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Critical Soil Concentrations of Cadmium, Lead, and Mercury in View of Health Effects on Humans and Animals

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I. Introduction

To assess the impact of elevated concentrations of metals in terrestrial ecosystems, a major distinction should be made in risks/effects of heavy metals related to (i) the soil ecosystem (soil organisms/processes and plants) and (ii) human health or animal health resulting from bioaccumulation. The latter effect is related to the phenomenon that a chemical accumulates in species through different trophic levels in a food chain, or secondary poisoning. Heavy metal accumulation in the food chain is specifically considered important with respect to cadmium (Cd), mercury (Hg), and, to a lesser extent, lead (Pb). Accumulation ultimately causes toxic effects on (i) humans by affecting food quality of crops (Kawada and Suzuki 1998) and animal products, as well as drinking water quality, and (ii) animal health by affecting fodder quality and by direct intake of contaminated soil (Adriano 2001). For both humans and animals, health effects arise mainly through accumulation in target organs such as kidney and liver (Satarug et al. 2000). Apart from direct health effects related to intake of food and soil, elevated metal levels in soil also lead to an increase in leaching losses of metals to groundwater and surface water, which will, after a considerable delay time, affect both drinking water quality and aquatic organisms (Crommentuijn et al. 1997).

An overview of the pathways of metals in terrestrial and aquatic ecosystems, including the pathways, considered in this review, is given in Table 1

Table 1. Receptors of Concern in Three Main Types of Terrestrial Ecosystems.

	Type of ecosystem		
Receptors of concern	Arable land	Grassland	Nonagricultural land
Ecosystem			
Soil microorganisms	+	+	+
Soil invertebrates	+	+	+
Plants	+	+	–
Wild plants	–	–	+
Human health/animal health			
Plants			
Food crops (human health)	+	–	–
Fodder crops (animal health)	–	+	–
Groundwater[a] (human health)	+	+	+
Animals			
Cattle (human animal health)	–	+	+
Birds/mammals (animal health)	+	+	+

[a]Refers specifically to groundwater used as drinking water.

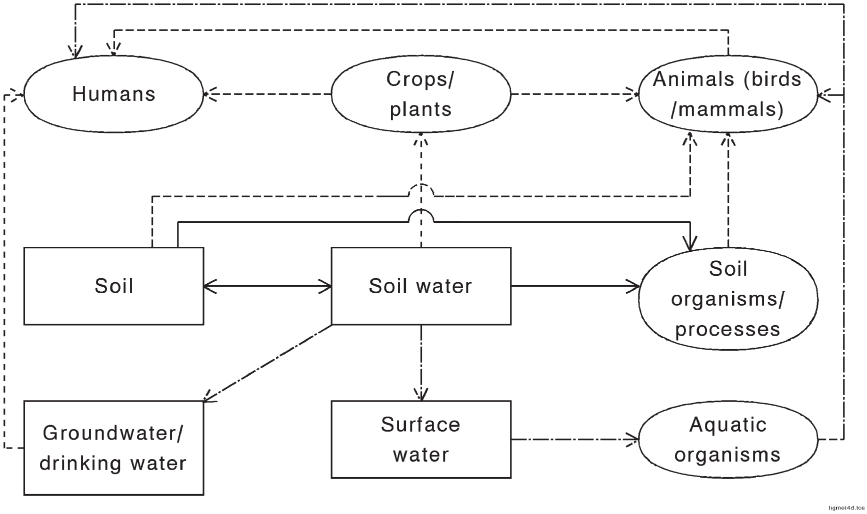

Fig. 1. Overview of the relationships and fluxes of metals from the soil to other compartments in terrestrial and aquatic ecosystems. Solid arrows are related to impacts on the soil ecosystem, discussed in another chapter (De Vries et al., this volume), whereas the dotted arrows refer to impacts on the health (or food quality) of plants, animals, and humans caused by accumulation in the food chain, discussed in this review. The hatched arrows are not considered as the paper focuses on terrestrial ecosystems.

and Fig. 1. This Chapter is limited to interactions in the soil (terrestrial ecosystems as well as agricultural systems) only. Hence, risks/effects of heavy metal uptake by consumption of aquatic organisms such as fish, which is specifically relevant for Hg (Meili 1997; Meili et al. 2003), is mentioned but no relationship can be established with the metal content in soil. Uptake of metals by humans is not included in Fig.1, although it plays a role for young children, especially for lead. Direct intake of soil in, for example, home gardens, is considered an important factor. The current Dutch soil quality standards for lead for home's gardens are in fact based partially on the ingestion of soil by children (VROM 1998). This aspect, however, is beyond the scope of this review. Here, we focus on the relationships in the soil–plant–animal chain, and exposure of humans to metals is considered within this "system" only. The relevant receptors in terrestrial ecosystems are presented in Table 1, with receptors considered here shown in bold.

At present, the transfer of metals, and chemicals in general, in food chains is generally described by bioconcentration factors (BCFs) and bioaccumulation factors (BAFs). These factors are based on the assumption of the existence of linear relationships between metals in soil and those in plants, earthworms, mammals, and other target organisms. The BCF is generally defined as the ratio of the test chemical concentration in an organism (e.g., plant, earthworm) to the concentration in water or soil at steady state. The BAF is defined as the ratio of the test chemical concentration in an organism to the concentration in its food at steady state (Jongbloed et al. 1994). BCFs are generally used for plants and invertebrates and are expressed in wet weight of tissue and dry weight of soil, whereas BAFs are generally used for accumulation by birds and mammals and are expressed on a wet weight basis.

The aim of this review is to illustrate that use of such constant accumulation factors is generally not adequate to describe metal transfer in the food chain. Here we show that there is a need to account for differences in soil properties when describing relationships between metal concentrations in soil and those in plants, water, and soil organisms. More specifically, we show how critical concentrations for Cd, Pb, and Hg in soil, in view of their potential impacts on human health and on animal health, can be derived by accounting for differences in soil properties. An analogous approach has been described by de Vries et al. (this volume) to derive critical concentrations for metals in soil and soil solution in view of ecotoxicological impacts on soil organisms and plants. Section II focuses on the derivation of critical concentrations for metals in soil in view of human health effects, resulting from intake of food crops, animal products, and drinking water. Section III is dedicated to the derivation of critical soil metal concentrations related to impacts on animal health, focusing on simple food chain models for birds and mammals feeding on worms and/or plants. In deriving such critical soil metal concentrations, use has been made of quality criteria or target values in crops and terrestrial fauna, which have been back-calculated to the soil using soil–plant, soil–soil invertebrate, plant–animal, and soil invertebrate–animal relationships, as discussed in detail in those subsections. We end with a critical evaluation of the assumptions related to the derivation and use of the critical soil metal concentrations (Section IV).

II. Critical Soil Metal Concentrations Related to Impacts on Human Health

Critical soil metal concentrations related to human toxicological effects can be derived from critical limits for humans (e.g., acceptable daily intake, ADI, in μg/kg/d) with an integrated model in which all relevant exposure pathways have been included. The ADI is the quantity of a compound to which man can be orally exposed, on the basis of body weight, without experiencing adverse effects on health. An example of such a model is CSOIL (Van den Berg and Roels 1991; Rikken et al. 2001), which derives a critical limit for soil from a given ADI value. This model includes many exposure routes to humans, such as intake from crops, meat, drinking water, and air and soil ingestion. The derivation of a critical soil limit related to an ADI by the CSOIL model depends strongly on many assumptions regarding the intake of food (Lijzen et al. 2001).

Here, it is assumed that critical soil metal concentrations related to human toxicological effects can be derived adequately from back-calculating food quality criteria (mg/kg) for metals in food crops, animal products (meat or milk), or target organs (e.g., kidney and liver) of cows/sheep and drinking water quality criteria (μg/L). Food quality and drinking water criteria quality criteria are thus used as an alternative to ADIs for humans to derive critical soil metal concentrations, thus avoiding the need of a comprehensive model on human exposure pathways. Next, we present an overview of quality criteria including a description how food quality criteria for crops can be derived from ADIs (II.A). We then illustrate how critical metal (Cd, Pb, and Hg) concentrations in soil can be derived as a function of soil properties from (i) food quality of crops (II.B), (ii) food quality of animal products, with an emphasis on grazing cows and sheep (II.C), and (iii) drinking water quality (II.D).

A. Health Impacts and Quality Criteria

For metals such as Cd, Pb, and Hg, no biological function is known. The possible health effects of exposure to cadmium, lead, and mercury have been investigated for many years, both for humans and for animals. A summary of those effects, based on studies summarized in reports published by, for example, the World Health Organization, the International Agency for Research on Cancer, the U.S Department of Health and Human Services, and Centers for Disease Control, is given in Jakubowski (2003). The major routes for human exposure are consumption of food, drinking of water, and, to a lesser extent, inhalation of air and intake of soil (children). In general, food is the dominant route of exposure of Cd and Pb of non-smokers (tobacco smoking can at least double the Cd intake), whereas the intake of fish is an important route of Hg intake (Anonymous 2000). In case of Cd and inorganic Hg, the kidney is the most sensitive and therefore most important target organism to protect. The target site for Pb toxicity is cognitive impairment associated with Pb levels in blood above 100 μg/L. This section contains an overview and discussion on (i) existing concepts that can be used to derive food quality criteria from ADI values and (ii) critical limits for Cd, Pb, and Hg in food crops and drinking water.

Derivation of Food Quality Criteria from Acceptable Daily Intakes

Food quality criteria, combined with soil–plant relationships, can be used to derive critical soil limits, thus avoiding the use of a detailed human exposure model while still using the concept of ADI. Next, we illustrate the relationship between food quality criteria and ADIs with the example of Cd in wheat. Wheat is considered one of the most important exposure pathways for humans.

Table 2. Relationships between Food Quality Criteria for Grain and Fish and Acceptable Daily Intakes (ADI).

