

# Spatially Explicit Integrated Risk Assessment of Present Soil Concentrations of Cadmium, Lead, Copper and Zinc in The Netherlands

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**Abstract** Historic and current agricultural and industrial activities have resulted in accumulation of Cd, Cu, Pb and Zn in soil. To estimate potential risks for ecosystems, agriculture and water quality, an integrated risk assessment was performed for The Netherlands. Risks of metal contamination were assessed on a national scale by comparing present soil concentrations of Cd, Pb, Cu and Zn with critical concentrations of those metals in view of agricultural impacts, ecological impacts and impacts on the quality of groundwater and surface waters. Results show that present soil metal concentrations cause few risks for agriculture or ecosystems; for less than 2% of the surface area present metal levels exceed critical limits. Critical limits for groundwater are only significantly exceeded for Pb (17% of the area), but critical limits for surface water are exceeded throughout the country for Cu and Zn. Taking critical limits used in The Netherlands, the area where exceedances take place is nearly negligible for Cd and low for Pb (less than 3%), but much larger (between 40% and 50%) for both Cu and Zn. Results from this study suggest that accumulation of heavy metals in Dutch soils at present primarily affects the quality of

surface waters. This stresses the need for harmonization of soil and water policy. Measures to reduce the load in surface waters to meet target levels, under conditions like those prevailing in The Netherlands, are bound to have an impact on land management.

**Keywords** Critical concentrations · Metals · Agricultural impacts · Food quality · Ecological impacts · Soil organisms · Aquatic organisms · Groundwater quality · Surface water quality

## 1 Introduction

In many areas in Europe heavy metals accumulate in soils due to emissions from industry, agriculture and traffic. This accumulation might lead to adverse effects on (1) the quality of agricultural products, (2) the functioning and species distribution of soil organisms (soil biodiversity), and (3) the quality of groundwater and surface waters. Eventually this may also pose risks to human health due to consumption of food and water. Heavy metal accumulation in the food chain has proven to be relevant for cadmium (Cd) and mercury (Hg), and to a lesser extent for lead (Pb; Jakubowski 2003). Ecotoxicological effects include impacts on plants like reduced development and growth of roots and shoots (toxicity symptoms), decreased nutrient contents in foliar tissues (physio-

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logical symptoms) and decreased enzymatic activity (biochemical symptoms) (e.g. Prasad 1995; Das et al. 1997). It also includes impacts on soil organisms, such as reduced species diversity, abundance and biomass, and changes in microbial processes, such as organic matter and nutrient turnover (e.g. Bengtsson and Tranvik 1989; Giller et al. 1998; Vig et al. 2003). When contaminants leach from soil to surface water they may affect aquatic organisms, including algae, crustacea and fish, through effects on gill functioning (e.g. Sola et al. 1995), nervous systems (e.g. Baatrup 1991), as well as growth and reproduction rates (e.g. Mance 1987).

Risk assessment of potential pollutants in soils at large scale levels requires knowledge of the relationships between pollutant concentrations and potential effects. This is conventionally done by the use of soil concentrations of the pollutant (variously termed, for example, ‘critical limits’, ‘quality standards’, ‘trigger values’) that define threshold levels above which further action (e.g. site-specific risk assessment, remediation) should be taken. Threshold concentrations used so far are more or less independent of soil properties, i.e. no account of bioavailability on risk has been considered. This may be sufficient where thresholds are used in a screening process as part of a tiered approach to risk assessment since conservative values can be chosen. However, at national and international scales, extensive assessment of risk by toxicity testing is not feasible, and the use of proper threshold concentrations is crucial. In this situation the relationships between soil properties and potential pollutant risk should be considered if possible.

Within the proposed EU Soil Framework Directive (EU 2006), multiple aspects of soil contamination have been recognized and guidelines have been formulated to strive towards a more sustainable land use which aims to prevent further accumulation and mitigate adverse effects of contaminants in soils. To assess current risks and whether current land use is sustainable, tools are needed to evaluate the present soil quality and the effects and threats of (long-term) inputs and accumulation of contaminants, such as metals, for the three major functions of soils in non-urban areas, i.e. food production, ecosystem support and protection of water bodies. At present, risk

assessments focus mainly on either single aspects of soil contamination or on point source contaminations in urban areas. Tools to perform an integrated risk assessment on a regional scale, thus identifying risk areas are scarce.

