McGrath, S. P. and Zhao, F-J. 2015. Concentrations of metals and metalloids in soils that have the potential to lead to exceedance of maximum limit concentrations of contaminants in food and feed. *Soil Use and Management.* 31 (Suppl. 1), pp. 34-45.

Soil Use and Management

*Soil Use and Management*, September 2015, **31** (Suppl. 1), 34–45 doi: 10.1111/sum.12080

REVIEW ARTICLE

# Concentrations of metals and metalloids in soils that have the potential to lead to exceedance of maximum limit concentrations of contaminants in food and feed

S. P. McGrath[1] & F. J. Zhao[1,2]

[1]*Rothamsted Research, Harpenden, Herts, AL5 2JQ, UK, and* [2]*College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing, 210095, China*

**Abstract**

This review focusses on the transfers of metals and metalloids from soil to food and feed, based mostly on UK information. Published information on the behaviour of a number of these contaminants in soil–plant systems is used to evaluate which elements are likely to transfer to food and feed. Data on the concentrations of metals and metalloids in soils and other soil properties in England and Wales are used in models to illustrate the likelihood of transfers exceeding the maximum concentration limits in food and feed in European legislation. Information from crop and herbage quality surveys is used to compare with the output from models. In most cases, the modelled or observed concentrations in food and feed do not reach the maximum allowable concentrations. Of all the contaminants considered, Cd appears to be most likely to exceed limit concentrations under UK conditions, but at present, there is some difficulty predicting Pb uptake and As uptake into the edible parts of crops from soil. However, crops exceeding the food limits are more likely to be grown if those crops are vegetables and if soil limit concentrations and best soil management practices have not been followed (e.g. maintenance of high soil pH in the case of cationic metals). We discuss the gaps and uncertainties for different metals and metalloids and show the need to review the situation if food or feed maximum concentration limits are changed as new information becomes available on toxicology and dietary exposure.

**Keywords:** Biosolids, toxicity, risk assessment, food standards, arsenic, cadmium, lead

## Introduction

As noted in the Soil Strategy for England, continued atmospheric deposition of contaminants and the increase in the spreading of organic and inorganic materials which may contain contaminants to land is an area of growing concern (Defra, 2009a). Materials used on land include organic wastes (e.g. composts, animal manure, sewage sludge) and inorganic by-products (e.g. recycled gypsum). These materials are spread on land because they can increase the levels of organic matter in soil, reduce fertilizer or lime requirements and provide the associated benefit of reduced landfilling or incineration. The nutrients and organic matter can have important agricultural and ecological benefits. However, these materials can also contain significant concentrations of contaminants, such as metals, which can accumulate in soil following repeated applications (Nicholson *et al*., 2008). The input of metals from various sources has been studied in the UK (Nicholson *et al*., 2003, 2008), as has the accumulation of metals in soils receiving sewage sludge, animal manures and composts (McGrath, 1987; Gibbs *et al*., 2006; Chaudri *et al*., 2007). New and future threats may emerge, for example, nanoparticles are noted in this respect in the Soil Strategy (Defra, 2009a).

This review is mainly focused on UK literature related to the concentrations of metals or metalloids in soils that have the potential to lead to exceedance of maximum concentration limits (MCL) in food. Contamination is taken to denote the presence of, in this case, metals or metalloids above background levels. But this does not necessarily mean that they are having a deleterious effect. 'Exceedance of maximum concentration limits' could imply that at certain

Correspondence: S. P. McGrath. E-mail: steve.mcgrath@rothamsted.ac.uk
Received June 2012; accepted after revision June 2013

 

concentrations, contaminants can be associated with detrimental effects on organisms (man in this case). However, it is difficult to establish causal relationships between exposure to contaminated soil and actual health impacts (Fera, 2009) and it is obviously not desirable to allow concentrations in food to become high enough to have actual effects. Therefore, various agencies have set limits in food and feed that are less than the levels at which effects on animal and human health can occur. These are predicted upper allowable limits and can change with time according to new knowledge and following review by the responsible agencies. However, it should be noted that there are other sources of environmental contamination of the food chain and that soil, considered here, is only one potential source.

The following sections give an assessment of how the contaminants behave in soils under different conditions, how they transfer to animals and plants used as food, and under what conditions they are likely to breach the MCLs in food consumed by humans. Many of the strongest emission sources of contaminants in soils have been controlled in the last 25 years through environmental regulation, but because contaminants can persist for long periods in soil, and their continued arrival in soils via pathways such as atmospheric deposition and the spreading of organic and inorganic materials on land, soils can continue to contain increased concentrations of contaminants or even increasing concentrations.

Metals and metalloids often accumulate in surface soil, and can be taken up by crops to different extents. Some of these are essential to plants and/or animals (e.g. Zn, Cu, Mn, Ni, Cr, Co, Mo), and deficiencies can occur when either the concentrations in soil are small or when the soil conditions limit their bioavailability. These elements can be toxic when present in large amounts, but this is unlikely to occur through the dietary route via soil and agriculture, for reasons discussed below. Other elements (such as Hg, Cd, Pb, Tl and As) are not thought to be required biologically and are toxic when they are present in sufficient concentrations.

## Limits in food or the diet

This review concentrates on contaminants that build up in soil and have the potential to lead to exceedance of limit values in food and highlights some of the gaps and uncertainties. To do this, it is necessary to examine the links between contaminant concentrations in soil and the exceedance of limit concentrations in food. Food in this sense should include the transfer from soil to plants to animals and animal products which are consumed, as well as plant foods that are consumed directly by humans. Direct transfer of contaminants from soil to animal (via soil ingestion) and then to humans is a potential route for contaminant transfer which is given some consideration below. In addition to concentrations, the amounts of specific foodstuffs consumed are important (e.g., As in rice; Meharg *et al*., 2009). European MCLs were used as examples of limit concentrations of contaminants in food (EC, 2006) and animal feed (EC, 2002, 2003).

Among the toxic metals/metalloids, food (or animal feeding stuff) limits are in place for Cd, F, Pb, Hg and Sn or being considered for As (Tables 1 and 2). Of these, F is only present in animal feed limits because animals were specifically exposed in the past near to strong point sources such as brickworks and aluminium smelters. Similarly, Sn is regulated only in canned foods, because there is a specific, acute risk of human exposure to tin from damaged or unlacquered cans. Exposure by this route has been minimized by introducing controls. Mercury is most harmful as methyl mercury, which is generally not found in terrestrial foods (except rice grown on Hg contaminated paddy soils, e.g. Feng *et al*., 2008). It is the commonest form in fish, which is why there are limits in seafood only. For these reasons, F, Hg and Sn will not be discussed further below.