Symptom incidence percentage	Cd limits		
	ADI_{total} (μg/d)	ADI_{grain} (μg/d)	Grain content[a] (mg/kg)
0.2	40	20	0.33
0.05	28	14	0.23
0.02	15	7.5	0.12
0.01	9	4.5	0.08

[a]Based on dividing the ADI by a net grain intake of 60 g/d (400 g/d times a body uptake efficiency of 15%).

Dose–response data for symptom incidence by humans for Cd exposure are presented by Sverdrup (2002). For Cd, the symptom is expressed as percent (%) incidence of tubular proteuria at the age of 40 yr. For Cd, ADIs are given as microgram per day (μg/d) for adult persons. Table 2 shows how the ADI values, related to incidence levels, that vary between 0.01% and 0.2% for Cd can be transferred to food quality criteria for grain, depending on the percent incidence accepted.

To perform the calculations for Cd, it is assumed that the total diffuse background exposure resulting from other exposure pathways is approximately equal to the exposure caused by eating bread or fish. For Cd, another important pathway is drinking water. In performing the calculations to derive a critical Cd content in grain, the daily intake of grain is set at 400 g and the body uptake efficiency, defined as the ratio between the total amount taken up by the body and the total administered dose, is assumed to equal 15%. The uncertainty of this coefficient, however, is large, and it can vary from 5% to 20% (Friberg et al. 1979). To derive a critical Hg content in fish, a weekly intake of 200 g of fish is assumed.

Based on a symptom incidence of 0.01%, being the standard risk level accepted for generic medical preparates, the acceptable Cd content in grain equals 0.08 mg/kg. Using a 10-fold-higher acceptable risk level (0.1%), the content increases to 0.28 mg/kg. The recommended food quality criterion for Cd in grain is 0.20 mg/kg (formerly 0.10 mg/kg), Which shows that the range in food quality criteria is in line with the range of calculated values.

Critical Limits for Cadmium, Lead, and Mercury in Food and Drinking Water

The major routes for human exposure are consumption of food, drinking of water, and inhalation of air, in case of smoking. The latter aspect is not considered here. In Table 3, an overview is given of relevant critical limits

Table 3. Overview of Food, Drinking Water, and Air Quality Criteria for Cd, Pb, and Hg in View of Human Health Effects.

		Critical limit			
Receptor	Unit[1]	Cd[a]	Pb[a]	Hg[a]	Source
Wheat	mg/kg	0.20 (0.10)[b]	0.2	0.03	Food quality criteria, EU 2001
Vegetables[c]	mg/kg	0.20	0.3	0.03	Food quality criteria, EU 2001
Drinking water	μg/L	3	10	1	WHO 2004

[a]All critical limits for food and fish are in mg/kg fresh weight.

[b]For wheat, the current critical limit is 0.20 mg/kg but we also investigated resulting critical soil concentrations using previous value of 0.10 mg/kg.

[c]Examples are endive, spinach, lettuce, etc.

for Cd, Pb, and Hg in this context, focusing on wheat in the case of food. Food is the main source of cadmium exposure in the general population (about 94%–99% of the total intake in nonsmokers). In this context, wheat is an important food product and, because wheat tends to accumulate Cd rather easily in the grain, this leads to the most sensitive critical limit for soil.

The EU regulation (EG) No. 466/2001 uses a limit for Cd of 0.2 mg/kg fresh weight in wheat grains. This limit was based on the principle "As Low As Reasonably Achievable" (ALARA) and is, therefore, not based on effects. There are, however, indications that from the point of view of protection of human health, the critical limit of 0.1 mg/kg fresh weight, which was used in the EU before 2001, is more appropriate. In the European Draft Risk Assessment Report for Cd Metal and Cd-Oxides (RAR-Cd; EC 2003), a Cd ADI for adult nonsmokers of 37–47 μg, referring to a body weight of 55–70 kg, respectively, was used to assess the current and future risk of Cd to populations by environmental exposure on a regional and continental scale. Assuming that 50% of the Cd ADI intake can be filled by grain diets, and assuming a daily intake of 200 g grains, the critical Cd content in grain would be 0.09–0.12 mg/kg wet wt. The assumed daily consumption of 200 g cereals is based on a range of 142–266 g in different European countries (EC 2003).

The assumption of 50% dietary Cd intake by wheat is based on (i) an estimate that 30%–50% of the dietary intake of Cd of the German population stems from consumption of flour and its products (Schütze et al. 2003a) and (ii) the fact that the calculated daily dietary Cd intake of 16–22 μg/d for Germans was in good agreement with the values reported in the RAR-Cd for the European population, which ranged between 10 and 21 μg/d. This value could be derived from German studies on food consumption behavior

(Kübler et al. 1995; Statistisches Bundesamt 1999) and data from the German food monitoring program (BgVV 1997). Consequently, an effects-based critical limit for Cd in wheat of 0.1 mg/kg wet wt was recommended for use in the framework of the Convention on Long-range Transboundary Air Pollution (Schütze et al. 2003b). In this study, we investigated the impact of using food quality criteria of both 0.20 mg/kg and 0.10 mg/kg fresh weight wet wt in wheat on critical soil Cd concentrations. A discussion on the reliability of the limits is continued in Section IV.

B. Derivation of Critical Soil Metal Concentrations from Food Quality Criteria for Crops

Approach

Figure 2 contains a schematic representation of the link between critical metal concentrations for soil and those for crops. A distinction was made between (i) food quality criteria in view of human health, (ii) fodder quality criteria in view of animal health, and (iii) phytotoxic levels in view of toxic effects on the crop itself. The latter aspect is not related to human health

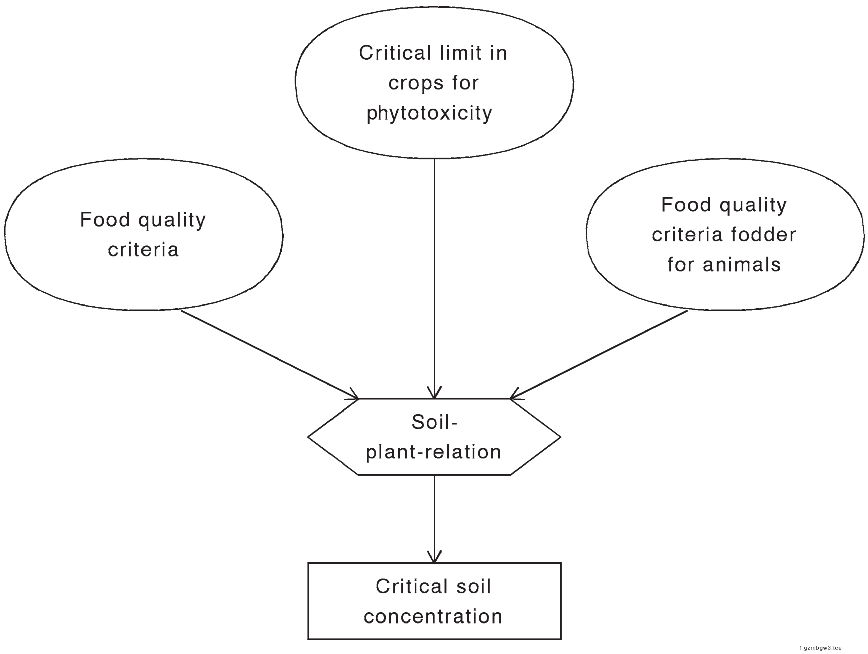

Fig. 2. Procedure that has been applied to derive critical limits for heavy metals in the soil from quality criteria in food crops in view of effects on humans (arable land) and in fodder in view of effects on animals (arable and grassland) and from critical limits in crops in view of phytotoxic effects (grassland and arable land).

but was included to be sure that the food quality criteria do not lead to situations where food crops are adversely affected. Because metal uptake by crops is plant specific, the kind of crop influences the derived limit for soil. It is thus necessary to derive relationships for the most sensitive crops to assess critical soil metal concentrations.

In most bioaccumulation models, including the aforementioned CSOIL model, a simple bioconcentration factor (BCF), often denoted as bioaccumulation factor (BAF), is used to calculate a metal content in plants from a total metal concentration in soil according to the following equation:

$$[M]_p = BCF_{sp} \cdot [M]_{s,tot} \quad (1)$$

where:

$[M]_{p(crit)}$ = metal concentration in plant (mg/kg)
$[M]_{s(crit)}$ = total metal concentration in soil (mg/kg)
BCF_{sp} = bioconcentration factor from soil to plant, being the ratio of metal concentration in plant to total metal concentration in soil (–)

Often a median BCF value based on many plant and soil data is used. Such an approach is only acceptable if a linear relationship between plant and soil content has been proven to exist, based on data. However, field data from various studies have shown that for most metals such a linear relationship does not exist. For certain metal–plant combinations, there is no relationship between soil and plant at all. To illustrate the absence of a simple relationship between metal contents in plant and soil, Fig. 3 gives an overview of Cd, Pb, and Hg contents in grass and wheat and in soil from Dutch agricultural fields. A poor relationship can be discerned only For Cd, but for Pb and Hg the BCF approach does not work. Instead, other factors, including above-ground uptake metals from atmospheric deposition, may be more important. For Pb, direct uptake is specifically relevant for vegetables, and for Hg it is often assumed that crop uptake is completely controlled by atmospheric deposition (De Temmerman and de Witte 2003a,b). Such relationships can be used to derive critical limits for these metals in the air, as summarized in De Vries et al. (2005). Furthermore, some crops can actively reduce the availability of metals in the rooting zone, thus reducing the application of any soil to plant relationship. When a relationship between the plant and soil heavy metal content is absent, it is impossible to derive critical soil metal concentrations from critical limits in plants and the use of a BCF gives a false impression of a limit thus derived.