In this paper, we assess current risks of metals in Dutch soils by comparing present and critical metal concentrations in (1) soil in view of agricultural and ecological impacts, while accounting for relationships between soil properties and potential pollutant risk and (2) groundwater and surface water in view of impact on water quality and aquatic organisms. More specifically, the critical metal concentrations are derived from criteria for each of the three functions listed below:

1. Food quality and health of crops/animals (agricultural impacts):
  - Food quality criteria for metals in agricultural crops or critical metal concentrations in view of crop health.
  - Food quality criteria for metals in animal products or critical metal concentrations in animal organs/acceptable daily intakes in view of toxic impacts on animal health.
2. Ecosystem health (ecological impacts):
  - Critical metal concentrations in soil solid phase or soil solution associated with adverse effects on soil ecosystems (soil biota: micro-organisms/invertebrates), soil processes (e.g. mineralization, nitrification, denitrification) or plants;
3. Water quality:
  - Quality criteria for metals in drinking water;
  - Critical metal concentrations in surface water in view of impacts on aquatic biota.

Recently a conceptual approach to derive critical limits in soil or soil solution from such criteria has been described and parameterized (De Vries et al. 2007a, b, 2008). In this paper we used this methodology to evaluate soil quality on a national scale and to identify areas where soil quality does not meet criteria for food quality, soil ecosystem health and water quality and where measures are required to mitigate adverse effects.

## 2 Methodological Approach

In this section, we first describe the general approach to calculate critical concentrations of the metals Cd, Pb, Cu and Zn in the soil solid phase and present concentrations in surface water and groundwater on a regional scale (Section 2.1). This is followed by a short description of the mathematical relations which we used to calculate (1) critical solid phase concentrations based on critical limits for agricultural and ecological targets and (2) present concentrations in surface waters and groundwater based on present soil solid phase concentrations (Section 2.2). Then we provide a description of the methods to derive regional scale input values for the calculations, i.e. soil properties, hydrology and present soil metal concentrations (Section 2.3). Finally an overview is given of critical limits for targets, which we used in our calculations (Section 2.4).

### 2.1 General Approach to Assess the Risk of Present Soil Metal Concentrations

Critical concentrations depend on the target to be protected. For the calculations we discriminated between different kinds of land use. Agricultural impacts were limited to managed grassland or arable land, whereas ecological impacts and impacts on water quality also included nature areas (see Table 1).

**Table 1** Receptors and impacts of concern in three main types of land use

| Target to protect                                       | Arable land | Grassland | Nature |
|---|-------------|-----------|--------|
| <b>Agricultural impacts</b>                             |             |           |        |
| Food crops (humans)                                     | +           | –         | –      |
| Fodder crops (animals)                                  | +           | +         | –      |
| Animal products (humans)                                | –           | +         | –      |
| Crop growth   | +           | –         | –      |
| Cattle health   | –           | +         | –      |
| <b>Ecological impacts</b>                               |             |           |        |
| Soil organisms (microbes/invertebrates), soil processes | +           | +         | +      |
| Plants  | +           | +         | +      |
| <b>Water quality impacts</b>                            |             |           |        |
| Drinking water  | +           | +         | +      |
| Aquatic organisms                                       | +           | +         | +      |