It should be noted that the existing limits for Cd and Pb are under review, and introduction of limits for As in rice is being considered. The main source of Cd for nonsmokers is food. For Cd, the European Food Safety Authority Panel on Contaminants in the Food Chain (EFSA, 2009a) recommended that the Provisional Tolerable Weekly Intake for this element should decrease by a factor of almost 3. The European Commission is considering decreasing the MCL in various food stuffs, for example, a proposal to amend the EU Food Regulation (EC, 2006) suggests that the maximum concentration in wheat may drop by half (FSA, 2009a). This would affect all of the evaluations of soil-to-food transfers below. For As, the diet is the main source of exposure in the EU, and a recently published opinion was that this should be decreased (EFSA, 2009b) as much as possible. It is thought that Pb intake should be as low as reasonably practicable because EFSA could not establish a threshold value for developmental neurotoxicity (FSA, 2009b).

## Behaviour in soil

Soil conditions can affect the build up and losses of contaminants and, therefore, their bioavailability and likely transfer through the food chain (Rooney *et al*., 2006; Chaudri *et al*., 2007; Li *et al*., 2008). Understanding the soil conditions that affect plant uptake is important in two respects: (i) these can be used to define soil-specific threshold values rather than a 'one fits all' approach (Rooney *et al*., 2006; Chaudri *et al*., 2007) and (ii) soil conditions that can be manipulated (e.g. pH) can form the basis of controls on the risk of contaminants entering the food chain in significant quantities. Metals that exist mainly as cationic

Table 1 Maximum concentration limits for metals/metalloids under EU Food Regulation 1881/2006 (EC, 2006)[a]

| Element | Commodity | Maximum limit mg/kg wet weight |
|---|---|---|
| Arsenic | None | – |
| Cadmium | Meat of cattle, pigs, sheep and poultry | 0.05 |
| | Horsemeat | 0.2 |
| | Liver of bovine animals, sheep, pig, poultry and horse | 0.5 |
| | Kidney of bovine animals, sheep, pig, poultry and horse | 1 |
| | Cereals excluding bran, germ, wheat and rice | 0.1 |
| | Bran, germ, wheat and rice | 0.2 |
| | Soybeans | 0.2 |
| | Vegetables and fruit excluding leaf, root and stem vegetables, fresh herbs, fungi, pine nuts, and potatoes | 0.05 |
| | Leaf vegetables, fresh herbs. Cultivated fungi and celeriac | 0.2 |
| | Stem vegetables, root vegetables and peeled potatoes | 0.1 |
| Lead | Milk | 0.02 |
| | Meat of cattle, pigs, sheep and poultry | 0.1 |
| | Offal of bovine animals, sheep, pigs and poultry | 0.5 |
| | Cereals, legumes and Pulses | 0.2 |
| | Vegetables and peeled potatoes, excluding brassicas, leaf vegetables, herbs and fungi | 0.1 |
| | Brassica vegetables, leaf vegetables and cultivated fungi | 0.3 |
| | Fruit excluding berries and small fruit | 0.1 |
| | Berries and small fruit | 0.2 |
| Mercury | Only seafood limits | – |
| Tin | Only canned food limits | – |

[a]Excluding seafood.

Table 2 Maximum concentration limits for metals/metalloids under EU Feed Regulation Directive 2002/32/EC and amendment 2003/100/EC (EC, 2002, 2003)

| Element | Type of feed | Maximum mg/kg at 88% DM | Maximum mg/kg DM |
|---|---|---|---|
| Arsenic | Feed | 2 | 2.3 |
| Cadmium | Feed | 1 | 1.1 |
| Lead | Green fodder | 40 | 45 |
| Fluorine | Feed | 150 | 170 |
| Mercury[a] | Feed | 0.1 | 0.11 |

[a]Hg added in No. 3281 Agriculture The Feeding Stuffs (England) Regulations 2005.

(positively charged) species tend to become more available at acid pHs and precipitate or are bound by soils under high pH conditions. Those metals or metalloids that form anionic (negatively charged) species usually react in the opposite way, being bound by positively charged sites, for example, on oxides at low pH and are less bound and, therefore, more available at high pHs. Other conditions can affect elements to variable extents, for example, high organic matter contents can bind metals like Cu and Pb strongly. Finally, the redox potential of soil (usually determined by the availability of oxygen, which in turn is influenced by the water status of soil) affects the chemical form and binding of redox sensitive metals/metalloids such as Mn, As and Cr.

## Concentrations in soils

Extensive data exist on the concentrations of some metals and metalloids in some 5600 soils of England and Wales in the National Soil Inventory (NSI) (McGrath & Loveland, 1992; Rawlins *et al.*, 2012). Monitoring of soils has also been carried out, and changes in Cd, Cr, Cu, Ni, Pb, V and Zn concentrations in UK soils between 1998 and 2007 assessed (Emmett *et al.*, 2010. The UK soils and herbage survey (Ross *et al.*, 2007) gives analyses for eleven metals and metalloids in soil and herbage from 122 rural and 29 urban sites in the UK.

Due to their potential toxicity at high concentrations to plants, animals and humans, soil maximum limit values for some metals have been published for the UK for the application of sewage sludge to agricultural soils (DoE, 1996). These are derived from European Directive 86/278/EEC on the use of sewage sludge on agricultural land in 1986. There was a lack of clarity on how values in the Directive were derived in relation to human (and animal) health, but this was later reviewed in a UK context by Carrington *et al.* (1998a,b).

Although the values apply only to land receiving sewage sludge, they also tend to be used as benchmarks in other situations, for example for land receiving bulky organic materials such as composts.

### Plant uptake and concentrations in food crops

A soil–plant barrier concept has been developed for metals and metalloids (Basta *et al*., 2005). This assumes that the mobility of these elements is influenced by soil or plant 'barriers' that can limit transmission of many metals through the food chain either due to soil chemical processes that limit solubility (soil barrier) or by plant senescence due to phytotoxicity (plant barrier). Applying this concept, a *soil barrier* is thought to limit transmission of trace elements, including Ti, Si, Zr, Au, Ag, V and Hg, that are very insoluble and/or strongly adsorbed in soil or in roots (Basta *et al*., 2005). Based on published *soil-to-plant transfer factors* (defined as the concentration in plant/concentration in soil), for a wide range of plant species, we would add Pb to this group with a soil barrier, although aerial deposition of soil or dust onto crops can result in some transfer into the food chain, although not strictly taken up into the plant tissues. These elements are less likely to be bioaccumulated in plant shoots or edible storage organs to levels that constitute risk to humans than metals that are not affected by the soil barrier. On the other hand, Basta *et al*. (2005) state that a *plant barrier* limits transmission of trace elements, including Zn, Cu, Ni, Mn, Cr, As and F because plant phytotoxicity occurs before they reach concentrations in the edible parts of plants considered harmful to consumers. However, in most soil conditions, uptake of Cr and As is limited due to lack of bioavailability in soil (but note that this is the case for As only under aerobic soil conditions). The elements Cd, Mo, Se and Tl are thought to a certain extent to pass the soil–plant barrier that limits transmission of many trace elements through the soil–crop–animal food chain. In addition, paddy rice grown in anaerobic soil is efficient in accumulating As (Xu *et al*., 2008; Meharg *et al*., 2009). Later, we deal in more detail with Cd, the most important example of an element without a strong soil–plant barrier.