Apart from the erroneous use of BCF values when a relationship is absent, it is often also inadequate to use BCFs even when such a relationship exists. In that case, better predictions of the metal content in plants can be obtained by a nonlinear relationship accounting for the impact of important soil properties that control the bioavailability of metals in soils, according to Brus et al. (2002) and Adams et al. (2004):

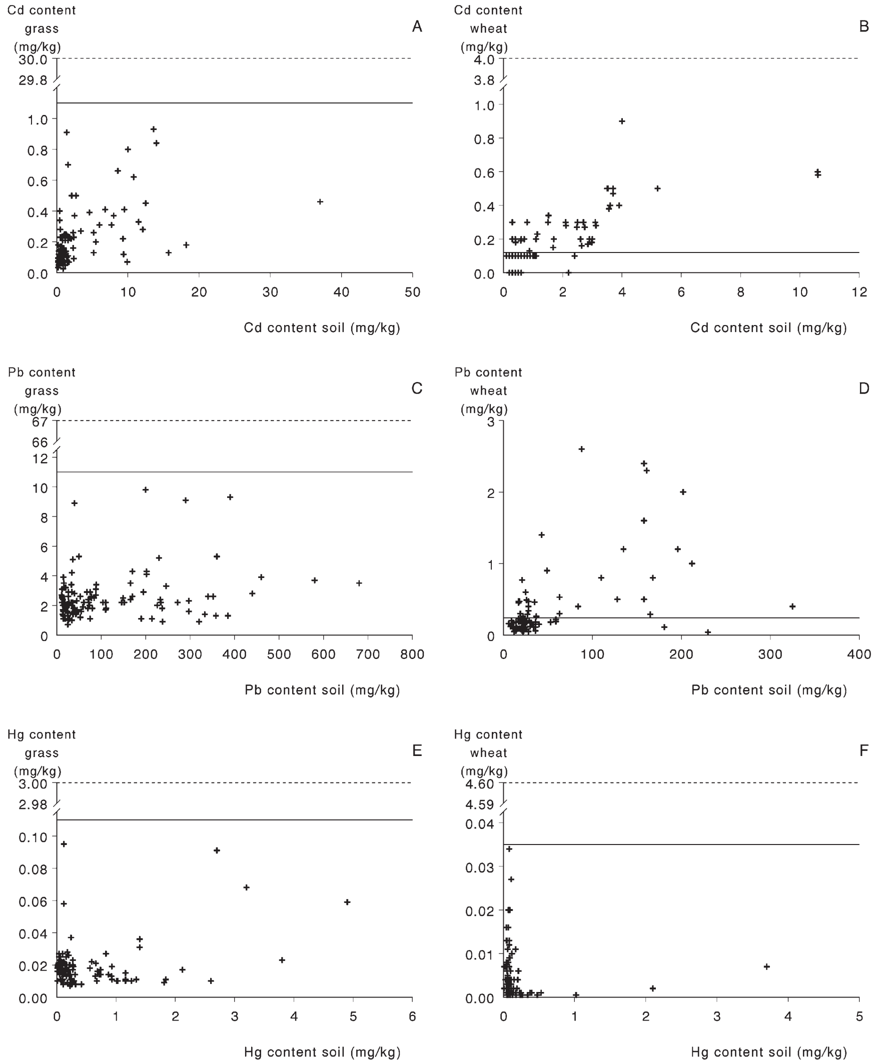

Fig. 3. Relationships between Cd, Pb, and Hg contents in grass and soil (A, C, E) and in wheat and soil (B, D, F). The solid line represents the fodder or food quality criteria as in Table 4, and the dashed line represents limits in view of phytotoxic effects on crops.

$$[M]_p = K_{sp} \cdot [M]^{n}_{s,tot} \qquad (2)$$

where:

K_{sp} = transfer constant from soil to plant ($mg.kg^{1-n}$)
n = coefficient describing the nonlinear relationship (–)

in which the value of K_{sp} depends on the content of organic matter and clay and the soil pH, according to:

$$\text{Log } K_{sp} = a + b \cdot pH - KCl + c \cdot \log[\text{clay}] + d \cdot \log[\text{OM}] \quad (3)$$

where:

[OM] = organic matter content in the soil (%)
[clay] = clay content in the soil (%)

A critical soil metal concentration can thus be calculated from the inverse nonlinear soil–plant relationship using a critical limit in a crop (food quality criteria, fodder criteria, or phytotoxicity limit), according to the following:

$$[M]_{s,tot(crit)} = ([M]_{p(crit)} / K_{sp})^{1/n} \quad (4)$$

where

$[M]_{p(crit)}$ = critical metal concentration in plant (mg/kg)
$[M]_{s(crit)}$ = critical total metal concentration in soil (mg/kg)

For each combination of crop and heavy metal, an evaluation of the resulting regression equation is needed to decide whether the predictions are accurate enough to be used in this approach. Furthermore, application of an inverse regression equation is warranted only when maximum measured metal contents in plants, used in deriving the relationship, do approach (and preferably exceed) the critical limits in plants. Otherwise, the derivation of critical soil metal concentrations from critical plant contents implies that the relationship is applied outside its range of derivation, which may lead to highly unreliable results (De Vries et al. 2007).

For Cd, Pb, and Hg in grass, maize, sugar beet, wheat, potatoes, lettuce, endive, and spinach, these being the main crops in the Netherlands, relationships were derived with the total soil concentration according to the following (see also Eqs. 2 and 3; Brus et al. 2002; Adams et al. 2004):

$$\log[M]_p = a + b \cdot pH + c \cdot \log[\text{clay}] + d \cdot \log[\text{OM}] + n \cdot \log[M]_{s,tot} \quad (5)$$

Values for the various coefficients (the exponent n and the parameters a, b, c, and d) were derived by multiple regression analyses. To derive these equations, data from field studies were used (Wiersma et al. 1986; Van Driel et al. 1988). In contrast to many laboratory studies, the soil samples from these field sites were not amended with metals and therefore reflect "real" field conditions. More information on the approach and datasets is given in De Vries et al. (2006). In general, relationships were reasonable to good for Cd, relatively poor for Pb, and absent for Hg. As an example, results for Cd and Pb for grass, maize, wheat, and lettuce are presented in Table 4.

For grass and maize, no relationships were found for Pb, and for wheat and lettuce the relations were very weak, most likely the result of processes

Table 4. Overview of Selected Soil–Plant Relationships for Cd and Pb.

Crop	Soil–plant relationship[a]	R^2
Grass		
Cd	$\log(Cd_{plant}) = 0.17 - 0.12*pH - 0.28*\log(OM) + 0.49*\log(Cd_{soil})$	0.53
Pb	No relationship found	—
Maize		
Cd	$\log(Cd_{plant}) = 0.9 - 0.21*pH - 0.32*\log(clay) + 1.08*\log(Cd_{soil})$	0.62
Pb	No relationship found	—
Wheat		
Cd	$\log(Cd_{plant}) = 0.35 - 0.15*pH - 0.39*\log(OM) + 0.76*\log(Cd_{soil})$	0.72
Pb	$\log(Pb_{plant}) = -0.25*pH - 1.42*\log(OM) + 1.14*\log(Pb_{soil})$	0.24
Lettuce		
Cd	$\log(Cd_p) = 2.55 - 0.33*pH - 0.19*\log(clay) - 0.39*\log(OM) + 0.85*\log(Cd_{soil})$	0.71
Pb	$\log(Pb_p) = -0.65 + 0.59*pH - 0.30*\log(OM) + 0.59*\log(Pb_{soil})$	0.40

[a]pH is pH_{KCl}, clay is clay content in %, and OM is organic matter content in %.

at the soil–root interface where lead uptake is actively blocked by plants. In situations with significant relationships, the sign of the coefficients (pH-KCl, clay, and OM) is negative, which implies that an increase in pH, clay content, and organic matter content leads to a lower metal content in crops. This result is in agreement with the impact of the aforementioned soil properties on the availability of metals in soil. For metals such as Cd and Pb, the availability and uptake by crops decreases with an increase in pH and organic matter or clay content.

Example of a Model Application

Here we illustrate how quality criteria in crops can be back-calculated to critical soil metal concentrations that are a function of soil properties (organic matter content, clay, content and soil pH), as these properties influence soil–plant relationships. An overview of the quality criteria (in mg/kg dry wt) used for the considered food crops (wheat, potato, lettuce, and endive) and fodder crops (grass, maize, and sugar beet) is given in Table 5. Table 5 also contains background information on the original food quality criteria given as fresh weight and an overview of critical limits in view of phytotoxic effects on crops, based on literature information. As expected, food and fodder quality criteria are much more stringent than limits in view of phytotoxic effects on crops. In De Vries et al. (2006), more detail information is given on the background of all the criteria.

As an example of the applicability of the methodology, critical Cd concentrations in soil have been calculated using the food quality criterion for lettuce and the relevant soil–plant relationship presented in Table 6. The

Table 5. Overview of Fodder and Food Quality Criteria for Cd, Pb, and Hg in View of Animal Health and Human Health and Limits in View of Phytotoxic Effects on Crops (all Limits are Given on the Basis of Dry Weight).

Quality criteria (mg/kg dry weight)							
		Food/fodder			Phytotoxicity		
Land use	Crop	Cd[a]	Pb[a]	Hg[a]	Cd[b]	Pb[b]	Hg[b]
Grassland	Grass	1.1	11	0.11	30[f]	67[j]	3[j]
Arable land	Maize	1.1	11	0.11	25[f]	38[j]	0.6[j]
Fodder crops	Sugarbeet	1.1	11	0.11	5[c]	—	1[c]
Arable land	Wheat	0.24	0.24	0.035	4[f]	—	4.6[j]
Food crops		(0.12)					
	Potato	0.42	0.42	0.13	5[c]	13[j]	1[c]
	Lettuce	4.0	6.0	0.60	10[e]	140[e,j]	1[c]
	Endive	3.3	5.0	0.50	15[f]	17[j]	1[c]

[a]The fodder quality criteria of Cd, Pb, and Hg for grass, maize, and sugarbeet are originally given as 1, 10, and 0.1 on the basis of 12% moisture content (food quality criteria; EU 2001). These data have been back-calculated to dry weight. The food quality criteria for wheat, potato, lettuce, and endive are originally given as fresh weight. In back-calculating to dry weight, the following moisture percentages were applied: wheat, 85% for the grain (the edible part); potato, 24%; lettuce, 5%; endive, 6%. For Hg, the food quality criteria are not considered applicable recently.