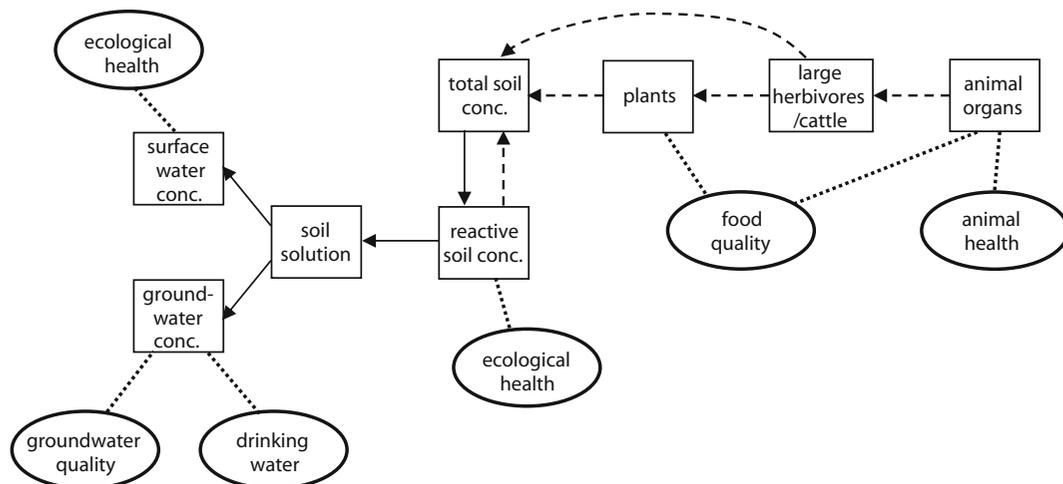
The critical total soil metal concentrations in view of agricultural impacts were derived from critical metal concentrations in plants or animal organs in terms of food quality or crop/animal health, combined with relationships for soil-plant transfer, soil-animal transfer and plant-animal transfer, as presented in Fig. 1. Food quality criteria for metals in crops or target organisms of grazing animals (liver and kidney) are available for Cd and Pb only, whereas data in view of toxic impacts on the crop or animal itself can be derived for all metals based on a tolerable daily intake (TDI). The critical soil metal concentrations in view of ecological impacts were derived from “no observed effect concentrations” (NOECs) for the reactive soil metal concentration in laboratory experiments and relationships between the total and reactive soil metal concentration (Fig. 1).

Critical limits for the quality of groundwater were based on existing criteria for drinking water. For surface water they were based on available limits derived from NOEC data for impacts on aquatic organisms. In this situation, however, present metal concentrations discharging to groundwater and surface water, due to leaching and runoff from soils, are unknown. Here, these concentrations were derived from the present total soil metal concentrations using a relationship for the soil-soil solution transfer (see solid arrows in Fig. 1). Application of a hydrological model allowed for a distinction between runoff to surface water and leaching to ground water (Fig. 1).

In the next section, we summarize the approaches that were used to calculate the relationships between compartments shown in Fig. 1. More details about the models applied here can be found in De Vries et al. (2007a, b, 2008).

### 2.2 Relations Used to Assess the Geographic Variation in Critical Soil Metal Concentrations and in Present Metal Concentrations Discharged to Surface Water and to Groundwater

*Calculation of Critical Soil Metal Concentrations for Food Quality* Critical soil metal concentrations were calculated from critical metal contents in plants in view of food quality or crop health. The approach is based on the assumption that the metal content in plants can be described by a multivariate non-linear relationship with the soil metal concentration, ac-



**Fig. 1** Relations between metals in different compartments, used to back calculate critical total soil metal concentrations from present total soil metal concentrations (*solid arrows*). Dotted lines without arrows indicate the link between criteria for metals in a compartment and the related impacts (*dotted arrows*) and to calculate present

counting for the impact of soil properties that control the (bio)availability of metals in soils (Brus et al. 2002; Adams et al. 2004), according to (see also De Vries et al. 2008):

$$\log M_{\text{plant(crit)}} = a_0 + a_1 \cdot \text{pH}_{\text{KCl}} + a_2 \cdot \log \text{OM} + a_3 \cdot \log \text{clay} + n \cdot \log M_{\text{tot(crit)}} \quad (1)$$

where  $M_{\text{plant(crit)}}$  is the critical limit for metal concentration in plant ( $\text{mg kg}^{-1}$ );  $M_{\text{tot(crit)}}$  is the critical total metal concentration in soil ( $\text{mg kg}^{-1}$ ); OM is the organic matter content in the soil (%); clay is the clay content in the soil (%);  $n$  is a coefficient describing the non-linear relationship between the metal concentration in plant and in soil (-).

Values for the various regression coefficients in Eq. 1 were derived for Cd, Cu, Pb and Zn in grass, maize, sugar beet, wheat, potatoes, lettuce, endive and spinach, being the main crops in The Netherlands (De Vries et al. 2008). The relationships obtained for Cd and Zn were much better than those for Cu and Pb. For the majority of crops, soil–plant relationships for Cu and Pb were not statistically significant and are not used. Furthermore, the critical limit of Zn in view of phytotoxic effects by far exceeds the measured plant values in the database which limits the application of the regression model (strong extrapolation). Critical soil concentrations, therefore, were only calculated for

concentrations in groundwater and surface waters from present total soil metal concentrations (*solid arrows*). Dotted lines without arrows indicate the link between criteria for metals in a compartment and the related impacts

Cd. Values for  $a_0$ – $a_3$  and  $n$  for Cd are given in Table 7 of the Annex.