Se and Mo can also be relatively easily taken up by food crops. However, it is highly unlikely that their accumulation in food crops would cause toxicity to humans, because the concentrations of these are small in UK soils. Where concentrations in soils are high, Mo can accumulate in pasture herbage and this can lead to Cu deficiency in ruminants (Thomson *et al*., 1972).

Thallium (Tl) is highly toxic to animals and humans and is readily taken up by some plants. A study in France showed very low Tl concentrations (<4 $\mu$g/kg dry weight) in wheat and maize grain from crops grown in soils varying widely in Tl concentration, but high concentrations of Tl in winter oilseed rape (*Brassica napus* L.) shoots and seeds, with the soil-to-plant transfer factor >1 (Tremel *et al*., 1997). Two other vegetable species, cabbage (*Brassica oleracea* cv *capitata* L.) and leek (*Allium porrum* L.), from a different location in France were also measured and showed transfer factors <1 (Tremel *et al*., 1997). The 2006 UK Total Diet Study showed low concentrations of Tl in foods and that, for average consumers, current dietary exposures to Tl are unlikely to be of toxicological concern (FSA, 2009b). However, where soils containing increased levels of Tl are used for growing food crops, based on the French study, there is potential for this to lead to increased uptake and accumulation. Further research should focus on vegetables (Brassica species) that are grown on soils with naturally increased levels of Tl.

Table 3 summarizes data from surveys of Cd, Pb and As concentrations in UK food crops. Chaudri *et al*. (1995) and Zhao *et al*. (2004) reported the ranges of Cd and Pb concentrations in wheat and barley grains collected representatively from major cereal-growing areas in the UK, which showed that >99% of the grain samples were below the MCLs. If the Cd limit in wheat were to be reduced from 0.2 to 0.1 mg/kg fresh weight (0.113 mg/kg dry weight based on 88.8% dry matter in cereals) to reduce dietary exposure of Cd (FSA, 2009a), 2.4% of the wheat grain would not be compliant. In a paired soil-crop survey which specifically included some land with elevated levels of Cd, Adams *et al*. (2004) found 4.5% of the wheat grain samples exceeding the current Cd MCL. A survey of 40 barley grain samples collected in 2000 from Scotland showed anomalously high concentrations of Pb, with a quarter of the samples exceeding the MCL (Zhao *et al*., 2004). However, it appears that these samples were surface contaminated during either sample collection or storage, as a brief washing of the grain decreased the Pb concentration markedly. Overall, most of the wheat and barley grain produced in the UK are compliant with the current Cd and Pb MCLs, although exceedance could occur if crops are grown at sites with increased concentrations, or if surface contamination of Pb can occur during storage and processing. Grain exceeding the limit would be diluted with other loads with low concentrations, and it is unlikely in the UK that grain from a single source would be consumed exclusively.

There are no nationwide surveys of Cd and Pb concentrations in vegetables and potatoes produced from commercial farms in the UK. There are, however, surveys of vegetables grown in urban and a few rural allotments. Moir & Thornton (1989) reported wide ranges of Cd and Pb in vegetables grown in 94 urban allotments in England, with the maximal values recorded exceeding the current EU food MCLs for both metals (Table 3). The percentage exceedance was not reported. Leafy vegetables such as spinach and lettuce showed the highest accumulation of Cd. The

Table 3 Concentrations of Cd, Pb and As in food crops (edible parts) in the UK

| Country | Crop | Element | DW or FW | Concentration (mg/kg) Minimum | Maximum | Mean | Median | *n* | % exceeding limit[a] | Note | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| UK | Wheat | Cd | DW | 0.004 | 0.31 | 0.043 | 0.037 | 1007 | 0.2 | 1982, 1992–1993, Nationwide, representative | Chaudri *et al.* (1995) |
| UK | Wheat | Cd | DW | 0.01 | 0.62 | 0.077 | 0.056 | 162 | 4.5 | 1998–2000, Nationwide, including some sites with elevated Cd | Adams *et al.* (2004) |
| UK | Barley | Cd | DW | <DL (0.003) | 0.10 | 0.019 | 0.014 | 215 | 0 | 1998–2000, Nationwide, including some contaminated sites | Adams *et al.* (2004) |
| UK | Wheat | Pb | DW | <DL (0.02) | 0.11 | – | 0.022 | 250 | 0 | 1998, Nationwide, representative | Zhao *et al.* (2004) |
| UK | Barley | Pb | DW | <DL (0.02) | 0.476 | – | 0.029 | 233 | 0.9 | 1998, Nationwide, representative | Zhao *et al.* (2004) |
| Scotland | Barley | Pb | DW | 0.078 | 0.309 | | 0.17 | 40 | 25[b] | 2000, representative | Zhao *et al.* (2004) |
| SW England | Wheat | As | DW | 0.013 | 0.50 | 0.07 | 0.038 | 37 | No limit | 2006, including As contaminated soils | Williams *et al.* (2007) |
| SW England | Barley | As | DW | 0.014 | 0.538 | 0.08 | 0.033 | 29 | No limit | 2006, including As contaminated soil | Williams *et al.* (2007) |
| Scotland | Wheat | As | DW | 0.010 | 0.213 | 0.03 | 0.021 | 29 | No limit | 2006, mostly from arable fields in Fife | Williams *et al.* (2007) |
| Scotland | Barley | As | DW | 0.033 | 0.049 | 0.04 | 0.038 | 6 | No limit | 2006, mostly from arable fields in Fife | Williams *et al.* (2007) |
| England | Broccoli | Cd | DW | 0.05 | 0.70 | 0.16 | | 82 | | 1987–1988, including 94 urban gardens and allotments | Moir & Thornton (1989) |
| | Cabbage | | | 0.05 | 0.28 | 0.12 | | 82 | | | |
| | Carrot | | | 0.04 | 1.08 | 0.25 | | 78 | | | |
| | Lettuce | | | 0.11 | 3.08 | 0.66 | | 78 | | | |
| | Parsnip | | | <0.025 | 0.59 | 0.10 | | 84 | | | |
| | Spinach | | | 0.18 | 10.4 | 1.62 | | 80 | | | |
| England | Cabbage | Pb | DW | 0.56 | 10.0 | 1.72 | | 82 | | 1987–1988, including 94 urban gardens and allotments | Moir & Thornton (1989) |
| | Carrot | | | 0.27 | 4.89 | 1.22 | | 78 | | | |
| UK | Vegetables[c] | As | FW | <0.0005 | 0.025 | 0.003 | 0.002 | 251 | | 2004, 6 urban and 6 rural allotments | Weeks *et al.* (2007) |
| | | Cd | FW | <0.0006 | 0.039 | 0.007 | 0.005 | | | | |
| | | Pb | FW | <0.0006 | 0.164 | 0.010 | 0.004 | | | | |

