Modelling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm

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Abstract. A predictive model of metal concentrations in crops was developed to optimize soil liming and sludge application strategies at a dedicated sewage sludge disposal site. Predictions of metal concentrations in plant tissue were derived from measured values of soil metal concentration, humus content and soil pH. The plant and soil data used to parameterize the model were collected on site using quadrat sampling of mature crop and underlying topsoil. The uptake model was used to map predicted metal concentrations in wheat grain and forage maize based upon a database of soil characteristics (metal content, % humus and pH) measured as part of a routine geochemical survey of the site. The effect of a management strategy to modify uptake of Cd by wheat by changing soil pH was investigated. The effect of soil dust adhering to maize plants at harvest was also simulated to investigate the importance of this pathway for Cd transfer to animal feed such as silage.

   The model gave satisfactory predictions for uptake of Cd and Zn but less useful simulations for Pb, Cu and Ni. The results for Cd uptake showed a greater dependence on soil pH in the case of wheat in comparison to maize. It is suggested that, for the study site, liming to pH 7.0 will reduce Cd concentrations in wheat grain to within EC legal standards. However the Cd content of maize may still exceed these guidelines, with a relatively minor contribution from contamination with soil dust.

Keywords: Heavy metals, plant uptake, sewage sludge, wheat, maize, models

INTRODUCTION

Intake of trace metals from dietary sources may represent a significant exposure pathway for human populations (Baes III *et al.* 1984; Reilly 1991). However, dietary exposure to trace metals is highly variable. For example, the major source of Pb in human diets is from postharvest processing of food (Bolger *et al.* 1996). For Cd, however, the principal exposure route for the general population is through uptake by food plants (López-Artíguez *et al.* 1993). Consequently, governments have imposed limits on the maximum concentrations of selected metals (Cd and Pb) in food products intended for human consumption (Commission Regulation 2001; Table 1). Where metal concentrations in crops exceed these limits, it may be possible to use this produce in animal feeds, in order to minimize the effect upon the human diet. However, animals fed a metal–enriched diet may have elevated concentrations of these metals in their tissues and milk (Baars *et al.* 1992; Crews *et al.* 1992). The greatest degree of metal accumulation occurs in offal, such as livers and kidneys (Beresford *et al.* 1999).

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Regular consumption of metal–enriched animal products may also lead to adverse health effects in humans (Reilly 1991). In response to this, the European Parliament intends to introduce new guidelines that reduce the maximum permissible concentrations of metals in animal feeds (Council Directive 1999; Table 1).

The UK Government encourages the application of sewage sludge to agricultural land as the best practicable environmental option for disposal (DETR 1999). Agricultural use of sludge reduces fertilizer costs, while increased organic matter content improves soil 'workability' and water holding capacity (Soffe 1995). However, sewage sludge may contain elevated concentrations of heavy metals. Over the past 30 years, there has been a substantial decrease in the inputs of metals to sewage (Smith 1996). For example, between 1962 and 1992 reported concentrations of Cd and Zn have been reduced by 98% and 80% respectively for sewage sludge produced in Nottingham, UK (Rowlands 1992). However, studies have shown elevated concentrations of metals in crops from farmland previously treated with sewage sludge (e.g. Hooda *et al.* 1997; Miner *et al.* 1997; Keller *et al.* 2001). Also, crops used for animal feed, such as forage maize, are often contaminated with soil particles adhering to plants at harvest. For example, Pinder &
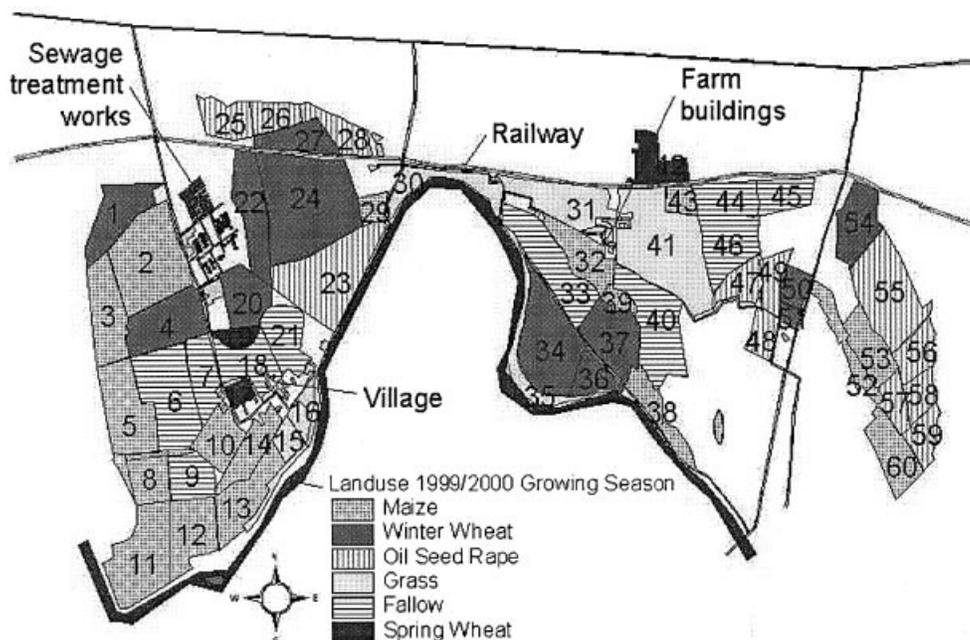
Figure 1. Site map showing land use for the 1999/2000 growing season, and the location of the sewage treatment works. Fields are numbered from 1–60.