*Calculation of Critical Soil Metal Concentrations for Animal Health and Quality of Animal Products* The derivation of critical soil metal concentrations from acceptable daily intakes (ADI) by animals was limited to grazing animals (cows). Furthermore, the derivation was limited to Cd, for which ADI values are relevant in view of impacts on human and animal health. Acceptable daily intakes (ADI) of those metals were related to critical metal contents in fodder (grass) and soil according to:

$$M_{\text{plant(crit)}} \cdot I_{\text{plant}} + M_{\text{tot(crit)}} \cdot I_{\text{soil}} = \text{ADI} \quad (2)$$

where ADI is acceptable daily intake of metals ( $\text{mg day}^{-1}$ );  $I_{\text{plant}}$  is intake of plants (fodder) ( $\text{kg day}^{-1}$ );  $I_{\text{soil}}$  is intake of soil ( $\text{kg day}^{-1}$ ).

The critical soil metal concentration was derived by combining Eqs. 1 and 2, in which  $M_{\text{tot(crit)}}$  was solved iteratively using a given ADI and given coefficients in the soil–plant relationship (see Table 7 for grass). The intake of plants,  $I_{\text{plant}}$ , and the intake of soil,  $I_{\text{soil}}$  was equal to  $16.9 \text{ kg day}^{-1}$  and  $0.41 \text{ kg day}^{-1}$ , respectively, assuming a constant intake of grass and soil throughout the year (De Vries et al. 2008). ADI values for Cd were based on food quality criteria for Cd in the kidney of cows using a methodology described in De Vries et al. (2007b).

*Calculation of Critical Soil Metal Concentrations for Ecological Health* Critical soil metal concentrations in view of ecotoxicological effects on soil organisms and plants were based on no observed effect concentrations (NOECs) for the concentration of added metal in laboratory experiments. These added metal concentrations were assumed to be in a reactive form and were related to soil solution pH and soil organic matter content, using a procedure described in Lofts et al. (2004) and De Vries et al. (2007a):

$$\log M_{\text{re(crit)}} = b_0 + b_1 \cdot \text{pH}_{\text{solution}} + b_2 \cdot \log \text{OM} \quad (3)$$

where  $M_{\text{re(crit)}}$  is the critical reactive metal concentration in the soil ( $\text{mg kg}^{-1}$ );  $\text{pH}_{\text{solution}}$  is the soil solution pH. Values derived for  $b_0$ ,  $b_1$  and  $b_2$  are given in Table 8 of the Annex. The reactive soil metal concentrations are metals that are potentially available for exchange with the soil solution. It excludes metals that are incorporated in mineral lattices which are not directly available for dissolution. For field soils, the reactive fraction is empirically established by an extraction using a 0.43 M  $\text{HNO}_3$  solution.

Critical total (added) metal concentrations were derived from the concentrations of reactive (added) metal according to (Römken et al. 2004):

$$\log M_{\text{tot(crit)}} = c_0 + c_1 \cdot \log M_{\text{re(crit)}} + c_2 \cdot \log \text{OM} + c_3 \cdot \log \text{clay} \quad (4)$$

Values derived for  $c_0$ – $c_3$  are given in Table 9 of the Annex. Since an added risk approach has been used by Lofts et al. (2004) and De Vries et al. (2007a) the addition of soil background concentrations is required to derive critical total soil metal concentrations. Background total soil metal concentrations were estimated from a large dataset of subsoil samples from 50 to 120 cm below ground level, which were assumed to have been subjected to little or no anthropogenic sources of metals. Background concentrations reflecting geochemical differences (Reimann and Garrett 2005) were derived using an empirical relation with soil properties, according to:

$$\log M_{\text{tot(background)}} = d_0 + d_1 \log \text{OM} + d_2 \log \text{clay} + d_3 \cdot \text{pH}_{\text{KCl}} \quad (5)$$

where  $M_{\text{tot(background)}}$  is total metal background concentration in the soil ( $\text{mg kg}^{-1}$ ). Values for the

regression coefficients are presented in Table 10 of the Annex.