**Table 3** (continued)

| Country | Crop | Element | DW or FW | Concentration (mg/kg) Minimum | Maximum | Mean | Median | *n* | % exceeding limit[a] | Note | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| UK | Herbage | As | DW | 0.5 | 3.21 | 0.56 | 0.50 | 366 | | 2002, rural locations, UK Soil and Herbage Pollutant Survey | Ross *et al.* (2007) |
| | | Cd | DW | 0.10 | 1.43 | 0.14 | 0.10 | | | | |
| | | Pb | DW | 0.47 | 84 | 2.12 | 1.00 | | | | |

[a]EC, 2006 maximum limits: 0.2 mg/kg Cd or Pb (fresh weight basis). The limits based on fresh weight have been converted to dry weight using the dry matter percentage presented by de Meeûs *et al.* (2002). [b]Likely, due to surface contamination during sampling or storage, because washing decreased grain Pb concentrations markedly. [c]See Weeks *et al.* (2007) for details of individual vegetables.

generally high concentrations of Pb and Cd in this survey reflect the fact that urban soils tend to be more contaminated with metals. A recent study of vegetables produced in 12 allotments in the UK (6 rural, 6 urban) reported generally low concentrations of Cd and Pb (Table 3), probably related to the similar metal concentrations in the rural and urban soils in this study (Weeks *et al.*, 2007).

The UK Soil and Herbage Pollutant Survey conducted by the Environment Agency in 2002 (Ross *et al.*, 2007) reported the ranges of As, Cd, Pb and other trace elements in herbage from 366 rural locations (Table 3). The maximal values are larger than the EU MCLs of these elements in animal feeding stuff, but the percentage exceedance is likely to be small, judged from the means and medians.

There are no nationwide surveys of As concentration in UK cereal grains. Williams *et al.* (2007) reported As concentrations in wheat and barley grains collected from two regions in the UK (Table 3). While those from Scotland (mainly Fife) can be considered to be in the normal range, the concentrations in many of the samples collected from south-west England (Devon and Cornwall) were high because soils had high (maximum 546 mg/kg) levels of As. The highest concentration in wheat grain reported by Williams *et al.* (2007) was 0.5 mg/kg on a dry matter basis, and this level could be of concern (but only if consumption levels are high and based on a single source of wheat) because As in wheat grain is present only in the most toxic inorganic forms (Zhao *et al.*, 2010a). Where soils do not contain increased levels of As (<20 mg/kg), the As concentrations found in wheat and barley grain are usually <0.05 mg/kg (Williams *et al.*, 2007; Zhao *et al.*, 2010b).

## Soil ingestion by livestock

Some metals may have the potential to transfer directly from the soil to be absorbed by grazing livestock (without passing through a plant), then transfer into the human food chain. Grazing livestock can ingest soil on its own or soil adhered to vegetation.

The amount of metal absorbed by this route depends on the quantity of soil ingested by the grazing animal, which varies depending on such factors as the livestock species, climate, grazing habits, time of year, sward cover and other factors such as stocking rates. It has been estimated that an average of around 6% of the dry matter intake is soil (Stark & Hall, 1992; Fries, 1996), although ingestion rates may be much higher under conditions of drought or over grazing, with Thornton & Abrahams (1983) suggesting that up to 18% of the cattle diet may be soil and can exceed 30% for sheep in late winter when there is little vegetation (Abrahams & Steigmajer, 2003). Concentrations of metals can be increased in foliage when sewage sludge is applied to land due to adherence of the sludge to foliage, and because the build up of metal is greatest in surface soil that animals are likely to consume. There is evidence that Cd and Pb accumulate in the liver and kidney, but not muscle tissues, of animals that feed on land that has received a number of applications of sewage sludge (Hillman *et al*., 2003). The risk to humans from this route is reduced but not eliminated for two main reasons: (i) the intake of offal is low in the average diet compared with muscle meat and (ii) to limit the risk of pathogen transfer to animals and amount of soil ingested in the case of sludged land, there is a no grazing or herbage harvesting period of 3 weeks after sludge application (DoE, 1996). However, worst-case scenarios could be more of an issue. An example would be people with a high consumption of offal, but this would be mitigated by the fact that it is unlikely that all of this particular dietary component would be derived from sludged land. Another case would be areas where the Code of Practice for Agricultural Use of Sewage Sludge was not adhered to, due to extreme weather conditions leading to poaching of soil, lack of herbage or poor management. It is worth noting that the Code of Practice for Agricultural Use of Sewage Sludge (DoE, 1996) does not apply to other routes of contamination of soils.

## Modelling metal transfer from soil to plants

A number of studies have attempted to establish empirical models to predict the transfer of metals from soil to crops (Legind & Trapp, 2010), Cd being the most successful case as its transfer from soil to crop is thought to be dependent on soil properties. These empirical models are generally based on a pH-dependent Freundlich equation. This equation was originally used to describe the solubility of metals in soils and can be extended to fit the relationship between soil and plant metal concentrations (equation 1; Brus *et al*., 2002; Brus & Jansen, 2004):

$$Q_{\mathrm{plant}} = AQ_{\mathrm{soil}}^{B} \tag{1}$$

where $Q_{\mathrm{plant}}$ and $Q_{\mathrm{soil}}$ are the metal concentrations in the crop and the soil, respectively, and $A$ and $B$ are the Freundlich coefficients. $A$ is assumed to be a log-linear function of soil properties such as pH, soil organic matter (SOM) and clay content, so that Eq. [1] can be converted to equation (2):

$$\begin{aligned}\log(Q_{\mathrm{plant}}) = A_0 + A_1\mathrm{pH} + A_2\log(\mathrm{SOM}) + A_3\log(\mathrm{clay}) \\ + B\log(Q_{\mathrm{soil}})\end{aligned} \tag{2}$$

The coefficients in equation (2), $A_{0\text{-}3}$ and $B$, are obtained by multiple regression using paired soil–plant datasets. In some cases, the coefficients for SOM or clay are not significant in the regression model and, therefore, these terms are excluded from the model. In the derivation of a soil guideline value for Cd using the Contaminated Land Exposure Assessment (CLEA) model in 2002, the relationship of log(CF) to soil pH was used, CF being the plant/soil concentration factor (Defra & EA, 2002a); this model is the same as equation (2) with the omissions of the SOM and clay terms, and the coefficient B being fixed at 1. Although the evidence reviewed in 2009 indicated increased Cd uptake by root and leafy vegetables at lower pH values, no quantitative relationship could be derived, and the 2002 approach was withdrawn and replaced with consideration of the CF only (EA, 2009a,b). Table 4 shows some examples of empirical models for Cd.