[b]For all crops, values are lower limits of ranges in phytotoxic contents.

The limits are based on the following sources:

[c]Kabata-Pendias and Pendias (1992), general crop-unspecific overview.

[d]Mortvedt et al. (1991).

[e]Smilde (1976).

[f]MacNicol and Beckett (1985), content at 10% reduction in yield.

[g]Dijkshoorn et al. (1979), content at 10% reduction in yield.

[h]Chang et al. (1992), content at 50% reduction in yield.

[i]Sheppard (1992), content at different percentages reduction in yield.

[j]Sauerbek (1983), content at different percentages reduction in yield.

Table 6. Calculated Critical Cd Contents in Soil in View of the Food Quality Criterion for Lettuce as a Function of Soil Properties.

Clay content (%)	Organic matter content (%)	Critical Cd content in soil (in mg/kg)		
		pH 5	pH 6	pH 7
2	2	0.61	1.4	3.3
2	5	0.88	2.1	4.8
2	10	1.2	2.7	6.4
20	2	1.9	4.4	10
20	5	2.8	6.5	15
20	10	3.7	8.6	20

example refers to a sandy soil with 2% clay and a clay soil with 20% clay. To illustrate the effect of differences in soil properties, the effect of low and high organic matter content (2%, 5%, and 10%) and pH (5, 6, and 7) was also established. Results suggest that it is essential to make a distinction in soil types considering their difference in soil properties. In acid sandy soils, the critical Cd content is below 1 mg/kg (Table 6), approaching the critical Cd content related to ecotoxicological impacts (see De Vries et al., this volume).

To illustrate impacts of major soil types, critical soil metal concentrations have been calculated on the basis of food quality criteria for Cd for the following three major soil types in agriculture:

Sandy soils (3% OM; 3% clay, pH_{KCl} 5.5)
Clay soils (3% OM; 25% clay, pH_{KCl} 6.5)
Peat soils (30% OM; 15% clay, pH_{KCl} 6.0)

Because of a rather strict food quality criterion for Cd in wheat and the fact that Cd accumulates rather easily in wheat grains, critical limits for wheat in soil are most strict with respect to food crops (Table 7). Using the present food quality criterion of 0.2 mg/kg fresh weight, results for sugar beet appear to just as strict. Using the previously used food quality criterion of 0.1 mg/kg fresh weight, wheat is always the most sensitive crop in terms of calculating critical soil metal concentrations. Wheat is a crop that is widely cultivated over Europe and has a relevant share in the total human food intake. Also, sufficiently adequate soil–plant relationships, compared to other edible parts of agricultural crops, exist that allow for the calculation of the critical soil metal content ($R^2 > 0.7$; see Table 4). Cd in wheat is,

Table 7. Calculated Critical Cd Contents in Soil in View of the Food Quality Criteria for Different Crops (as in Table 4) and Soil Types.

		Critical Cd content in soil (mg/kg)			
Land use	Crop	Sand	Clay	Peat	All soils
Grassland	Grass	9.3	37	14	37
Arable land	Maize	2.6	7.6	5.3	6.1
	Sugar beet	0.94	3.3	2.0	2.2
	Wheat[a]	1.1 (0.46)	1.8 (0.72)	4.6 (1.9)	2.6 (1.1)
	Potato	5.3	9.3	14	10
	Lettuce	1.5	5.8	9.5	6.4
	Endive	0.93	5.3	8.3	5.8

[a]Values in brackets for wheat are results of calculations with the previously used food quality criterion of 0.1 mg/kg fresh weight, whereas the standard results are calculated with the present value of 0.2 mg/kg fresh weight.

therefore, an appropriate indicator of human health effects of Cd on arable land. Phytotoxic concentrations of Pb and Cd in food crops are in all cases much higher than limits related to human health; thus, there is no need to investigate critical loads of metals related to phytotoxic effects.

C. Derivation of Critical Soil Metal Concentrations from Food Quality Criteria for Animal Products

Approach

Figure 4 shows how critical metal concentrations for the soil have been derived from food quality criteria in animal products/organs related to human health and from acceptable daily intake by animals related to animal health. The latter aspect was included to be sure that the food quality criteria for humans do not lead to situations in which animal health is adversely affected. The derivation was limited to grazing animals, which are most sensitive due to ingestion of soil in addition to intake of grass. Figure 4 shows that such a derivation requires information on quality criteria or target values for metals in animal products, grass and soil intake, and

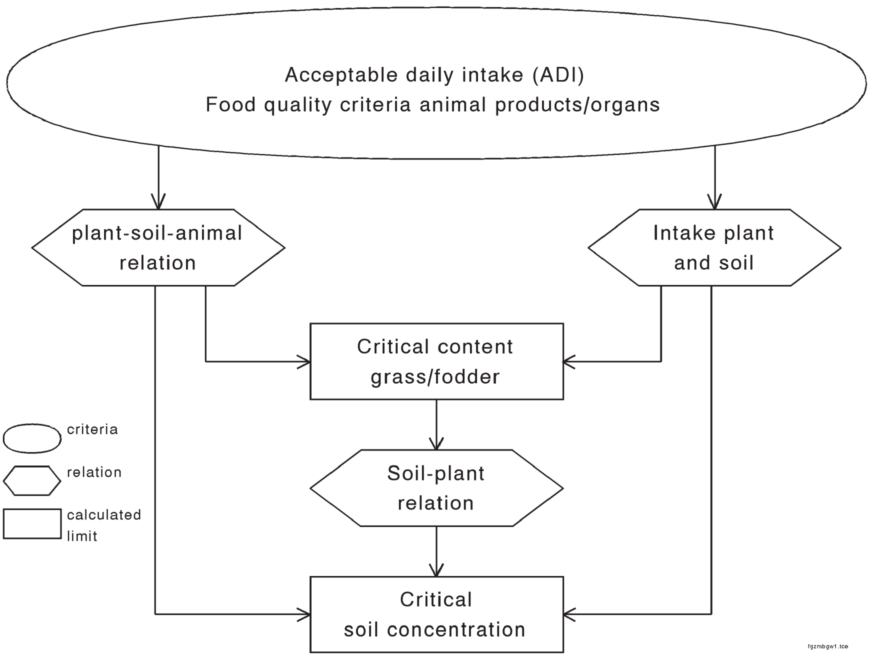

Fig. 4. Procedure that has been applied to derive critical limits for heavy metals in the soil (on grassland) from food quality criteria in animal products/organs in view of effects on humans and from acceptable daily intakes in view of toxic effects on animals.

soil–plant and plant–animal product relationships, including the effects of soil properties on these relationships.

When information is available on ADIs of metals, this can be used to obtain information on critical metal contents in fodder and soil according to:

$$[M]_{p(crit)} \cdot Ip + [M]_{s,tot(crit)} \cdot Is = ADI \tag{6}$$

where:

ADI = acceptable daily intakes of metals (mg/d)
Ip = intake of plants (fodder) (kg/d)
Is = intake of soil (kg/d)

A combination of Eq. 2 and Eq. 6 gives:

$$K_{sp} \cdot [M]^{n}_{s,tot(crit)} \cdot Ip + [M]_{s,tot(crit)} \cdot Is = ADI \tag{7}$$

From Eq. 7, the value of $[M]_{s,tot(crit)}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp}, Ip, and Is. For those metals where no soil–plant relationship is available, median values of the metal content in the crop ($[M]_p$) can be used to calculate the corresponding critical soil metal content, according to:

$$[M]_{s,tot(crit)} = (ADI - [M]_p \cdot Ip)/Is \tag{8}$$

When information is available on food quality criteria in animal organs/products, this can be used to calculate an ADI by assuming the following:

- The availability of metals to animals is the same for metals present in plant products and soil, which implies that the transfer coefficients of metals from soil to animal product and that from plant to animal product is equal (see Fig. 4); this allows the calculation of an average concentration of metal in fodder, based on a certain intake of grass and the inevitable additional ingestion of soil.
- There is a direct linear relationship between metal content in animal organs/products and metal content in fodder (use of a BAF from plant to animal organ, BAF_{pa}).
- The intake of metals by other sources (water and air) is negligible.

Using these assumptions, the relationship between metal content in animal organs/products and in soil can be approximated as:

$$[M]_{ao(crit)} = \left(\frac{[M]_{p(crit)} \cdot Ip + [M]_{s,tot(crit)} \cdot Is}{Ip + Is} \right) \cdot BAF_{pa} \tag{9}$$

where:

$[M]_{ao(crit)}$ = food quality criteria for metal content in animal organ (mg/kg)
BAF_{pa} = bioaccumulation factor from plant to animal organ/product (mg/kg fresh weight/mg/kg dry weight)

A combination of Eq. 6 and 9 gives:

$$ADI = [M]_{ao(crit)} \cdot (Ip + Is) / BCF_{pa} \tag{10}$$

This again allows the calculation of $[M]_{s,tot(crit),}$ either iteratively from Eq. 7 or directly from Eq. 8.

Example of a Model Application

An example of a model application is limited to cows and sheep. Quality criteria or target values for metals in kidney, liver, and meat of those animals were used and back-calculated to the soil using soil–plant and plant–animal relationsships. In Table 8, an overview is given of the critical contents of Cd, Pb, and Hg used in view of food safety (food quality criteria) and animal health. An estimate of the ADI based on these criteria is given in Table 9 using Eq. 10 and the plant–animal bioconcentration factors given in the same table. The dry mass intake of grass by cows and sheep was assumed to be equal to 16.9 and 2.5 kg/d, respectively, and 0.41 and 0.10 kg/d of soil, assuming that the animals are always in the field ("worst case scenario"). Data for cows are based on McKone and Ryan (1989) and those for sheep on Huinink (2000).