Table 1. Summary of European Legislation on maximum permissible concentrations of cadmium and lead in soils and foodstuffs.

Metal	Animal Feed (mg kg⁻¹ fw)[a]	Food for Human Consumption (mg kg⁻¹ fw)[b]			
		Milk	Meat	Offal	Cereals
Cd	1.00	–	0.05	0.50	0.20
Pb	10.0	0.02	0.10	0.50	0.20

[a]Council Directive 1999. [b]Commission Regulation 2001

McLeod (1988) used measurement of non-bioavailable soil elements in maize tissue to estimate soil adherence and suggested that foliar contamination was 1.80 ± 0.33 g soil kg⁻¹ plant (dw). Studies with rodents have shown that on average 43% of soil-adsorbed Cd is bioavailable once ingested (Schilderman et al. 1997). Adult humans typically absorb 7.0–15% of ingested Pb, while 40–53% of ingested Pb may be bioavailable to infants (Ruby et al. 1999). Therefore, if soil is sufficiently contaminated, adhered soil particles may lead to elevated concentrations of metals in feeds such as silage and hence increased metal loadings in meat and milk products.

Arable land to which sewage sludge is applied must be managed in order to keep metal concentrations in soils below EC guideline values (Council Directive 1986; Statutory Instrument 1989). Uptake of metals by crop plants must also be managed to comply with proposed EC legal standards (Commission Regulation 2001; Council Directive 1999). One method of achieving this in sludge-amended soils is to maintain a high soil pH as the proportion of 'bioavailable' metal decreases with increasing pH (Berglund & Reidel 1983). Application of lime to sludge-amended soils has been shown to reduce crop Cd concentrations by about 20% and Zn concentrations by about 35% for each pH unit increase up to pH 7.0 (Preer et al. 1995). Other management tools available to operators of sludge-amended sites are limited but include grain-blending, choice of crop and sludge disposal policy.

The aims of this study were:
(1) to develop a model of metal uptake by wheat and maize using matched soil and plant samples from a 'dedicated' sewage-sludge disposal site and thereby predict crop metal offtake across the site using geochemical survey data for the estate;
(2) to simulate the management effects of elevated soil pH values, through application of lime, on metal uptake by wheat and maize;
(3) to investigate the importance of contamination of crops with soil dust for metal concentrations in ensiled maize.

METHODS

Site description
This study was carried out at a dedicated sewage sludge disposal site, operated by a major water company in the UK, during the 1999/2000 growing season. Figure 1 shows a map of the site and the land use for the 1999/2000 season. The site is farmed as a dairy and cereal growing enterprise but is subject to the operational constraints associated with 'dedicated site' status, under the UK Sludge (Use in Agriculture) Regulations (Council Directive 1986). Parts of the farm have been used for sewage sludge disposal for over 100 years, formerly by surface spreading, and more recently by subsurface injection. Of the 900 ha site, 719 ha are used for growing crops or pasture. The main crops grown during the 1999/2000 season were forage maize

(200 ha) and winter wheat (192 ha). For maize, the whole above-ground biomass is silaged and used as animal feed on site. Wheat grain is either used on site or sold to the animal feed industry.

Sampling procedure and analysis
Samples of winter wheat (var. Equinox) were collected from the estate during August 2000, immediately prior to harvest. Four representative samples were harvested from fields 1, 4, 20, 22, 24, 36, 37 and 51 (Figure 1). From geochemical surveys of the site, commissioned by the water company, it was apparent that these fields provided a representative range of the soil metal concentrations found on the estate (Heaven & Delve 1997). Fields 20, 22 and 36 are in the first quartile for Cd concentrations in the soil, fields 37 and 51 in the second quartile, field 24 in the third quartile and fields 1 and 4 in the fourth quartile.

Sampling of plant and topsoil was undertaken using four quadrats (0.25 m^2) located in a grid pattern across individual fields. Wheat stems were cut 10 cm above ground level, using stainless steel secateurs. Corresponding topsoil samples were taken to a depth of 20 cm using a stainless steel auger; five auger samples were taken, in a grid pattern, from within each quadrat. Wheat samples were dried at 60 °C for 48 hours and threshed to remove the grain. Grain samples were ground using a stainless steel mill. Soil samples were air dried and sieved to <2.00 mm prior to grinding for acid digestion.

A similar approach was adopted for sampling maize (var. Melody) and the underlying topsoil in October 2000, just prior to harvest. Four representative samples were harvested from fields 5, 8, 12, 14, 29 and 52 (Figure 1). Six plants (two rows of three plants) were sampled from each location. Plant material was washed in tap water to remove adhered soil particles and subsequently shredded using a PTFE and stainless steel shredder. All shredded maize plants (including stems, leaves and cobs) were dried together at 80 °C for 72 hours. Sub-samples (50 g dw) were milled using a stainless steel mill.