The models presented in Table 4 were used to predict the potential for Cd accumulation in different crops, grass or vegetables across England and Wales, using the soil data from the National Soil Inventory (NSI) for England and Wales (McGrath & Loveland, 1992). In the NSI database, total soil Cd was determined by flame atomic absorption, which had a high detection limit (0.2 mg Cd/kg soil). A recent re-analysis of the NSI soils using a more sensitive method (X-RF) showed lower Cd concentrations (Rawlins *et al*., 2012), with the median being 0.36 of the old value. This factor was used to correct for the over-estimation of soil Cd in the NSI dataset. Table 4 shows the range and the median of the predicted Cd concentrations in the crops, if they were grown in all soils ($n$ = 5577) across the country, and the percentage of the predicted concentrations that could exceed the respective MCL. The cumulative frequency distributions of selected crops (wheat, barley and leafy vegetables) are presented in Figures 1 and 2.

These calculations show that exceedance of the Cd MCL is likely to be rare (0–1.6%) for wheat grain, barley grain, cabbage and potato grown in England and Wales. For wheat and barley grain, the predictions are in agreement with the nationwide survey data showing few samples exceeding their respective MCLs (Chaudri *et al*., 1995; Adams *et al*., 2004), thus giving confidence to the model predictions. In contrast, leafy and root vegetables (including lettuce and carrot) have the potential to be more problematic, with the prediction that 24–53% of potential sites could lead to Cd concentrations that exceeded the MCL, if these crops were grown on them. However, it is not known what proportion of these sites actually are used to grow these vegetables. While there are no national survey data for these vegetable crops to back up the model predictions, it is known that these plants do tend to accumulate more Cd in their edible parts (Kuboi *et al*., 1986; Alexander *et al*., 2006). High concentrations of Cd were also reported by Moir & Thornton (1989) in some vegetables grown in urban allotments. An important reason causing Cd exceedance in the model outputs is low soil pH (suggesting that many of these sites are not being maintained at pH ≥6.0 for agricultural use). If soil pH is maintained at ≥6.0, as would be expected in normal agricultural practices, exceedance of the Cd MCL can be decreased markedly to ≤1.5% for most vegetable crops (Figure 2). The only exception is root

Table 4 Empirical models for predicting Cd transfer from soil to crops or cattle and the applications of the models to the NSI database

| | | | | Predicted Cd in plant (mg/kg dry weight) or kidney (mg/kg fresh weight) | | | Cd limit (mg/kg)[a] | | | % sites that could exceed Cd limit if crops grown at all sites | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant | Model | Model *n* | Reference | Minimum | Maximum | Median | Fresh weight | Dry weight | Dry matter%[b] | At observed pH | At pH >6 |
| Wheat grain | log (Grain Cd) = 0.12 + 0.43 log (Soil Cd) – 0.16 pH | 246 | Adams *et al.* (2004) | 0.011 | 0.46 | 0.08 | 0.2 | 0.225 | 88.8 | 1.6 | 0.14 |
| Wheat grain | log (Grain Cd) = 0.086 + 0.542 log(Soil Cd) – 0.126 pH – 0.218 log(SOM) | 102 | Brus & Jansen, 2004 | 0.01 | 0.67 | 0.067 | 0.2 | 0.225 | 88.8 | 0.3 | 0.2 |
| Barley grain | log (Grain Cd) = 0.20 + 0.82 log (Soil Cd) – 0.24 pH | 84 | Adams *et al.* (2004) | 0.001 | 0.46 | 0.018 | 0.1 | 0.113 | 88.8 | 1.2 | 0.18 |
| Grass | log (Grass Cd) = 0.168 + 0.489log (Soil Cd) – 0.125 pH – 0.283 log(SOM) | 115 | Brus *et al.* (2002) | 0.012 | 0.77 | 0.077 | | | | | |
| Grass to cattle kidney transfer | Kidney Cd = $(Cd_{grass} \times M_{grass} \times f_{grass} + Cd_{soil} \times M_{soil} \times f_{soil})/(M_{grass} + M_{soil})$ [c] | – | Brus *et al.* (2002) | 0.037 | 3.64 | 0.27 | 1.0 | | | 0.2 | 0.2 |
| Leafy vegetables | Ln(Plant Cd) = 11.206 + Ln(Soil Cd) –1.634 pH | – | Defra & EA (2002a) | 0.001 | 351 | 1.06 | 0.2 | 3.03 | 6.6 | 33.5 | 1.5 |
| Root vegetables | Ln(Plant Cd) = 11.174 + Ln (Soil Cd) –1.646 pH | – | Defra & EA (2002a) | 0.001 | 325 | 0.95 | 0.1 | 0.667 | 15 | 53.2 | 39.4 |
| Broccoli | log(Plant Cd) = –0.0023 + 0.294 log(Cd on SOC) – 0.153 pH [d] | 84 | Hough *et al.* (2004) | 0.038 | 0.804 | 0.20 | 0.05 | 0.333 | 15 | 9 | 0.4 |
| Cabbage | log(Plant Cd) = –0.611 + 0.120 log(Cd on SOC) – 0.623 pH [d] | 107 | Hough *et al.* (2004) | 0.000 | 0.003 | 0.0001 | 0.05 | 0.333 | 15 | 0 | 0 |
| Carrot | log(Plant Cd) = 1.24 + 0.355 log(Cd on SOC) – 0.311 pH [d] | 126 | Hough *et al.* (2004) | 0.034 | 4.11 | 0.49 | 0.1 | 0.847 | 11.8 | 26.3 | 0.4 |
| Lettuce | log(Plant Cd) = 2.02 + 0.318 log(Cd on SOC) – 0.359 pH [d] | 88 | Hough *et al.* (2004) | 0.072 | 14.2 | 1.43 | 0.2 | 3.03 | 6.6 | 23.9 | 0.02 |

[a]EC, 2006 maximum concentration limits. [b]Dry matter percentages are from de Meeûs *et al.* (2002). [c]$M_{grass}$, amount of grass consumed by cattle = 15 kg/day; $M_{soil}$, amount of soil consumed by cattle = 0.5 kg/day; $f_{grass}$ and $f_{soil}$, the transfer coefficient of Cd from grass or soil to animal kidney, respectively, both = 2.99. [d]Cd normalized by the mass of soil organic carbon, that is, *n*, mg Cd per kg soil organic matter.

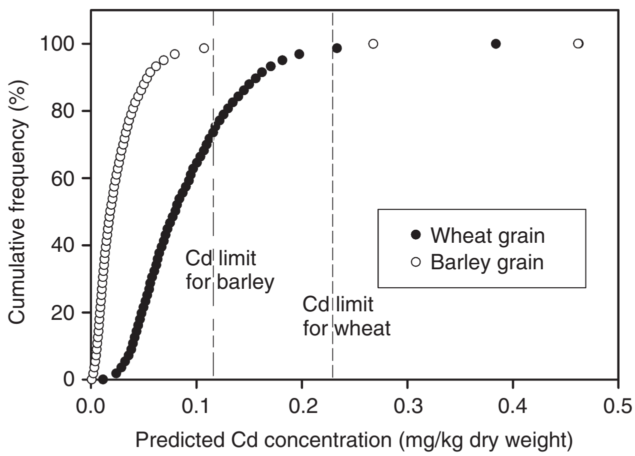


**Figure 1** Frequency distribution of predicted Cd concentrations in wheat and barley grains, using the models of Adams *et al.* (2004).