Because there are no reliable soil–plant relationships for grass for any of the metals involved, critical soil concentrations of Cd, Pb, and Hg were calculated from the ADI, according to Eq. 8. To achieve this, measured median values of the metal content in grass were used (Wiersma et al. 1986). As the median plant metal content is hardly affected by the metal content of the soil or the soil type, the calculated critical soil concentrations hardly

Table 8. Critical Contents of Cd, Pb, and Hg in Animal Products and Animal Organs of Cows and Sheep in View of Food Safety (Food Quality Criteria, EU 2001) and Animal Health (Puls 1988) (all Limits are Given on the Basis of Fresh Weight).

		Critical limit (mg/kg)					
		Food safety			Animal health		
Animal	Organ	Cd	Pb	Hg[a]	Cd	Pb	Hg
Cow	Kidney	1.0	0.5	0.05	5	3	1.4
	Liver	0.5	0.5	0.05	1.4	2	2
	Meat	0.05	0.1	0.05	0.02	—	—
Sheep	Kidney	1.0	0.5	0.05	4	5	1
	Liver	0.5	0.5	0.05	2	5	4
	Meat	0.05	0.1	0.05	—	0.1	—

[a]For Hg, the food quality criteria have recently been abandoned. For sheep, the food quality criteria have been assumed equal to those for cows.

Table 9. Plant–Animal Bioconcentration Factors and Calculated Acceptable Daily Intake (ADI) of Cd, Pb, and Hg in Cows and Sheep in View of Impacts on Food Safety and Animal Health.

		BAF_{pa}[a,b] (mg/kg fresh weight/mg/kg dry weight)			ADI food safety (mg/d)			ADI animal health (mg/d)		
Animal	Organ	Cd	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Hg
Cow	Unspecific	—	—	—	—	—	—	63[c]	2380[c]	28[c]
	Kidney	2.99	0.086	0.638	5.8	101	1.4	29	604	38
	Liver	0.554	0.0404	0.158	16	214	5.5	44	857	219
	Meat	$3.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	262	1332	941	105	—	—
	Minimum	—	—	—	5.8	101	1.4	29	604	28
Sheep	Kidney	2.08	—	0.468	1.25	—	0.28	5	—	5.6
	Liver	1.85	—	0.0572	0.70	—	2.3	2.8	—	182
	Meat	$2.9 \cdot 10^{-3}$	—	$9.4 \cdot 10^{-4}$	45	—	138	—	—	—
	Minimum	—	—	—	0.70	—	0.28	2.8	—	5.6

[a]Estimates for BAF_{pa} for cows are based on Van Hooft (1995).
[b]Estimates for BAF_{pa} for sheep are based on Beresford et al. (1999). The values used are the upper estimates of the ranges given in this publication.
[c]Direct estimates for the ADI, unrelated to the various animals, are based on NOEC data in mg/kg bw/d for the oral intake of food and soil by Ma et al. (2001). The values were multiplied by a body weight of 70 kg to get an ADI in mg/d.

Table 10. Overview of Critical Metal Contents in Soil on Grassland in View of Food Safety (Effects on Kidney) and Animal Health Calculated on the Basis of a Median Metal Plant Content and a Median BCF Value.

		Critical metal contents (mg/kg)			
		Food quality (kidney)		Animal health	
Metal	Soil type	$[M]_p$(50%)	BCF (50%)	$[M]_p$(50%)	BCF (50%)
Cd	Sand	10	1.3	67	6.5
	Clay	5.3	2.3	62	12
	Peat	9.6	2.0	66	10
Pb	Sand	155	41	1382	245
	Clay	155	124	1382	743
	Peat	159	106	1386	634
Hg	Sand	2.6	0.25	68	5.1
	Clay	2.7	1.3	68	28
	peat	2.5	0.68	67	14

differ between soils. This point is illustrated in Table 10, presenting calculated critical soil concentrations of Cd, Pb, and Hg based on the ADI in view of target values for the kidney of cows (the most sensitive animal organ) and in view of impacts on their health. For illustrative purposes, Table 10 also shows the values that would result from using median BCF values. Use of such values suggest an impact of soil type, but this only occurs because the ratio of metal contents in plant and soil differs between soil types without any real relationship involved. Results show that the critical soil metal concentrations are generally much higher than those derived from ecotoxicological impacts, as presented by De Vries et al. (this volume). Results for Cd and Hg for sheep (for Pb data that are lacking to allow the calculation, see Table 9) are highly comparable (De Vries et al. 2006). At the critical soil concentration derived by median plant metal contents, soil ingestion is the dominant pathway leading to critical metal concentrations in the kidney (calculated contribution, 61%–99%; De Vries et al. 2006).

D. Derivation of Critical Soil Metal Concentrations from Drinking Water Quality Criteria

Approach

The critical total Cd, Pb, and Hg concentration in soil related to human health effects can also be based on quality criteria (critical limits) for drinking water (WHO 2004). The WHO guideline includes the following quality criteria for Cd, Pb and Hg in view of drinking water quality: Pb 10 mg/m^3, Cd 3 mg/m^3, and Hg 1 mg/m^3 (see Table 3). In several countries, such as the Netherlands, it is required that those concentrations should thus not be exceeded in groundwater used as drinking water. Based on the concentration in the soil pore water as a first estimate of the concentration in groundwater, an estimate of the related critical metal concentration in soil can be made using transfer functions that relate (i) the total dissolved metal concentration to the reactive soil metal concentration and (ii) the reactive soil metal concentration to the total soil metal concentration. Such transfer functions do exist for Cd and Pb (Römkens et al. 2004) as well as for Cu and Zn (these metals are not considered here) but not for Hg.

The reactive soil metal concentration can be derived from the total dissolved metal concentration according to:

$$[M]_{s,re} = K_f \cdot [M]_{ss}^n \tag{11}$$

where:

$[M]_{ss}$ = concentration of heavy metal M in the soil solution (mmol/L)
$M_{s,re}$ = reactive concentration of heavy metal M in the soil, in this case, a 0.43 M HNO_3 extractable content (mol/kg)
K_f = Freundlich coefficient (1/g * [(L^n)/($mmol^n$)])

The value of K_f is calculated as a function of the content of organic matter, clay, and pH extract according to:

$$\log K_f = \alpha_0 + \alpha_1 \cdot \log [OM] + \alpha_2 \cdot \log [clay] + \alpha_3 \cdot pH\ H_2O \tag{12}$$

where:

$\alpha_0 \ldots \alpha_3$ = regression coefficients
pH H_2O = pH in extract or soil solution

Values for the various regression coefficients were derived from laboratory experiments where soil samples were equilibrated with different extracting solutions at a 1:2 soil solution ratio. The result is a database with approximately 1400 soil soil solution records representing almost all Dutch soil types (Römkens et al. 2004). The coefficients for Eq. 12 are shown in Table 11.

Table 11. Values for the Coefficients α_0, α_1, α_2, α_3, and n in the Relationships Relating Dissolved Total Concentrations and Reactive Soil Concentrations of Cd and Pb, According to Eq. 12 after Römkens et al. (2004).

Metal	α_0	α_1	α_2	α_3	n	R^2	se(Y)
Cd	–4.85	0.58	0.28	0.27	0.54	0.79	0.33
Pb	–2.96	0.83	0.02	0.25	0.68	0.57	0.55

Table 12. Values for the Coefficients β_0-β_3 in the Relationships (Eq. 13) Relating Reactive, (0.43 N HNO_3), and Pseudo-total (Aqua Regia) Soil Concentrations of Cd and Pb, Using a Dutch Dataset (Römkens et al. 2004). The Relationships Hold for both $[M]_{tot}$ and $[M]_{re}$ in mg/kg.

Metal	β_0	β_1 $[M]_{re}$	β_2 [OM]	β_3 [clay]	R^2_{adj}	Se(Y)[a]
Cd	0.028	0.877	0.009	0.081	0.96	0.10
Pb	0.323	0.810	0.035	0.136	0.92	0.13

[a]The standard error of the *y*-estimate on a logarithmic basis.

In this equation, dissolved organic carbon (DOC) was not included although it was available in the database. For applications on a regional or even national scale, however, data on DOC are usually not available, which was the main reason to exclude DOC from the model. For Cd, the effect of including DOC was rather small and the quality of predicted Cd concentrations was not significantly affected by removing DOC from the list of soil properties included. For Pb, however, the quality of model predictions was somewhat less when DOC was omitted from the equation. This result is not surprising because almost all Pb present in the soil solution is bound to DOC (Römkens et al. 2004).

In many countries, the regulation regarding critical metal concentrations in soil is based on total, aqua regia extractable, metal concentrations (actually being pseudo-total as aqua regia does not dissolve all metals). In the model relating the dissolved metal concentration to the metals in the solid phase, only the reactive fraction was included. To correct for this, the total metal concentration has to be derived from the criteria for the total contents because the total metal content equals the reactive and the not-reactive fraction. The total aqua regia extractable metal is derived from the reactive metal concentration and the content of organic matter and clay according to the following:

$$\log [M]_{s,tot} = \beta_0 + \beta_1 \cdot \log [M]_{s,re} + \beta_2 \cdot \log [OM]_s + \beta_3 \cdot \log [clay] \qquad (13)$$

with the parameters given in Table 12 (see also the chapter by De Vries et al. in this volume).

Example of a Model Application

As an example of the applicability of the methodology, critical Cd and Pb contents have been calculated using drinking water quality standards and the relevant transfer functions presented in Table 13. The example refers to the same sandy soil and clay soil used before in deriving critical Cd contents in view of food quality criteria. Results again suggest show that it is essential to consider differences in soil types to derive relevant critical limits. In both acid and near-neutral sandy soils, the critical Cd content is below 1 mg/kg

Table 13. Calculated Critical Total Cd and Pb Contents in Soil in View of Drinking Water Quality Criteria as a Function of Soil Properties.