Plant samples were digested in concentrated HNO$_3$ and analysed for Cd, Cu, Ni, Pb and Zn by flame atomic absorption spectrophotometry (FAAS). Where measured metal concentrations were found to be less than ten times the concentration of blank digests, further plant tissue samples were redigested in Primar high purity concentrated HNO$_3$ and analysed using graphite furnace AAS (GFAAS). Soil samples were digested using *Aqua Regia* (75% conc. HCl, 25% conc. HNO$_3$) and analysed using FAAS. Soil pH (1:2.5 H$_2$O) and loss on ignition (LOI) at 550 °C were also determined.

The geochemical surveys of the site supplied by the water company did not include any measure of soil organic matter content. Therefore, a second series of 103 soil samples, based upon a 200 m × 300 m grid pattern across the whole estate, were collected and assayed for LOI. The resulting values were converted to %C assuming %C=0.58 LOI (Rowell 1997). From this data values of %C were then assigned to the 100 m geochemical sampling grid used by Heaven & Delve (1997) for the most recent geochemical survey (n=484).

Analytical quality control was addressed in several ways. All digestions were performed in triplicate. A standard reference material, tomato leaves (SRM 1573a, National Institute of Standards and Technology) with certified mass fractions of Cd, Cu, Ni and Zn was used to validate the digestion and analysis by AAS. Two independent operators performed the entire process of sample digestion and analysis. A high level of reproducibility was attained with R^2 of 0.96 (Cu), 0.98 (Cd) and 0.96 (Zn) between the two analyses.

Modelling solubility and plant uptake of metals
Metal solubility in soils may be modelled using an equation based upon a pH-dependent Freundlich relation (Jopony & Young 1994). This can be used to predict free metal ion activity in the soil pore water [M^{2+}] from total soil metal content [M_{soil}] and soil pH. As humus is often considered to be the primary adsorber of metal ions in the soil (Sauvé *et al.* 2000), a further refinement is to assume that metals are exclusively adsorbed on humus to increase comparability between soils. Total metal concentrations in the soil [M_{soil}] were therefore re-expressed as if adsorbed on organic carbon [M_C]. The activity of free metal ions [M^{2+}] was then predicted from [M_C], (mg kg^{-1} C) and soil pH:

$$p(M^{2+}) = \frac{p[M_C] + k_1 = k_2 pH}{n_F} \qquad (1)$$

Where k_1, and k_2 are empirical, metal-specific constants and n_F is the power term from the Freundlich equation.

Metal uptake by vegetables is often characterized by a soil→plant transfer factor, TF, (e.g. Baes III *et al.* 1984). However, the 'Free-Ion Activity Model' (FIAM) suggests that uptake may be controlled by metal ion activity in the soil pore water (Parker & Pedler 1997). Therefore, in this study, the transfer factor was expressed as the quotient of metal concentration in the plant [M_{plant}] to metal ion activity in soil pore water [M^{2+}] derived from Equation 1:

$$TF = \log \frac{[M_{plant}]}{(M^{2+})} \qquad (2)$$

Equations 1 and 2 can be combined into a single expression relating [M_{plant}] to pH and [M_C] (Equation 3):

$$\log[M_{plant}] = C + \beta_1[pH] + \beta_2 \log[M_C] \qquad (3)$$

Where C, β_1 and β_2 are empirical metal- and crop-specific constants. Values of C, β_1 and β_2 were derived by minimizing the error (Residual Standard Error, RSD) in the prediction of [M_{plant}] from measured values of pH and [M_C] in Equation 3.

Model calibration and validation
Generalised cross validation (Shao 1993) was used to estimate the model prediction error and assess whether sufficient data had been used to efficiently parameterize Equation 3. This procedure involves leaving nv observations out of the full parameterization dataset (n), parameterizing

the model using the reduced dataset ($n - nv$), and estimating the prediction error (RSD) using the nv data. The selection of nv from n must represent all possible data selections. There are $\binom{n}{nv}$ different ways to split the dataset, so Monte Carlo cross validation was undertaken to obtain a numerical solution by randomly selecting $nv = 2, 4, 8, 16,\ldots, n$. For each value of nv the random selection of the omitted data values was repeated 10^5 times. Checks were undertaken to ensure this adequately sampled the $\binom{n}{nv}$ possible data selections. The Monte Carlo cross validation was performed using a programme written in object-orientated Pascal.

Soil management strategies
Using the geochemical survey data ($[M_{soil}]$ and pH) reported by Heaven & Delve (1997), combined with our new measurements of LOI to derive values of $[M_C]$, values of $[M_{plant}]$ were predicted for the entire cultivated area of the farm. To make comparisons with current legislation (Table 1) estimates of $[M_{plant}]$ were converted to fresh weight concentrations using conversion factors of 0.34 (mature forage maize, Xiccato *et al*. 1994) or 0.85 (postharvest wheat grain, HGCA 2001). These data were used to map metal uptake by either wheat grain or maize (whole plant) across the whole estate.