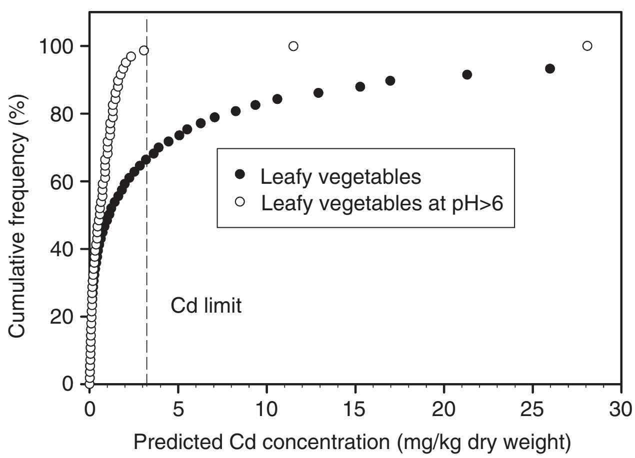


**Figure 2** Frequency distribution of predicted Cd concentrations in leafy vegetables, using Defra & EA (2002a) model.

vegetables assessed with the plant transfer function used in the CLEA model, which still shows 39% of sites with exceedance; examples might be if these crops were grown on soils with high levels of Cd. The model of Hough *et al.* (2004) for carrot, however, predicts that the exceedance would decrease from 26% to 0.4% if the soil pH is maintained at ≥6.0, in line with leafy vegetables.

Brus *et al.* (2002) used a soil-to-grass transfer model coupled with a grass-to-cattle transfer model (Table 4) to predict concentrations of Cd in cattle kidney in the Netherlands. When these models are applied to the soils in England and Wales, it is predicted that in only 0.2% of situations would the kidney Cd concentration exceed the 1.0 mg/kg fresh weight limit (EC, 2006). Also, no scenario is predicted to exceed the feed Cd MCL of 1.1 mg/kg dry weight (EC, 2002).

It should be pointed out that extrapolation of the empirical models beyond the range of soil types or properties that were used to construct the model may not be valid. The uncertainty associated with model calculations is also difficult to assess (Legind & Trapp, 2010). Nevertheless, the model calculations described above appear to be consistent in revealing that the potential issue of specific concern lies in the Cd accumulation by vegetable crops if they are grown in soils with increased Cd, whereas for cereals and grassland, the likelihood of exceeding the current MCLs in broad scale agriculture is very small.

In the light of the recent EFSA opinion on the need to reduce Cd exposures (EFSA, 2009a), there are proposals to reduce the Cd MCLs in offal and cereal (wheat) by half (FSA, 2009a). Using this scenario, 28% of wheat and 3% cattle kidney are predicted to exceed the limits, if all soils in the NSI survey were used to grow wheat or grass for cattle and without adjustment of soil pH. This is likely to be an overestimate because not all soils are used in this way, and the pH of the soils would be adjusted to achieve optimum crop growth.

In contrast to Cd which is taken up by plant roots, the main entry route of Pb to plants is via atmospheric deposition (Tjell *et al.*, 1979; Dalenberg & Vandriel, 1990). For this reason, no correlations were found between Pb concentration in wheat or barley grain and soil properties (Zhao *et al.*, 2004). An empirical model for predicting Pb concentration in wheat grain was presented by Brus & Jansen (2004), although it explained only 36% of the variance in the grain Pb concentration. When this model is applied to the NSI data, the predicted wheat grain Pb ranges from 0.01 to 10.4 mg/kg dry weight, with 65% exceeding the 0.235 mg/kg DW MCL (EC, 2006). The high percentage of exceedance is not supported by the nationwide survey data (Zhao *et al.*, 2004), suggesting that applying the Pb model of Brus & Jansen (2004) to the soils in England and Wales is not valid. For vegetable crops, Hough *et al.* (2004) also presented empirical models for predicting Pb concentration using soil properties. Apart from the fact that these models are generally poor in accounting for the variance of the data (Legind & Trapp, 2010), some models also contain negative coefficients for the soil Pb and positive coefficients for soil pH, meaning that plant Pb concentration would decrease with soil Pb concentration and increase with soil pH, which is unlikely to be correct. Based on the evidence available, it is concluded that the Pb concentrations of edible parts of food plants cannot be predicted reliably from soil measurements.

For residents with allotments, the CLEA model estimated that consumption of home-grown vegetables and ingestion of soils attached to vegetables contribute 22% and 7%, respectively, of the mean exposure to Pb (Defra & EA, 2002b). However, the Defra/EA soil guideline value (Defra & EA, 2002b) for Pb was withdrawn in 2009 (EA, 2009d).

No empirical models for As accumulation in food crops have been reported to date, but may be needed as a result of the EFSA opinion to reduce As intake by humans from food

(EFSA, 2009b). In the derivation of the soil guideline value for inorganic As, the Environment Agency used fixed soil-to-plant transfer factors for various vegetables and fruits, implying a linear relationship between plant and soil As concentrations (EA, 2009c). Williams *et al*. (2007) showed a log–log linear relationship, with considerable scatter, between soil As and grain As for wheat and barley in the UK. This is an area of uncertainty.

Little knowledge exists on interactions between contaminants in terms of uptake and accumulation within plants and animals and, therefore, food. It is known for example that Zn and Cd act in many cases as analogues and that there is competition for uptake, with Zn almost always present in much higher concentrations. So, when assessing the impact of Cd, Zn availability needs to be considered. However, models for even this well-known interaction are not yet available in the literature.

## Conclusions

Among the toxic metals/metalloids, there are maximum concentration limits in food (or animal feeding stuff) in place for Cd, F, Pb, Hg and Sn, or being considered for As in food. These were used here as an upper limit to assess the significance of concentrations in food and feed, derived from soil. For other metals/metalloids, there are no MCLs in food or feed. Cadmium is the metal that was found to be more likely to be present in soils and taken up by food crops in amounts that exceed its limit in food than other metals/metalloids. Models describing the transfer of Cd from soil to plants and animals have been developed, but no models exist for uptake into crops from soils for As and those for Pb appear to be unreliable.

Applying models for Cd uptake to the soils in England and Wales shows compliance with the MCL for cereals, potato and herbage in most soils, whereas vegetables may be more problematic if they are grown in soils containing increased concentrations of Cd in combination with low pH. The UK Total Diet Studies are based on composite samples of different food groups and did not identify any specific concerns (FSA, 2009b). This is backed up by surveys of cereal grains and herbage which show that a very small percentage of samples exceed the current limits for Cd. However, there are no national surveys to back up model predictions of transfer from soil to vegetables.