*Calculation of Present Groundwater and Surface Water Concentrations* A two-step approach was used to calculate dissolved concentrations in leachates to groundwater and in runoff to surface water (Bonten et al. 2008). First, dissolved metal concentrations in the soil solution were calculated from reactive solid phase metal concentrations using a scaled Freundlich isotherm according to (De Vries et al. 2007b):

$$M_{\text{re}} = K_f \cdot [M]^n \quad (6)$$

where  $[M]$  is the concentration of dissolved metals in the soil solution ( $\text{mg l}^{-1}$ );  $n$  is the Freundlich exponent (–);  $K_f$  is the Freundlich coefficient ( $\text{mg}^{1-n} \text{kg}^{-1} \text{l}^n$ ), with  $K_f$  being derived as (Römken et al. 2004):

$$\log K_f = e_0 + e_1 \cdot \log \text{OM} + e_2 \cdot \log \text{clay} + e_3 \cdot \text{pH}_{\text{solution}} + e_4 \cdot \log [\text{DOC}] \quad (7)$$

where  $\text{pH}_{\text{solution}}$  is pH in soil solution;  $[\text{DOC}]$  is the dissolved organic carbon concentration in the soil solution ( $\text{mg C l}^{-1}$ ). Values for the regression coefficients  $e_0$ – $e_4$  are shown in Table 11 of the Annex.

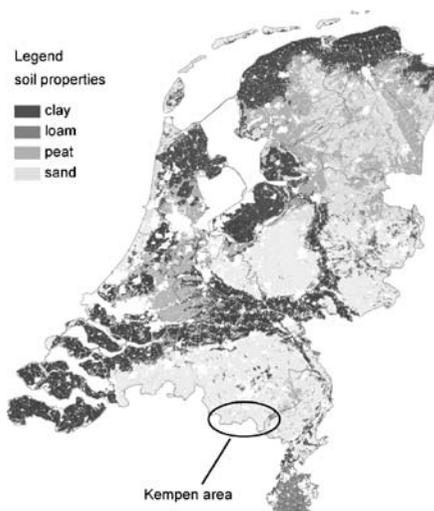
Metal concentrations discharged to surface waters were derived by multiplying soil solution concentrations of all soil horizons within a soil profile with lateral drainage flows of each horizon and dividing the resulting flux by the total lateral drainage flow (flux weighted average concentration). The metal concentration discharged to groundwater was set equal to the predicted soil solution concentrations in the soil horizon at the average groundwater level, in areas where such discharge occurs. The hydrological flows (seepage, lateral drainage, evaporation, transpiration), which were used to calculate metal leaching to groundwater and surface waters, were based on results of the STONE model (Wolf et al. 2003). Water fluxes, available on a daily basis for the period 1971–2000, were aggregated to long term (30 year) averages for each unit, as described below.

### 2.3 Spatial Schematization of Input Parameters

The approach which has been described above was applied to all rural and nature areas of The Nether-

lands, thereby taking into account regional variations in soil properties, land use, hydrological characteristics and present total metal contents. This required a spatial schematization of these parameters as input for the assessment. To do so, 6,405 units, being unique combinations of soil properties, land use and climate conditions, were defined representing the total agricultural and nature area of The Netherlands. These units were taken from the model 'STONE' (Wolf et al. 2003), which has previously been used to calculate nitrogen and phosphate leaching to surface waters in The Netherlands. Each unit is an aggregation of 250×250 m grid cells. The number of grid cells within a unit differs between 4 and 3,482. Soil properties of the units were based on the Dutch Soil Information System (Van der Pouw and Finke 1999), which contains soil properties (organic matter, clay, pH-KCl) of approximately 1,500 soil profiles. For each unit, soil properties were attributed to the different horizons of the soil profile to a depth of 13 m below surface level. The value for the pH in soil solution was derived by a regression equation with pH-KCl (pH-soil solution=0.82×pH-KCl+1.79, unpublished). In Fig. 2, the soil map of The Netherlands is shown, major soil types (sand, clay, peat and loess soils) can be distinguished.

The geographic variation in total present soil metal concentrations was based on an interpolation procedure of measured concentrations in soil samples,



**Fig. 2** Geographic distribution of major soil types in The Netherlands

taking into account differences in soil properties and land use. This allowed for a more detailed risk assessment than a direct interpolation of measured concentrations, because the number of measured soil concentrations is relatively small compared to the number of measured soil properties. The total present metal concentrations were calculated using a two-step approach (Bonten et al. 2008). In the first step linear regression relations were derived between soil metal concentrations, soil properties (organic matter, clay content, pH-KCl) and land use. The regression models were fitted by ordinary least squares. These regression models were then used to estimate the metal concentrations at the centres of the 250×250 m grid. In the second step, the errors of the regression estimates were calculated at the sampling locations of measurements of metal concentrations. These errors are the differences between the estimates obtained with the regression model (first step) and the actual measured concentrations in each point. These errors were interpolated to the grid centres using simple kriging (Goovaerts 1997), and added to the regression estimates of the first step.