Clay content (%)	Organic matter content (%)	Critical Cd content (in mg/kg)		Critical Pb content (in mg/kg)	
		pH 4	pH 6	pH 4	pH 6
2	2	0.17	0.52	8.4	21
2	5	0.28	0.83	16	41
2	10	0.40	1.2	26	66
20	2	0.37	1.1	12	30
20	5	0.59	1.8	23	58
20	10	0.85	2.5	37	94

Table 14. Calculated Critical Total Cd and Pb Contents in Soil in View of Drinking Water Quality Criteria for Different Soil Types.

Metal	Soil use	Critical metal content (mg/kg)		
		Sand	Clay	Peat
Cd	Agriculture	0.55	1.9	4.0
	Nature	0.24	1.2	1.4
Pb	Agriculture	24	53	196
	Nature	12	31	77

(Table 13), approaching the critical Cd content related to ecotoxcological impacts on soil organisms living in the soil (see De Vries et al., this volume).

To illustrate the impact of major soil types, critical total soil metal concentrations have been calculated on the basis of drinking water criteria for Cd for the following three soil types:

- Sandy soil (3% organic matter, 3% clay, and a pH H_2O of 5.5 in agriculture and a pH H_2O of 4.0 in nature)
- Clay soil (3% organic matter, 25% clay, and a pH H_2O of 6.5 in agriculture and a pH H_2O of 6.0 in nature)
- Peat soil (30% organic matter, 15% clay, and a pH H_2O of 6.0 in agriculture and a pH H_2O of 4.0 in nature)

Results thus obtained for those soil types illustrate that the lowest critical Cd and Pb contents are calculated for sandy soils in nonagricultural areas (Table 14). A discussion on the relevance of such limits is continued in Section IV.

III. Critical Soil Metal Concentrations Related to Impacts on Animal Health

Approach

Figure 5 shows the schematic representation of the link between acceptable daily intake (ADI) of animals and critical soil metal concentrations, distinguishing between birds, feeding on worms only, and mammals, feeding on birds and plants. Bioaccumulation of chemicals from soil to worm-eating birds and mammals takes place in at least two steps: first, the transfer from soil to food (plants and/or invertebrates; usually based on a BCF), which is followed by the transfer from food to higher organisms (small birds and mammals) using a BAF. The food chain of soil → plant (grass) → cattle has been described in our previous chapter for agricultural soils. This food chain is also relevant for grazing cows and sheep. In this case, the parameterization of the model is slightly different, but the overall result is comparable to that presented in Table 10 (De Vries et al. 2006). In this section, we focus on the food chain of soil → soil invertebrate → mammal/bird.

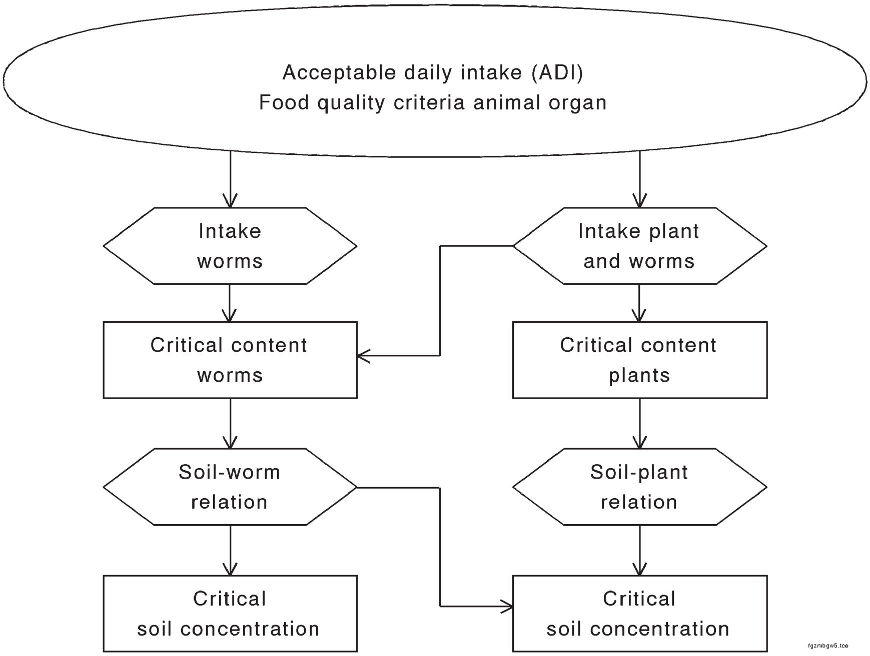

Fig. 5. Indicator and target organism and procedure that has been applied to derive critical limits for heavy metals in the soil from criteria in animal organs in view of toxic effects on animals.

Assuming that a mammal or bird feeds on soil invertebrates only, the simplest model to calculate a critical metal content in the soil, $[M]_{s(crit),}$ based on this food chain is the use of a bioconcentration factor, according to (Romijn et al. 1991a,b):

$$[M]_{s,tot(crit)} = [M]_{in(crit)} / BCF_{in} \tag{14}$$

in which:

$[M]_{in(crit)}$ = critical metal concentrations in terms of no observed effect concentrations (wet wt) of the food (invertebrate), corrected for the species of concern (mammal or bird: mg/kg)
BCF_{in} = bioconcentration factor, representing the ratio between the concentration in the invertebrate (the food of the species of concern) and the concentration in soil ($kg_{dry\ soil}/kg_{wet\ food}$)

The methodology has been used previously by Van de Plassche (1994) to derive critical soil metal contents for Cd, Cu, and methyl Hg, using the formula in the general sense of invertebrates, not only worms. Van de Plassche (1994) applied extra correction factors in Eq. 14 to extrapolate the results from toxicity studies in the laboratory to field conditions. These correction factors refers to differences in metabolic rate, caloric food content, food assimilation efficiency, pollutant assimilation efficiency, and species sensitivity to the pollutant in the laboratory and in the field situation. BCF values used by Van de Plassche (1994) have, however, not been corrected for soil characteristics, thus leading to a single critical limit value for Cd, Cu, and methyl Hg for all soils. A more sophisticated approach is the use of a BCF, which depends on soil characteristics, comparable to that of the soil–plant relationship as presented by Ma and van der Voet (1993) for Cd in earthworms. The dependence of critical metal contents in soil on soil characteristics implies that impacts of Cd on earthworms occur through the soil solution because the partitioning of Cd from the soil to the soil solution is influenced by the same soil characteristics.

As with the soil–plant relationships, the metal content in earthworms can, however, better be related to the metal content in soil in a nonlinear way, while accounting for the impact of soil properties. In this study we used such an approach (compare Eq. 2):

$$[M]_w = K_{sw} \cdot [M]_{s,tot}^m \tag{15}$$

where:

$[M]_w$ = metal concentration in worm (mg/kg)
K_{sw} = transfer constant from soil to worm ($[kg/mg]^m$)

in which the value of K_{sw} depends on the cation-exchange capacity (CEC) and the soil pH according to (compare Eq. 3, after Ma 1983):

$$\text{Log } K_{sw} = a_0 + a_1 \cdot \log(CEC) + a_2 \cdot pH \tag{16}$$

where:

CEC = cation-exchange capacity ($mmol_c$/100g)

By combining Eqs. 15 and 16, a critical soil limit can thus be calculated from an ADI using an inverse nonlinear soil–worm relationship according to:

$$[M]_{s,tot(crit)} = ([M]_{w,crit}) / K_{sw})^{1/m} \tag{17}$$

where:

$[M]_{w,crit}$ = critical limit for metal concentration in worm (mg/kg)

Application of the data of Ma (1983) to Eq. 15 and 16 for Cd and Pb, while deriving the CEC from the clay and organic matter content according to Helling et al. (1964), resulted in parameter values presented in Table 15 with a rather close match between data for internal levels of both metals in worms and model fit.

Below we further describe the approach to calculate critical metal concentrations in soil from critical metal contents in target organs and acceptable daily intakes, distinguishing between vermivores, feeding on worms only, and omnivores, feeding on both plants and worms.

For vermivores, the intake of earthworms is considered to be the dominant source of metals. Available information on the ADI of such a vermivore can be used to derive a critical metal content in the earthworm (the food) according to:

$$[M]_{w(crit)} = ADI / I_w \tag{18}$$

where:

I_w = Daily intake of earthworms (kg/d)

Equation 18 is based on the assumption that the vermivore eats earthworms only. Direct information on the acceptable daily metal intake is generally not available. However, this information can be derived from a critical metal content in the kidney of the vermivore and the critical time period in which this critical content is reached according to De Vries et al. (2007):

Table 15. Overview of Parameters in the Transfer Function for Metal Accumulation in Earthworms, Based on Data by Ma (1983).

	Parameters				
Metal	a_0	a_1 (CEC) $mmol_c$/100 g	a_2 (pH)	n mg/kg	R^2
Cd	2.69	–0.38	–0.14	0.51	0.72
Pb	1.92	–0.99	–0.22	1.16	0.61

$$[M]_{org(crit)} = [M]_{w(crit)} \cdot I_w \cdot f_{ass,org} \cdot T_{dy} \cdot T_{crit} / W_{org} \tag{19}$$

which by combination with Eq. 18 leads to

$$ADI = \frac{M_{org(crit)} \cdot W_{org}}{f_{ass,org} \cdot T_{dy} \cdot T_{crit}} \tag{20}$$

where

$[M]_{org\,(crit)}$ = critical limit for metal content in target organ (kidney) (mg/kg)
W_{org} = dry weight of the organ (kg)
$f_{ass,org}$ = assimilation fraction of the metal in food to the target organ (–)
T_{dy} = number of days during the year that the species is exposed to polluted food (d/yr)
T_{crit} = critical time period (reproductive phase of the species), in which the metal content in the target organ should stay below the critical limit (yr)

The kidney is used because this is the most sensitive organ for the intake of Cd, Pb, and Hg. The critical time period is set equal to the reproductive phase of the species.