If the MCLs for Cd and Pb in food or feed are lowered in future, this will affect the likely crops and areas that may exceed the limits. This situation needs to be kept under review. The potential for uptake and toxicity of nanoparticles, including those that are likely to be deposited on soils (Mueller & Nowack, 2008; e.g. those containing Ag, Ce, Ti and Zn), is uncertain at present and the subject of ongoing research.

Finally, it is not clear whether the concentrations of contaminants of interest here (As, Cd and Pb) are increasing or decreasing in soils over time, due to the small changes over time (Emmett *et al*., 2010; note As was not monitored). This is likely to be affected by local conditions including inputs and soil conditions and requires substantial effort to characterize and understand these processes and to accurately detect any changes.

## References

Abrahams, P.W. & Steigmajer, J. 2003. Soil ingestion by sheep grazing the metal enriched floodplain soils of mid-wales. *Environmental Geochemistry and Health*, **25**, 17–24.

Adams, M.L., Zhao, F.J., McGrath, S.P., Nicholson, F.A. & Chambers, B.J. 2004. Predicting cadmium concentrations in wheat and barley grain using soil properties. *Journal of Environmental Quality*, **33**, 532–41.

Alexander, P.D., Alloway, B.J. & Dourado, A.M. 2006. Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environmental Pollution*, **144**, 736–45.

Basta, N.T., Ryan, J.A. & Chaney, R.L. 2005. Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. *Journal of Environmental Quality*, **34**, 49–63.

Brus, D.J. & Jansen, M.J.W. 2004. Uncertainty and sensitivity analysis of spatial predictions of heavy metals in wheat. *Journal of Environmental Quality*, **33**, 882–90.

Brus, D.J., de Gruijter, J.J., Walvoort, D.J.J., de Vries, F., Bronswijk, J.J.B., Romkens, P. & de Vries, W. 2002. Mapping the probability of exceeding critical thresholds for cadmium concentrations in soils in the Netherlands. *Journal of Environmental Quality*, **31**, 1875–84.

Carrington, E.G., Davis, R.D. & Pike, E.B. 1998a. Review of the scientific evidence relating to the controls on the agricultural use of sewage sludge. Part 1 - the evidence underlying the 1989 Department of the Environment code of practice for agricultural use of Sludge and the sludge (use in agriculture) regulations. Final Report to the Department of the Environment, Transport and the Regions, Department of Health, Ministry of Agriculture, Fisheries and Food and UK Water Industry Research Limited. Report No: DETR 4415/3. Available at: www.defra.gov.uk

Carrington, E.G., Davis, R.D., Hall, J.E., Pike, E.B., Smith, S.R. & Unwin, R.J. 1998b. Review of the scientific evidence relating to the controls on the agricultural use of sewage sludge. Part 2 - evidence since 1989 relevant to controls on the agricultural use of sewage sludge. Final Report to the Department of the Environment, Transport and the Regions, Department of Health, Ministry of Agriculture, Fisheries and Food and UK Water Industry Research Limited. Report No: DETR 4454/4. Available at: www.defra.gov.uk

Chaudri, A.M., Zhao, F.J., McGrath, S.P. & Crosland, A.R. 1995. The Cadmium content of British wheat grain. *Journal of Environmental Quality*, **24**, 850–5.

Chaudri, A.M., McGrath, S.P., Gibbs, P.A., Chambers, B.J., Carlton-Smith, C.H., Godley, A., Bacon, J.R., Campbell, C.D. & Aitken, M.N. 2007. Cadmium availability to wheat grain in soils treated with sewage sludge or metal salts. *Chemosphere*, **66**, 1415–1423.

Dalenberg, J.W. & Vandriel, W. 1990. Contribution of atmospheric deposition to heavy metal concentrations in field crops. *Netherlands Journal of Agricultural Science*, **38**, 369–79.

Defra (Department for Environment, Food and Rural Affairs). 2009a. Safeguarding our Soils. A Strategy for England. www.defra.gov.uk; accessed 19/08/2013.

Defra & EA (Department for Environment, Food and Rural Affairs and the Environment Agency). 2002a. *Soil guideline values for cadmium contamination*, pp. 1–15. Environment Agency, Bristol.

Defra & EA (Department for Environment, Food and Rural Affairs and the Environment Agency). 2002b. *Soil guideline values for lead contamination*, pp. 1–15. Environment Agency, Bristol.

DoE (Department of the Environment). 1996. *Code of practice for agricultural use of sewage sludge*. Department of the Environment, London.

EA (Environment Agency). 2009a. *Soil Guideline Values for cadmium in soil*. Science Report SC050021, pp. 1–11. Environment Agency, Bristol.

EA (Environment Agency). 2009b. *Supplementary information for the derivation of Soil Guideline Values for cadmium*. Science Report SC050021/Technical review cadmium, pp. 1–24. Environment Agency, Bristol.

EA (Environment Agency). 2009c. *Soil guideline values for inorganic arsenic in soil*, pp. 1–11. Environment Agency, Bristol.

EA (Environment Agency). 2009d. *Soil Guideline Value reports*. Available at: http://www.environment-agency.gov.uk/research/planning/64015.aspx; accessed 19/08/2013.

EC (European Commission). 2002. Directive 2002/32/EC on undesirable substances in animal feed. *Official Journal of the European Union*. L 140/10-21.

EC (European Commission). 2003. Directive 2003/100/EC amending Annex I to Directive 2002/32/EC on undesirable substances in animal feed. *Official Journal of the European Union*. L 285/33-37.

EC (European Commission). 2006. Commission Regulation 2006/1881/EC setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Union* L 364/5-24.

EFSA (European Food Safety Authority). 2009a. Scientific opinion on cadmium in food. *EFSA Journal*, **980**, 1–139.

EFSA (European Food Safety Authority). 2009b. Scientific opinion on arsenic in food. *EFSA Journal*, **7**(1351), 1–199.

Emmett, B.A., Reynolds, B., Chamberlain, P.M., Rowe, E., Spurgeon, D., Brittain, S.A., Frogbrook, Z., Hughes, S., Lawlor, A.J., Poskitt, J., Potter, E., Robinson, D.A., Scott, A., Wood, C. & Woods, C. 2010. Countryside Survey: Soils Report from 2007. Technical Report No. 9/07 NERC/Centre for Ecology & Hydrology 192pp. (CEH Project Number: C03259).

Feng, X., Li, P., Qiu, G., Wang, S.F., Li, G.H., Shang, L.H., Meng, B., Jiang, H.M., Bai, W.Y., Li, Z.G. & Fu, X.W. 2008. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou Province, China. *Environmental Science and Technology*, **42**, 326–332.

Fera (Food and Environment Research Agency). 2009. Potential health effects of contaminants in soil. Final report project SP1002 to Defra. www.defra.gov.uk; accessed 19/08/2013.

Fries, G.F. 1996. Ingestion of sludge applied organic chemicals by animals. *Science of the Total Environment*, **185**, 93–108.

FSA (Food Standards Agency). 2009a. Food Contaminants. Update Bulletin November 2009.

