids, thermally hydrolysed	**Biosolids, lime stabilised**	**Compost**	**Distillery, bioplant sludge**	**Separated digestate liquor**	**Separated digestate fibre**
Dry matter (%)	**30**	**50**	**30**	**2.5**	**4**	**25**
Heavy metal	g/t	g/t	g/t	g/t	g/m^3	g/t
Zinc	90	115	65	5	10	10
Copper	60	190	14	220	5	5
Nickel	25	4	5	0.2	1.5	3
Cadmium	0.4	0.5	0.3	0.006	<0.01	<0.1
Lead	30	15	29	0.8	0.5	0.5
Mercury	0.2	0.02	0.1	0.02	0.05	0.4
Chromium	8	10	5	0.3	0.25	5
Molybdenum	2	1.6	0.3	N/A	N/A	N/A
Selenium	0.5	0.5	N/A	N/A	N/A	N/A
Arsenic	1.5	10	N/A	N/A	N/A	N/A
N/A – not determined						

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