When information on the ADI of an omnivore is available, this can be used to derive a critical metal content in the earthworm and the plant according to:

$$Ip \cdot [M]_{p(crit)} + Iw \cdot [M]_{w(crit)} = ADI \tag{21}$$

A combination of Eqs. 2, 16, and 21 leads to:

$$Ip \cdot K_{sp} \cdot [M]^{n}_{s,tot(crit)} + Iw \cdot K_{sw} \cdot [M]^{m}_{s,tot(crit)} = ADI \tag{22}$$

Equation 22 is based on the implicit assumption that the omnivore lives on one type of plant only. In principle, relationships have to be derived for all plant species that are a significant part of the diet of the omnivore. From Eq. 22, the value of $[M]_{s(crit)}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp}, K_{sw}, Ip, and Iw. When a significant soil–plant relationship does not exist, a constant plant metal content (e.g., a median or 95th percentile value) should be used to calculate the soil content, according to:

$$[M]_{s,tot(crit)} = ((ADI - Ip \cdot [M]_p)/(Iw \cdot K_{sw}))^{1/m} \tag{23}$$

As with the vermivores, the value of ADI can be derived from a critical metal content in the kidney of the omnivore and the critical time period in which this critical content is reached, using Eq. 20.

Example of a Model Application

Below we illustrate the approach using data for soil–plant and soil–worm relationships and available target values for the kidney. The black-tailed

Table 16. Calculated Acceptable Daily Intake of Cd and Pb by the Black-Tailed Godwit and the Badger.

Animal	$[M]_{org(crit)}$ (mg/kg) Cd	Pb	M_{org} (kg)	$f_{ass,org}$ (−) Cd	Pb	T_{dy} (d/yr)	T_{crit} (yr)	ADI (mg/d) Cd	Pb
Godwit[a]	200[c]	90[d]	3.85×10^{-3}	5×10^{-3}	1.5×10^{-4}	122	5	0.253	0.114
Badger[b]	200[c]	90[d]	65×10^{-3}	5×10^{-3}	1.5×10^{-4}	365	4	1.781	0.801

[a]Apart from the critical Cd and Pb contents in the kidney, $[M]_{org(crit)}$, all data are based on Bosveld et al. (2000).

[b]Apart from the critical Cd and Pb contents in the kidney, all data are based on Klok et al. (1998).

[c]The critical limit of Cd in the kidney of vertebrates varies is based on a LOEC of 100–350 mg/kg (Nicholson et al. 1983; Cooke and Johnson 1996; Pascoe et al. 1996). In this chapter, we used an intermediate value of 200 mg/kg.

[d]This critical limit is based on Ma (1996).

godwit, a small bird, was taken as a representative of the vermivores and the badger was chosen as a representative of the omnivores. For the badger, the intake of earthworms (*Lumbricus terrestris*) forms the largest part of their diet, for which well-grazed pastures are preferred. Badgers, however, also eat grass, fruits, and nuts, cereals such as wheat or oats, bulbs and tubers, etc. In short, badgers are opportunists and will consume whatever is available, but earthworms are the preferred food item. To illustrate the approach, we assumed that the badger lives on worms and grass only. The calculation of critical soil metal concentrations has been limited to Cd and Pb, as information for Hg needed to calculate ADI values and critical metal contents in worms was not available.

Estimates of the ADI, as well as the parameters required to perform the calculation, are given in Table 16. From the ADI values, the critical metal content in soil was calculated assuming an intake of worms (wet wt) of 0.1 kg/d by the godwit and 0.5 kg/d by the badger and a dry matter percentage for worms of 16%. The intake of plant material by the badger was also set at 0.5 kg/d. Table 16 also includes results for the badger, based on the assumption that they feed on worms only (worst case situation; compare Eqs. 17 and 23).

Results of the critical metal concentrations for cadmium and lead in soil based on ADIs of those metals by the godwit and badger, determined by the target values for those metals in the kidney, are given in Table 17. A distinction has been made between agricultural and nonagricultural soil based on the expected difference in soil pH. With respect to clay and organic matter content, use was made of the values presented earlier. The pH values used are the following:

Table 17. Overview of Critical Total Cd and Pb Concentrations in the Soil Based on Acceptable Daily Intakes of Those Metals by the Black-Tailed Godwit and Badger.

		Critical Cd content (mg/kg)		Critical Pb content (mg/kg)	
Soil use	Soil type	Black-tailed godwit	Badger	Black-tailed godwit	Badger
Agriculture	Sand	0.14	0,26 (0,28)	123	157 (165)
Agriculture	Clay	0.66	1,2 (1,3)	534	668 (718)
Agriculture	Peat	1.0	1,9 (2,0)	1024	1297 (1378)
Nature	Sand	0.067	0,12 (0,13)	69	88 (92)
Nature	Clay	0.47	0,82 (0,92)	412	514 (554)
Nature	Peat	0.33	0,60 (0,65)	426	539 (573)

Data for the badger are based on a daily intake of 0.5 kg worms and 0.5 kg plant material.

Values in brackets are based on a daily intake of worms only.

- Sandy soil: 5.5 for agriculture and 4.5 for nature
- Clay soil: 6.5 for agriculture and 6.0 for nature
- Peat soil: 6.0 for agriculture and 4.5 for nature

Results show that calculated critical soil Cd concentrations are very low, especially on sandy soils (see Table 17). Calculated values are (much) lower than those based on ecotoxicological criteria (see De Vries et al., this volume). Often, the values are also below present Cd concentrations in soils, which implies a present risk for these worm-eating mammals and birds. In contrast to Cd, critical Pb concentrations are high (Table 17) and far above, up to ten times, the critical concentrations related to ecotoxicological impacts (see De Vries et al., this volume) and the generally observed present Pb concentrations.

IV. Discussion

A. Uncertainties in Deriving Critical Soil Metal Concentrations from Food Quality Criteria for Crops

Uncertainties in Food Quality Criteria

The derivation of critical soil metal concentrations based on critical content in crops is based on the idea that products from agricultural soils have to meet standards for food. The choice of the standard has a profound impact on the level of the critical metal content in soils., in case of a significant soil–plant relationship, as derived for Cd; this holds specifically for wheat, which is a dominant source of Cd exposure to humans. The use of the recommended food quality criterion of 0.20 mg/kg causes a large difference in critical soil Cd concentration compared to the formerly used value of 0.10 mg/kg. Many studies mention considerable gaps in knowledge, particularly in assessing the risk to human health from exposure to dietary Cd. On one hand, new scientific results (Ikeda et al. 2003; Simmons et al. 2003; Chaney et al. 2004; Reeves and Chaney 2004; Reeves et al. 2005) induced discussions whether even the currently used official European critical Cd limits of 0.2 mg/kg (fresh weight) for cereals might possibly be too low. Based on a meta-analysis of human surveys in Japan, Ikeda et al. (2003) presented evidence on a threshold in urinary Cd before renal tubular dysfunction occurred that was clearly higher than thresholds reported in European studies. The latter were, however, not related to evidence of Cd disease but of predisease conditions. On the other hand, there are indications that the 0.10 mg/kg criterion is already too high. In the derivation of a Cd ADI for adult nonsmokers of 37–47 μg (EC 2003), an absorption rate of dietary Cd by the human body of only 3% was assumed. The Cd absorption rates by the human body include some uncertainties and, if a higher absorption rate were to be applied, e.g., the frequently used value of 5% (Kalberlah 1999), the derived ADI would be lower, thus lowering the acceptable Cd level in grain. Furthermore, the EC CSTEE (2004) stated that sensitive parts of the population are not sufficiently considered in the RAR-Cd and recommended the use of more conservative approaches for risk assessment in general. This precautionary approach is in line with statements from the WGE (2004), the EC DG Industry (1997), JECFA (2000), and SCOPE (2003) that there is no safe level for Cd in food.

Uncertainties in Soil–Plant Relationships for Metals

Several aspects play an important role when deriving soil to plant relationships to be used for the derivation of the soil critical metals concentrations:

1. *Impact of plant species* (variation between cultivars as well as crops). The uptake of metals is known to vary between crops. In general, crops such as lettuce and wheat tend to accumulate more metals than crops such as beans and tomatoes. Thresholds for agriculture should therefore be based on the more sensitive crops. Once the criteria for sensitive crops are met, the cultivation of other crops is secured. Variations in uptake of metals between cultivars, however, also play a considerable role. In the data used for the derivation of the soil to plant relationships for the Netherlands, several cultivars were planted, this being one reason why the quality of soil to plant relationships is often rather poor.

2. *Validity of data for specific conditions*. The availability of metals in soils, and hence the uptake of metals by crops, depends on soil conditions

and soil properties such as clay content, organic matter, and pH. Differences in type of clay minerals and organic matter quality in soils between different climatic regions may cause different uptake patterns. Also, the uptake of water is rather different in soils in semiarid regions compared to those in moderate climates. The data used here are likely to be representative for conditions that prevail in northwestern parts of Europe, but care should be taken using plant to soil relationships based on these data in other climatic zones. When looking for data to derive critical limits in soil, care should be taken that these data should cover the range of interest in both soil properties as well as the metal content in soils and crops. The highest plant metal content should at least be equal to the food quality standard chosen to avoid extrapolation of the regression equations.

3. *Use of data from experiments performed using hydroponic solutions and in greenhouses*. Differences in conditions between experiments (in greenhouses and lysimeters) and those in the field will cause different uptake patterns of metals from soils. In general, growing conditions in most plant uptake experiments are kept constant. Plants are watered frequently, and the nutrient status is often maintained by adding ample supplies of fertilizer, which will affect the uptake of metals from these soils. To obtain critical limits valid at field conditions, data from field experiments should therefore be used.

4. *Availability of data for specific combinations of metals and crops.* For Cd, Pb, and Hg the number of data for the crops of interest is rather large due to the extensive monitoring of soil and crops by Wiersma et al. (1986). However for other metals such as Cu and Zn, no such national inventories are yet available.