Cadmium uptake by fodder crops may cause the greatest concern at sites in receipt of sewage sludge. To reduce Cd concentrations in crops, the main management strategy employed by the estate is to maintain elevated soil pH levels through the application of lime. Although soil pH across the site ranged from 5.7–8.0 (Heaven & Delve 1997), the majority (81%) of soil samples were between pH 6.0 and 7.0. To investigate the effect of altering pH, uniform soil pH values of 6.0 and 7.0 were applied to the whole estate and Cd uptake by maize and wheat calculated. Equation 3 was also used to assess the (uniform) soil pH value that resulted in a mean concentration of Cd in wheat grain that was within the legal standards ($\leqslant 0.20 \text{ mg kg}^{-1}$ fw, Table 1). As wheat grain is mixed on-site prior to sale as part of the normal storage practices, a weighted mean concentration of metal in wheat grain for the whole site was used.

Residual soil contamination on ensiled maize
In order to predict metal concentrations in maize, soil particles that were adhered to the plant surface were removed by washing before drying, acid digestion and analysis. However the production of silage from harvested maize plants is unlikely to remove adhered soil particles, which could be a significant source of metal contamination in animal feed (Hinton *et al*. 1995). The potential increase in the Cd concentration in maize from residual soil contamination was estimated by accounting for both uptake and contamination of leaves by soil splash and deposition of dust (Equation 4).

$$\text{Cd}_{maize} = \text{Cd}_{uptake}(1 - \text{P}_{soil}) + \text{Cd}_{soil}\text{P}_{soil} \qquad (4)$$

Where Cd_{maize} is the total concentration of Cd in maize including soil contamination, Cd_{uptake} is the predicted uptake of Cd in maize calculated using Equation 3, Cd_{soil}

is the concentration of Cd in the soil and P_{soil} is the proportion, by weight, of soil in the harvested maize biomass. In this study, a value of P_{soil} of 0.01 or 0.02 was used to represent typical levels of soil deposition on maize surfaces reported by Pinder & McLeod (1988).

Equation 4 was used to predict Cd uptake by maize from a 'typical' (mean) soil on the estate (% LOI = 11.4%; soil pH = 6.8) for a range of soil Cd concentrations (1.00 mg kg^{-1} to $45.0 \text{ mg, >kg}^{-1}$) which covers the full range of soil Cd concentrations reported by Heaven & Delve (1997).

Comparison of EC limits for Cd in wheat grain with EC sludge regulations for Cd in soil
The EC has proposed limits for concentrations of potentially toxic metals in soils, above which the application of sewage sludge to that soil must be evaluated (European Union 2000). Using the parameterized model, it was possible to assess the pH-dependent limits for soil Cd against the EC limit for the concentration of Cd in wheat grain (Table 1). Equation 3 was used to estimate the maximum permissible concentration of Cd in the soil that resulted in values of $[\text{Cd}_{wheat}]$ within EU legislation (i.e. $[\text{Cd}_{wheat}] = \leqslant 1 \text{ mg kg}^{-1}$ fw for the purpose of animal feed, or $[\text{Cd}_{wheat}] = \leqslant 0.2 \text{ mg kg}^{-1}$ fw for human consumption) across the pH range covered by the EU sludge regulations limit values for Cd in soil. Maximum permissible $[\text{Cd}_{soil}]$ values were estimated for each pH level assuming a minimum and maximum soil organic carbon content of 1 and 10% respectively.

RESULTS AND DISCUSSION

Plant metal concentration $[M_{plant}]$
Regression analysis of $[M_{plant}]$ against pH and $[M_C]$ (Equation 3) gave significant results ($P < 0.001$) for uptake of all five metals by both wheat and maize, except Pb and Cu uptake by wheat. Table 2 presents the values of C, β_1 and β_2 (Equation 3), together with the percentage variance (γ_o) for Equation 3. For maize, γ_o ranged from 41% (Ni) to 86% (Cd), with a mean γ_o value of 61% across all five metals. For wheat, values of γ_o ranged from 9% (Pb) to 92% (Cd); the mean γ_o value was 51% across all five metals. However, the individual model parameters (β_1, β_2) displayed a lower statistical significance (P value). The P values for C are not reported as Equation 3 is a logarithmic relation and so it is not meaningful to determine whether the value of C was significantly different from zero. Generally, parameter values of the coefficient for pH (β_1) were not as reliable as for β_2. This may have been due to the narrow pH range (mean pH=6.18, standard deviation=0.4) found at the site relative to the range of log$[M_C]$ (e.g. mean=1.77 mg Cd kg^{-1} C, standard deviation = 0.71). The significance of β_1 (pH-dependence) for Cd uptake by wheat was much greater than for Cd uptake by maize. Narrow soil pH ranges are typical of agricultural sites. Therefore, it would not be recommended that these parameter values be applied to another site without re-parameterization.

The model produced a small value of RSD for Cd, Cu, Ni, Pb and Zn. The cross-validated RSD (RSD$_{cv}$) was calculated for all 10 uptake models (Table 2). This is an

Table 2. Parameter values for metal uptake by maize and wheat (Equation 3). n represents the number of observations; C, β_1 and β_2 are the constants ($\pm$SE) from Equation 3; γ_o denotes the percentage variance accounted for by the model. The Residual Standard Deviation (RSD) and corresponding cross-validated RSD (RSD$_{CV}$) are shown for each model.