FSA (Food Standards Agency). 2009b. Measurement of the concentrations of metals and other elements from the 2006 UK total diet study. Food Standards Agency, London. Food Survey Information Sheet 01/09 Available at: http://www.food.gov.uk/science/surveillance/fsisbranch2009/survey0109.

Gibbs, P.A., Chambers, B.J., Chaudri, A.M., McGrath, S.P., Carlton-Smith, C.H., Bacon, J.R., Campbell, C.D. & Aitken, M.N. 2006. Initial results from a long-term, multi-site field study of the effects on soil fertility and microbial activity of sludge cakes containing heavy metals. *Soil Use and Management*, **22**, 11–21.

Hillman, J.P., Hill, J., Morgan, J.E. & Wilkinson, J.M. 2003. Recycling of sewage sludge to grassland: a review of the legislation to control of the localization and accumulation of potential toxic metals in grazing systems. *Grass and Forage Science*, **58**, 101–111.

Hough, R.L., Breward, N., Young, S.D., Crout, N.M.J., Tye, A.M., Moir, A.M. & Thornton, I. 2004. Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. *Environmental Health Perspectives*, **112**, 215–221.

Kuboi, T., Noguchi, A. & Yazaki, J. 1986. Family dependent cadmium accumulation characteristics in higher plants. *Plant and Soil*, **92**, 405–15.

Legind, C.N. & Trapp, S. 2010. Comparison of prediction methods for the uptake of As, Cd and Pb in carrot and lettuce. *SAR and QSAR in Environmental Research*, **21**, 513–525.

Li, H.F., Gray, C., Micó, C., Zhao, F.J. & McGrath, S.P. 2008. Phytotoxicity and bioavailability of cobalt to plants in a range of soils. *Chemosphere*, **75**, 979–986.

McGrath, S.P. 1987. Long term studies of metal transfers following applications of sewage sludge. In: *Pollutant transport and fate in ecosystems* (eds P.J. Coughtrey, M.H. Martin & M.H. Unsworth), pp. 301–317. Special Publication No.6 of the British Ecological Society, Blackwell Scientific, Oxford.

McGrath, S.P. & Loveland, P.J. 1992. *The soil geochemical Atlas of England and Wales*. Blackie, Glasgow.

de Meeûs, C., Eduljee, G.H. & Hutton, M. 2002. Assessment and management of risks arising from exposure to cadmium in fertilisers. I.. *Science of the Total Environment*, **291**, 167–87.

Meharg, A.A., Williams, P.N., Adamako, E., Lawgali, Y.Y., Deacon, C., Villada, A., Cambell, R.C.J., Sun, G., Zhu, Y.G., Feldmann, J., Raab, A., Zhao, F.J., Islam, R., Hossain, S. & Yanai, J. 2009. Geographical variation in total and inorganic arsenic content of polished (white) rice. *Environmental Science and Technology*, **43**, 1612–1617.

Moir, A.M. & Thornton, I. 1989. Lead and cadmium in urban allotment and garden soils and vegetables in the United Kingdom. *Environmental Geochemistry & Health*, **11**, 113–119.

Mueller, N.C. & Nowack, B. 2008. Exposure modeling of engineered nanoparticles in the environment. *Environmental Science & Technology*, **42**, 4447–4453.

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

Nicholson, F.A., Chambers, B.J., Smith, S.R., Riddell-Black, D., Butler, A.P., Rose, S.C. & Lamb, R. 2008. *Sources and Impacts of*

*Past, Current and Future Contamination of Soil*. Final report for Defra Project SP0547.

Rawlins, B.G., McGrath, S.P., Scheib, A.J., Breward, N., Cave, M., Lister, T.R., Ingham, M., Gowing, C. & Carter, S. (2012) *The advanced soil geochemical Atlas of England and Wales*. British Geological Survey, Keyworth. Available at: http://www.bgs.ac.uk/gbase/advsoilatlasEW.html

Rooney, C.P., Zhao, F.J. & McGrath, S.P. 2006. Soil factors controlling the expression of copper toxicity to plants in a wide range of European soils. *Environmental Toxicology and Chemistry*, **25**, 726–732.

Ross, S.M., Wood, M.D., Copplestone, D., Warriner, M. & Crook, P. 2007. *Environmental concentrations of heavy metals in UK soil and herbage*. UKSHS Report Number 7. Environment Agency, Bristol.

Stark, B.A. & Hall, J.E. 1992. Implications of sewage sludge application to pasture on the intake of contaminants by grazing animals. In: *Effects of organic contaminants in sewage sludge on soil fertility* (eds J.E. Hall, D.R. Sauerbeck & P. L'Hermite), pp. 134–157. Comission of the European Communities, Luxemburg.

Thomson, I., Thornton, I. & Webb, J.S. 1972. Molybdenum in black shales and incidence of bovine hypocuprosis. *Journal of the Science of Food & Agriculture*, **23**, 879–891.

Thornton, I. & Abrahams, P. 1983. Soil ingestion - a major pathway of heavy metals into livestock grazing contaminated land. *Science of the Total Environment*, **28**, 287–294.

Tjell, J.C., Hovmand, M.F. & Mosbaek, H. 1979. Atmospheric lead pollution of grass grown in a background area in Denmark. *Nature*, **280**, 425–426.

Tremel, A., Masson, P., Garraud, H., Donard, O.F.X., Baize, D. & Mench, M. 1997. Thallium in French agrosystems.2. Concentration of thallium in field-grown rape and some other plant species. *Environmental Pollution*, **97**, 161–168.

Weeks, C.A., Brown, S.N., Vazquez, I., Thomas, K., Baxter, M., Warriss, P.D. & Knowles, T.G. 2007. Multi-element survey of allotment produce and soil in the UK. *Food Additives and Contaminants*, **24**, 877–885.

Williams, P.N., Villada, A., Deacon, C., Raab, A., Figuerola, J., Green, A.J., Feldmann, J. & Meharg, A.A. 2007. Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. *Environmental Science & Technology*, **41**, 6854–6859.

Xu, X., McGrath, S.P., Meharg, A. & Zhao, F.J. 2008. Growing rice aerobically markedly decreases arsenic accumulation. *Environmental Science and Technology*, **42**, 5574–5579.

Zhao, F.J., Adams, M.L., Dumont, C., McGrath, S.P., Chaudri, A.M., Nicholson, F.A., Chambers, B.J. & Sinclair, A.H. 2004. Factors affecting the concentrations of lead in British wheat and barley grain. *Environmental Pollution*, **131**, 461–468.

Zhao, F.J., Stroud, J.L., Eagling, T., Dunham, S.J., McGrath, S.P. & Shewry, P.R. 2010a. The accumulation, distribution and speciation of arsenic in wheat grain. *Environmental Science & Technology*, **44**, 5464–5468.

Zhao, F.J., McGrath, S.P. & Meharg, A.A. 2010b. Arsenic as a food-chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. *Annual Review of Plant Biology*, **61**, 535–559.