5. *Use of "historic" data to derive soil to plant relationships.* Most data used in this study are based on monitoring efforts during the early 1980s. After that time, atmospheric deposition of lead, especially, has decreased considerably because of the shift to lead-free fuel. Because Pb uptake is related to atmospheric deposition, plant data from the pre-lead-free fuel era might not be applicable to current conditions. The fact that little or no relationship between soil and plants for lead could be obtained may be partially related to the fact that the plant metal level was controlled (partly) by atmospheric deposition. Differences in atmospheric deposition usually are less pronounced than differences in the soil Pb levels and soil properties across the Netherlands.

Despite some obvious points of concern raised above, the model concept presented here is already a step ahead compared to the common concept used (BSF). It has been shown that uptake of metals by crops can be described by nonlinear equations more accurately compared to linear bioaccumulation factors. Differences in critical levels between soil types are large and need to be considered when trying to derive relevant protection levels for different soil types. At present, more complex models exist to predict plant uptake and heavy metal availability in soil. However, these models require a rather extensive parameterization that is, usually, hard to obtain for application in different soil types. An advantage of the approach described here is that it can be easily applied to a regional or even national scale because the input required is usually available.

B. Uncertainties in Deriving Critical Soil Metal Concentrations from Food Quality Criteria for Animal/Products

Uncertainties in the derivation of critical soil concentrations from critical metal contents in animal organs/products from cows and sheep are determined by uncertainties in the acceptable daily intake (ADI), the daily intake of plant and soil, and in the transfer rates of metals from soil to grass to the consuming animal. Uncertainties in the intake of plant and soil are comparatively limited. Regarding soil–plant relationships, the uncertainties have already been mentioned. Most uncertain, however, is the hypothesized linear relationship between metal content in animal organs/products and metal content in fodder. The use of a constant bioaccumulation factor from plant to animal organ, BAF_{pa}, is a crucial assumption in deriving ADI values from critical metal contents in animal organs/products (see Eq. 10). Schütze et al. (2003a) made a literature review on the relationships between Cd in environment/fodder and Cd in animals (organs and muscle of wildlife and cattle). In several studies (Hapke et al. 1977; Crössmann 1981; Schinner 1981; Hecht 1982; Holm 1983), it could be shown that there is a relationship. The overall conclusion was, however, that a mathematical quantification of the carry-over could not be done.

The carry-over rates to a certain organ depend not only on the Cd intake but also on animal species, animal age, and the composition of fodder. In particular, with respect to Cd, there is a strong interlink to Zn uptake. We also must be aware that the differences in metal contents in fodder are usually low compared with the gradients in studies and surveys reported in the literature. The correlation between metal in fodder and in animal product is probably much weaker in cases of unpolluted soils. Another crucial assumption is that the availability of metals present in plant products and soil to animals is the same. This assumption also needs verification. In summary, when ADI values are not available, the derivation of a soil critical concentration is highly uncertain.

C. Uncertainties in Deriving Critical Soil Metal Concentrations from Drinking Water Quality Criteria

Uncertainties in Transfer Functions from Soil to Soil Solution

The points raised in relation to the soil to plant relationships are to a large extent also valid for the soil to water relationships. Data (especially the range therein) used to construct the relationships should match the range in environmental conditions. Again, differences in geology and specific sources of contamination (nature of the contamination) have a profound impact on the distribution of metals between soil and soil solution. As such, the approach outlined here is merely a conceptual approach (valid for the Netherlands, of course), and care should be taken when using the relationships presented here under rather different circumstances.

Using a Critical Metal Concentration in Soil Solution Based on Drinking Water Quality Criteria

An important methodological aspect is the fact that critical soil concentrations calculated from groundwater standards (based on drinking water quality criteria) assume that the metal concentration in soil solution can be used as an estimate of the concentration in groundwater. This is only the case in a steady-state situation, assuming a constant dissolved metal concentration with depth. Because steady state is generally not attained, the approach presented here is a worst case. At a given critical soil concentration, the water draining from the topsoil, for which the calculations are made, will generally contain more metals than upper groundwater because of ongoing retention in the lower parts of the soil profile. Only a dynamic modeling approach can account for these changes in the soil profile. In this way, one can calculate the time period before the dissolved metal concentration reaches a critical value in groundwater. Such a calculation should be made using the critical metal input (critical load) to the soil, accounting for differences between the critical and original soil metal concentration at each soil depth until groundwater, is reached. When this time period is longer than a target period (e.g., 100 years), one may not want to use such limits for regulation purposes.

D. Uncertainties in Deriving Critical Soil Metal Concentrations from Critical Metal Contents in Organs of Worm-Eating Birds

The assessment of critical soil metal concentrations from critical metal contents in organs of worm-eating birds is influenced by the uncertainty in all the factors affecting the calculation, including the ADI of the worm-eating animal, the intake of worms, and the soil to worm relationships. Data on the intake of worms are comparatively reliable. As with the soil–plant relationships, the data used to construct soil–worm relationships are specific for Dutch circumstances with respect to clay mineralogy, organic matter quality, etc., but in these circumstances, they seem quite reliable. As with the calculation for cows and sheep, the largest uncertainty is related to the acceptable daily intake. The uncertainty of the ADI value is, among others, determined by the uncertainty in critical internal level for metal in the target organ of the worm-eating animal and the assimilation fraction of the metal in food to the target organ (see Eq. 20). Both uncertainties are relatively large. In addition, it is important to mention that the back-calculated soil concentrations assumes a homogeneous feeding habit area of the animal. Because animals move around, the quality of the food they consume differs from one location to the other, depending on local conditions. The size of the feeding area also affects to what extent this difference affects the exposure of animals. The earthworms will remain bound to a certain area, but birds and mammals, such as the badger, that are feeding on the worms dwell in a much larger area, and the variability in the degree of contaminants (spatial variation in the amount of metals in soil, for example), will affect the levels of metals present in the food obtained from one site compared to another. This aspect is spatially averaged in back-calculating the concentrations.

V. Conclusions

Major conclusions that can be derived from the presented analyses in this chapter follow.

1. The impact of soil properties on critical soil metal concentrations in view of human health and animal health impacts is mainly relevant for Cd, because of the occurrence of rather significant soil–plant, soil–solution, and soil–worm relationships. For Hg, the effects are unclear and presently cannot be included. There are no soil–soil solution, soil–plant, or soil–worm relationships. Only in grazing animals is a back-calculation possible because of ingestion of contaminated soil as the dominant pathway. However, this calculation is highly uncertain. For Pb, impacts of soil properties can be relevant in case of worm-eating animals and in view of impacts on groundwater quality from the occurrence of rather significant soil–solution and soil–worm relationships. Critical soil concentrations for Pb related to impacts on animal health and human health are, however, generally much higher than those related to ecotoxicological impacts (the same is true for Hg).

2. The largest uncertainties in deriving critical soil concentrations in view of human health and animal health are related to soil concentrations that are derived from food quality criteria or internal critical limits of animal organs; this is mainly because the metal transfer rates from soil to food (either plants such as grass or small animals such as worms) to animals vary considerably, and model approaches are still in development. Both the availability of the metal in the food or soil consumed by animals and the actual internal uptake by animals are concerns. Furthermore, there is a large uncertainty in the internal critical level in organs for both aboveground and belowground organisms (see Bruus Pedersen et al. 2000).

3. Critical Cd concentrations in view of health effects on animals and humans are sometimes lower than those related to ecotoxicological impacts on soil organisms/processes and plants. This point is illustrated in Table 18,

Table 18. Calculated Critical Total Cd Contents in Soil in View of Impacts on Soil Organisms/Soil Processes, Food Quality of Wheat, and Health of Worm-Eating Birds and Mammals.

		Critical Cd content (mg/kg)		
Land use	Impact on	Sand	Clay	Peat
Nature[a]	Soil organisms (pH 4.5)	0.89	2.8	13
Arable land	Wheat	0.46	0.72	1.9
Nature[a]	Drinking water	0.24	1.2	1.4
Nature[a]	Impacts on worm eating mammals (badger)	0.13	0.92	0.65
Nature[a]	Impacts on worm-eating birds (godwit)	0.067	0.47	0.33

[a]Apart from the critical Cd and Pb contents in the kidney, $[M]_{org(crit)}$, all data are based on Bosveld et al. (2000).

showing calculated critical total Cd concentrations in soil related to food quality criteria for wheat, drinking water quality, and acceptable daily intakes of worm-eating birds and mammals. Specifically, for acid sandy soils the calculated critical concentrations are (much) lower than critical metal concentrations related to ecotoxicological impacts (see also De Vries et al., this volume). Despite the uncertainties involved, this implies that present Cd concentrations in the rural area may affect both agricultural and non-agricultural systems.

Summary

Assessment of the risk of elevated soil metal concentrations requires appropriate critical limits for metal concentrations in soil in view of ecological and human toxicological risks. This chapter presents an overview of methodologies to derive critical total metal concentrations in soils for Cd, Pb, and Hg as relevant to health effects on animals and humans, taking into account the effect of soil properties. The approach is based on the use of nonlinear relationships for metals in soil, soil solution, plants, and soil invertebrates, including soil properties that affect metal availability in soil. Results indicate that the impact of soil properties on critical soil metal concentrations is mainly relevant for Cd because of significant soil–plant, soil–solution, and soil–worm relationships. Critical Cd levels in soil thus derived are sometimes lower than those related to ecotoxicological impacts on soil organisms/processes and plants, which is especially true for critical soil Cd concentrations in view of food quality criteria for wheat, drinking water quality, and acceptable daily intakes of worm-eating birds and

mammals. There are, however, large uncertainties involved in the derivation from assumptions made in the calculation and uncertainties in acceptable daily intakes and in relationships for Cd in soil, soil solution, plants, and soil invertebrates. Despite these uncertainties, the analyses indicate that present Cd concentrations in parts of the rural areas are in excess of the critical levels at which effects in both agricultural and nonagricultural systems can occur.

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