Metal/Crop	n	C	$\beta_1{}^a$	$\beta_2{}^a$	$\gamma_o{}^b$	RSD	RSD$_{CV}$
Cd/Maize	24	1.50 ± 1.06	$-1.12\text{x}10^{-2}\pm0.16$ (0.65)	$8.36\text{x}10^{-1}\pm0.11$ (<0.001)	86^{***}	0.26	0.30
Cu/Maize	24	1.32 ± 0.22	$-4.22\text{x}10^{-2}\pm0.03$ (0.17)	$4.97\text{x}10^{-2}\pm0.03$ (0.10)	45^{***}	0.05	0.06
Ni/Maize	24	$-1.49\text{x}10^{-2}\pm0.54$	$-3.24\text{x}10^{-2}\pm0.07$ (0.54)	$1.78\text{x}10^{-1}\pm0.09$ (0.07)	41^{***}	0.11	0.14
Pb/Maize	24	$1.39\text{x}\pm2.59$	$-6.44\text{x}10^{-1}\pm0.29$ (0.04)	$6.87\text{x}10^{-1}\pm0.47$ (0.16)	52^{***}	0.47	0.52
Zn/Maize	24	$-6.58\text{x}10^{-1}\pm0.83$	$-6.82\text{x}10^{-2}\pm0.09$ (0.48)	$7.67\text{x}10^{-1}\pm0.13$ (<0.001)	81^{***}	0.15	0.18
Cd/Wheat	27	1.40 ± 1.15	$-4.39\text{x}10^{-1}\pm0.15$ (0.01)	$7.62\text{x}10^{-1}\pm0.15$ (<0.001)	92^{***}	0.17	0.17
Cu/Wheat	27	1.36 ± 0.50	$-1.48\text{x}10^{-2}\pm0.04$ (0.52)	$-4.86\text{x}10^{-2}\pm0.08$ (0.57)	12^{*}	0.06	0.06
Ni/Wheat	27	-1.65 ± 1.68	$-2.01\text{x}10^{-2}\pm0.13$ (0.68)	$7.30\text{x}10^{-1}\pm0.33$ (0.04)	54^{***}	0.23	0.26
Pb/Wheat	27	$-6.96\text{x}10^{-1}\pm3.44$	$7.51\text{x}10^{-1}\pm0.21$ (0.73)	$3.33\text{x}10^{-2}\pm0.71$ (0.96)	9^{NS}	0.38	0.40
Zn/Wheat	27	4.87 ± 1.52	$-6.11\text{x}10^{-1}\pm0.07$ (<0.001)	$2.04\text{x}10^{-1}\pm0.27$ (0.47)	87^{***}	0.12	0.13

[a] Numbers in parenthesis indicate statistical significance (P)
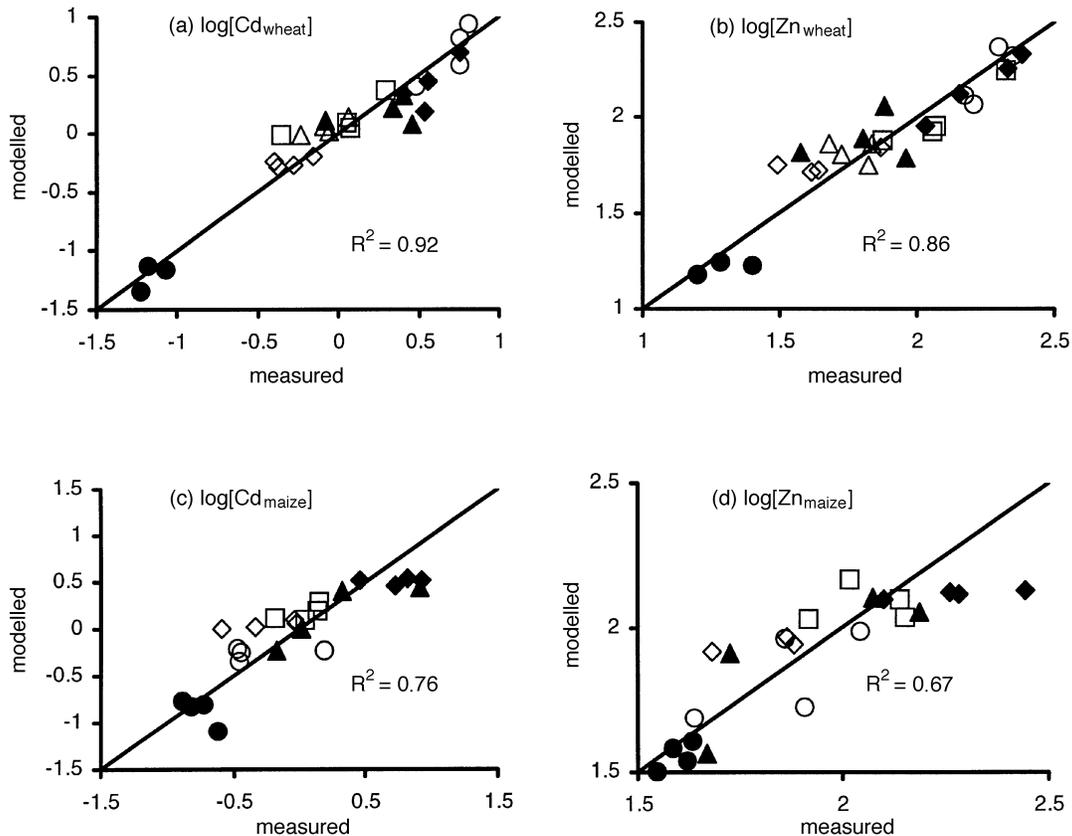[b] Statistical significance: * for $P<0.1$, ** for $P<0.01$, *** for $P<0.001$, and NS for $P>0.1$.