The general relations and the differences for interpolation were derived using a large database that contains analyses of 4,363, 4,373, 3,713 and 3,712 individual soil samples for Cd, Pb, Cu and Zn, respectively. This database contains data from Provincial monitoring Networks, the National Soil Monitoring Network of RIVM and the former Institute for Soil Fertility in Haren as summarized in Brus et al. (2002), combined with data from a recent survey of metal background concentrations (Lamé et al. 2004) and more recent data from the provincial monitoring networks. The metal contents reported are 'total' contents, usually determined with Aqua Regia. Samples from locations with specific (point) source contaminations were excluded. A distinction was made between samples from agricultural sites and from nature sites. The relations had the following form for the topsoil:

$$\log M_{\text{tot}} = f_0 + f_1 \cdot \log \text{OM} + f_2 \cdot \log \text{clay} + f_3 \cdot \text{pH}_{\text{KCl}} \quad (8)$$

Values for  $f_0$ – $f_3$  are given in Table 12 of the Annex. For the subsoil a depth dependent relation was

derived based on subsoil samples and topsoil samples from the same sampling point:

$$\begin{aligned} \log M_{\text{tot},z} = & g_0 + g_1 \cdot \log z + g_2 \cdot \log M_{\text{tot},z=0} \\ & + g_3 \cdot \log \text{OM} + g_4 \cdot \log \text{clay} \\ & + g_5 \cdot \text{pH}_{\text{KCl}} \end{aligned} \quad (9)$$

where  $z$  is the depth of the soil layer ( $m$ );  $M_{\text{tot},z}$  is the total metal soil concentration at depth  $z$  ( $\text{mg kg}^{-1}$ ). Values for the regression coefficients  $g_0$ – $g_5$  are presented in Table 13 of the Annex. When attributing metal concentrations to soil layers in the subsoil, the maximum value according the depth dependent relation (Eq. 9) and the background concentration (Eq. 5) was used. These subsoil metal concentrations were used for calculating metal concentrations leaching to surface waters and groundwater.

#### 2.4 Critical Limits for Arable Crops, Animal Products and Water Quality

Critical limits for target receptors include: (1) critical Cd concentrations in plants and acceptable daily intakes of Cd in view of effects on crop growth or animal health and (2) critical dissolved metal (Cd, Pb, Cu and Zn) concentrations in groundwater and in surface water. The reason for the limitation of agricultural impacts to Cd has been described in Section 2.2. The food quality criteria for Cd that were used to make the calculations are given in Table 2.

**Table 2** Overview of fodder and food quality criteria for Cd in view of animal health and human health in  $\text{mg kg}^{-1}$  based on EU regulations EC 1881/2006 (human food) and EC 32/2002 (animal fodder)

| Land use     | Crop        | Quality criterion ( $\text{mg kg}^{-1}$ fw) | % Dry weight    | Quality criterion ( $\text{mg kg}^{-1}$ dw) |
|--------------|-------------|---|-----------------|---|
| Grassland    | Grass       | 1   | 88 <sup>a</sup> | 1.1   |
| Fodder crops | Maize       | 1   | 88 <sup>a</sup> | 1.1   |
|              | Sugar beet  | 1   | 88 <sup>a</sup> | 1.1   |
| Arable land  | Wheat-grain | 0.2   | 85              | 0.24  |
|              | Potato      | 0.1   | 24              | 0.42  |
|              | Lettuce     | 0.2   | 5               | 4.0   |
|              | Endive      | 0.2   | 6               | 3.3   |

<sup>a</sup> In case of grass, maize and sugar beet, the quality criteria do not represent fresh weight but criteria at a dry weight of 12% moisture content (food quality criteria, EU 2001)

Critical limits related to phytotoxic effects on crops are always much higher than food quality criteria for Cd (see also De Vries et al. 2008) and were thus not used here.