Figure 2. Predicted vs. measured Cd and Zn concentrations (mg kg^{-1}, log scale) in wheat grain (a and b) for the fields sampled, where ▲ = field 1, ◆ = field 4, □ = field 20, ○ = field 22, ◇ = field 36, △ = field 37 and ● = field 50. Predicted vs. measured Cd and Zn concentrations in forage maize (c and d) for the fields sampled, where ▲ = field 5, ◆ = field 8, □ = field 12, ○ = field 14, ◇ = field 29 and ● = field 52. In all cases the solid line represents the 1:1 ratio.
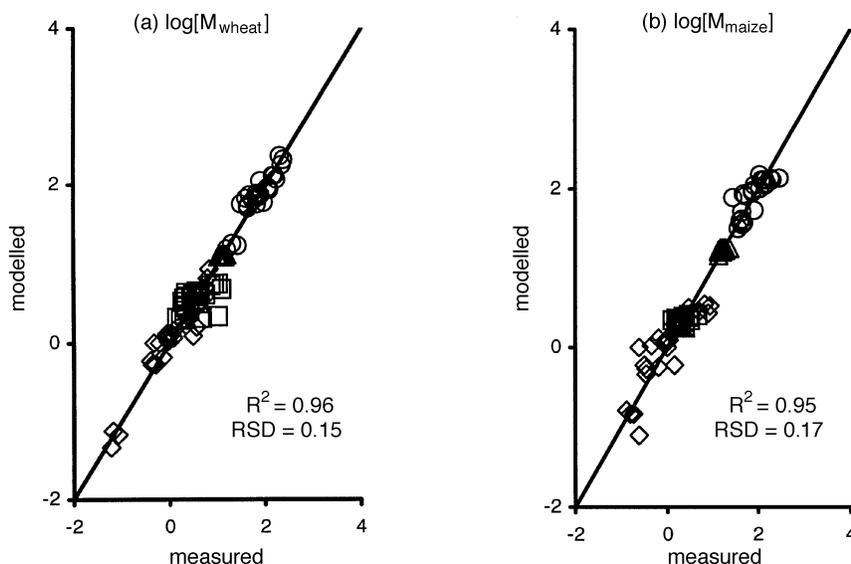
Figure 3. Predicted vs. measured Cd ($\diamond$), Cu ($\triangle$), Ni ($\square$) and Zn ($\bigcirc$) concentrations (mg kg^{-1}, log scale) in (a) wheat grain and (b) forage maize for the samples used in this study. The solid line represents the 1:1 ratio.

estimate of the model uncertainty when it is applied to a new dataset. In all cases values of RSD_{cv} were close to, but greater than, the regression RSD, suggesting that these models are robust and can be applied generically. Despite this, large uncertainty was associated with the estimates of β_1 and β_2 for the models of Pb and Cu uptake by wheat (Table 2). This may be due to the limited scatter displayed by these data.

Figure 2 shows predicted against measured Cd and Zn concentrations in wheat grain and forage maize for the fields sampled. Figure 3 shows predicted against measured metal concentrations in wheat grain and forage maize for Cd, Cu, Ni and Zn. Predicted Pb concentrations in both crops were poorly correlated with measured values (Table 2). This may indicate that the majority of Pb found in the plant material was the result of atmospheric deposition. Dalenberg & Van Driel (1990) suggested that 73–95% of the concentration of Pb in wheat grain was a result of atmospheric deposition. By contrast, only 21% of the concentration of Cd measured in wheat grain was from atmospheric sources. This estimate was made by comparing the specific activity of plants grown in the same radiolabelled soil, where half the plants were exposed to the atmosphere while the other half were grown in a dust-free environment. In this study, the predictions made for Pb uptake by wheat were worse than those made for maize, possibly because the wheat samples were not washed prior to digestion. Maize samples were washed as the whole plant was to be processed for analysis and there was clear evidence of considerable soil deposition on the maize leaves. This difference can be seen in Table 2 where Equation 3 accounts for a very small proportion of the variance in log[Pb$_{wheat}$] (9%) but 52% of the variance in log[Pb$_{maize}$].

The geochemical data collected in 1997 (Heaven & Delve 1997) were used to predict uptake of metals by crop plants for the entire estate. For example Figure 4 shows maps of predicted Cd uptake by wheat grain and forage maize. Both
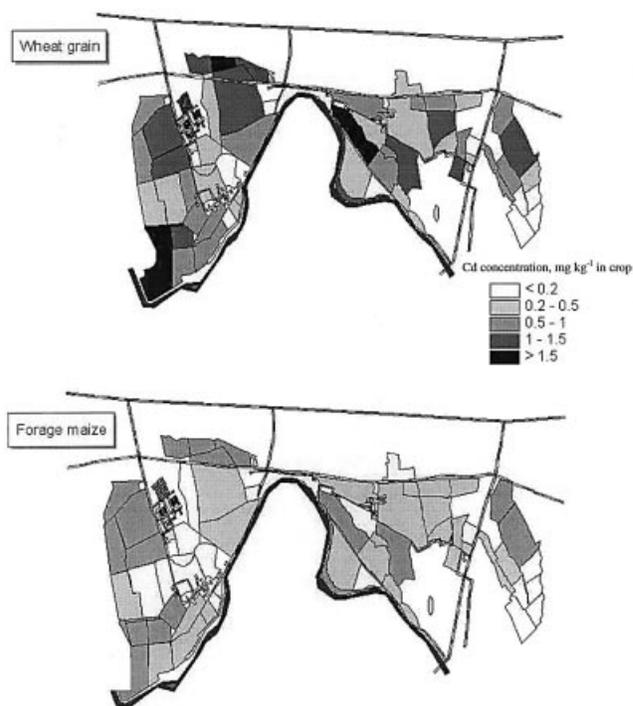

Figure 4. Spatial distribution of simulated Cd uptake by (a) wheat grain and (b) forage maize from the 1997 geochemical data reported by Heaven & Delve (1997).

crops display a similar pattern of uptake with the largest Cd concentrations occurring in the southeast corner of the site and in fields north of the railway line. These areas correspond with fields where the historical practice of lagooning of sewage sludge has occurred for the longest period of time. Overall, concentrations of Cd in forage maize are less than in wheat grain, with a greater number of
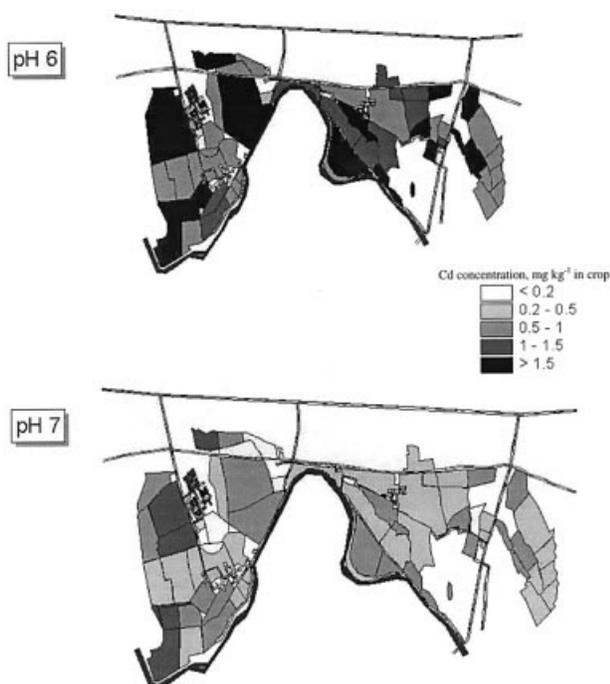
Figure 5. Spatial distribution of simulated Cd uptake by wheat grain under a given soil pH management scheme of either pH 6 or pH 7.

prediction values less than the Council Directive limit for animal feed ($1.0 \, \text{mg Cd kg}^{-1}$ fw; Table 1) (Figure 4).

Management scenarios
Figure 5 compares the effect of uniform soil pH values of 6 and 7 on the predicted concentrations of Cd in wheat grain across the whole estate. If the current soil pH values across the estate were increased to pH 7.0, the majority (>50%) of grain produced on the estate would have Cd concentrations below the limit for animal feed set by European legislation (Table 1). However, for simulated grain blending, a uniform pH of 7.5 was needed to achieve a weighted mean Cd concentration in wheat grain of $1 \, \text{mg kg}^{-1}$ (fw) for the whole site. Rowell (1997) suggests that a soil solution in equilibrium with calcite ($CaCO_3$) for a typical calcareous soil ((Ca^{2+})=0.002 M and P_{CO2}=0.003) will have a pH of 7.4. This suggests that solid $CaCO_3$ must be maintained in the soil in order to achieve the soil pH necessary to reduce Cd uptake into wheat grain to the desired level. This emphasizes the need for a stringent liming policy as part of the management plan for such sites.

Residual soil contamination
Figure 6 shows the modelled Cd content in maize from a combination of plant uptake and hypothetical leaf contamination of 0%, 1% and 2% for a field with the mean soil conditions on the estate (LOI=11.4%, pH=6.8). There was a slight increase (about 4.0%) in Cd concentrations in harvested maize with every 1% increase in soil contamination of foliage. The decrease in the Cd concentration in harvested maize due to increasing soil pH to 7.5 (Figure 6, broken line) was only about 2.0% for every pH unit. This simulation suggests that removal of adhered soil from
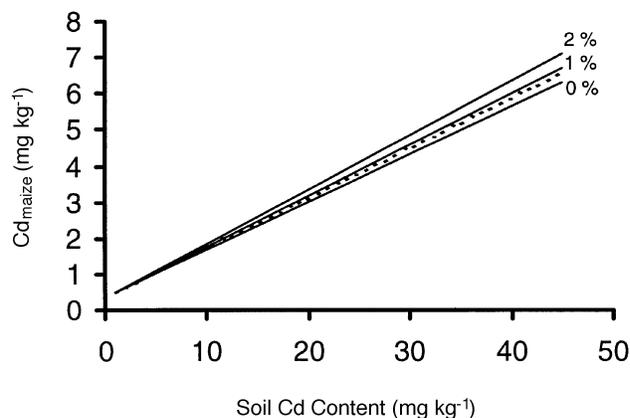

Figure 6. Cadmium concentration in harvested maize due to 0%, 1% and 2% residual soil contamination. Soil characteristics include pH 6.8 and % LOI=11.4 %. The broken line (---) represents the Cd concentration in harvested maize when the soil pH is increased from 6.8 to 7.5, assuming 1% residual soil contamination.
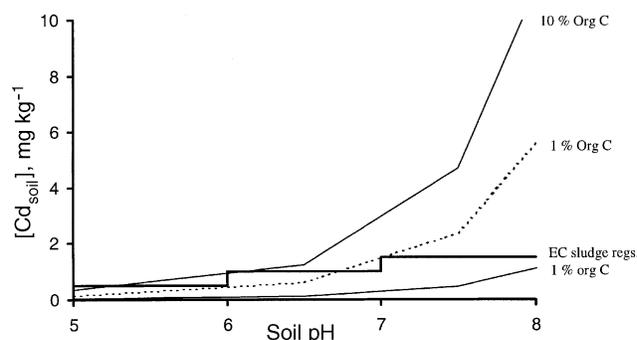

Figure 7. Comparison of EC limits for Cd in wheat grain with EC sludge regulations for Cd concentration in soils (stepped line). The solid line (—) represent the maximum permissible Cd concentrations in soil that will result in a Cd concentration in wheat less than EC limits for human consumption ($<0.2 \, \text{mg Cd kg}^{-1}$ fw) for a soil with 1% or 10% organic carbon. The broken line (---) represents the maximum permissible Cd concentration in soil that will result in a Cd concentration in wheat less than EC limits for animal feed ($<1 \, \text{mg Cd kg}^{-1}$ fw) for a soil with 1% organic carbon.

harvested maize plants may reduce Cd concentrations in animal feeds such as silage. However, even under conditions of heavy residual soil contamination, removal of adhered soil only has the potential to decrease [Cd_{maize}] by 4% (~$0.02 \, \text{mg Cd kg}^{-1}$ fw). Increasing soil pH from pH 6 to pH 7 also has little effect on [Cd_{maize}], reducing it by about $0.01 \, \text{mg Cd kg}^{-1}$ (fw) due to the low pH-dependence of uptake. However, as previously discussed, Table 2 shows that the coefficient value for pH (β_1) was relatively unreliable due to a limited soil pH range.

Comparison of EC limits for Cd in wheat grain with EC sludge regulations for Cd concentration in soils
The model for Cd uptake by wheat was run iteratively to estimate values for [Cd_{soil}] which gave rise to [Cd_{wheat}] values equal to those prescribed by the EC for human and animal feed (Table 1). Figure 7 shows a comparison of these model-derived values of [Cd_{soil}] with the EC sludge

regulations limits for Cd concentrations in soil. Figure 7 suggests that the sludge limits are quite conservative, except where soil pH is low (pH 5 – 6) or where % organic carbon is very small. However most sewage-sludge amended soils have high organic matter contents and dedicated sites operate fairly stringent liming policies to maintain soil pH >6. If the concentration of Cd in the soil exceeds the limit values, sewage sludge may still be applied after evaluation of the following aspects: uptake of Cd by plants, intake of Cd by animals, groundwater contamination, and long-term effects on biodiversity in particular on soil biota (European Union 2000).

CONCLUSIONS

Reasonable predictions of the metal concentration of maize and wheat crops were possible from values of soil metal content, pH and LOI. The average values of RSD for predictions of metal uptake by maize and wheat (mg kg^{-1}) were 0.21 and 0.19 log units respectively. However, poor γ_o values suggest that models for Pb uptake by both crops require consideration of atmospheric deposition.

Adjustment of soil pH by liming seems to be a good management strategy for reducing concentrations of metals in wheat grain to levels below those proposed within European legislation for animal feed (Table 1). However, a stringent liming policy would be required to maintain a soil pH >7.0. The viability of this would depend on the cost of such an operation. The simulation suggests that concentrations of metals in maize are only slightly affected by pH but may be improved by washing depending upon the prevailing levels of contamination by soil dust. However this is unlikely to be feasible on a farm scale.

The approach described in this study was reasonably successful. This supports the simulation of bioavailability based on simple soil geochemical survey data, as utilized by some risk assessment models such as CLEA (DEFRA and Environment Agency 2002). Similar models could be re-parameterized for situations where the uptake of metals by plants is of concern, such as the uptake of potentially toxic metals by vegetables grown in urban gardens and allotments.

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