The calculated acceptable daily intake (ADI) of Cd in view of a target value of  $1.0 \text{ mg kg}^{-1}$  for the kidney of cows (the most sensitive animal organ) was equal to  $5.8 \text{ mg day}^{-1}$  (De Vries et al. 2008). The ADI in view of impacts on the health of cows, based on NOEC data in  $\text{mg kg}^{-1} \text{ bw day}^{-1}$  for the oral intake of food and soil by Ma et al. (2001) was  $63 \text{ mg day}^{-1}$ . Consequently, only the ADI value in view of human health effects was used to calculate the critical soil Cd concentrations.

Critical dissolved metal concentrations in groundwater and in surface water used are listed in Table 3. For groundwater, critical limits used included drinking water quality criteria (WHO 2004) and target values for groundwater used in The Netherlands (TV-NL, VROM 2007). WHO drinking water limits appear to be much higher than Dutch target values and the latter were thus crucial in assessing the risk of present metal leaching from agriculture in The Netherlands. For surface waters, maximum tolerable risk (MTR) values, based on NOEC data for impacts on aquatic organisms (Crommentuijn et al. 1997) were used for The Netherlands. Equivalent values used across the EU are based on recent Risk Assessment reports for Cd (European Chemicals Bureau 2007), Cu (European Copper Institute 2007), Pb (Lead Development Association International 2007) and Zn (National Institute of Public Health and Environment (RIVM) 2004). For both the Dutch MTR as well as the EU-RAR values a separate analysis was performed to test the sensitivity of the results for the differences between both sets of critical limits. For Cd, Pb and Zn EU-RAR based critical limits are slightly lower than those used in The Netherlands (MTR), whereas the reverse is true for Cu, the EU RAR being approximately five times as high as the MTR NL (Table 3).

The ways in which bioavailability has been accounted for in deriving MTR values for aquatic organisms in the EU RAR's depends on the metal of interest. For Pb, bioavailability is not yet implemented at all. For Cd, the effect of hardness is the main factor controlling bioavailability considered at present whereas for Cu and Zn effects of pH, DOC and hardness are accounted for. The presented MTR

**Table 3** Overview of critical limits used to calculate critical limits (all in  $\mu\text{g l}^{-1}$  dissolved)

| Metal | Critical limit groundwater ( $\mu\text{g l}^{-1}$ ) |       | Critical limit surface water ( $\mu\text{g l}^{-1}$ ) |                  |
|-------|---|-------|---|------------------|
|       | Drinking water value <sup>a</sup>                   | TV NL | EU RAR  | MTR NL           |
| Cd    | 3   | 0.4   | 0.19  | 0.4 <sup>b</sup> |
| Pb    | 10  | 15    | 9.5   | 11 <sup>b</sup>  |
| Cu    | 2,000   | 15    | 7.8   | 1.5 <sup>b</sup> |
| Zn    | 3,000 <sup>a</sup>                                  | 65    | 8.8 <sup>c</sup>                                      | 9.4 <sup>b</sup> |

<sup>a</sup> These values were not used in Dutch drinking water value, no WHO value available

<sup>b</sup> The MTR values for the Netherlands are the sum of the PNEC-added plus a background value. PNEC-added values for Cd, Pb, Cu and Zn are 0.34, 11.0, 1.1, and 6.6  $\mu\text{l}^{-1}$  respectively. Background additions for Cd, Pb, Cu and Zn are 0.08, 0.44, 0.15, and 2.8  $\mu\text{l}^{-1}$  respectively. The resulting MTR levels are truncated

<sup>c</sup> The EU-RAR value for Zn is based on a PNEC-added of 7.8  $\mu\text{l}^{-1}$  (RIVM 2004) and a background correction of 1.0  $\mu\text{l}^{-1}$

values refer to a specific ‘average’ water composition. Also a safety factor of 2 is applied for Cd and Zn accounting for aspects such as the endpoints and the diversity and representativity of the taxonomic groups covered. For Pb and Cu, such a safety factor is not included.

For Cd, Pb and Cu, the critical limits in the EU RAR’s values refer to a total dissolved concentration, but for Zn the value refers to an *added* concentration. This requires the use of a background Zn concentration. The natural background level for dissolved zinc concentrations determined for Dutch surface water is equal to 1.0  $\mu\text{g l}^{-1}$  (Van de Meent et al. 1990), equal to the background level for the North Sea (Cleven et al. 1993). This deviates from the background correction used in the derivation of the Dutch MTR where a background value of 2.8  $\mu\text{g l}^{-1}$  was used (Crommentuijn et al. 1997) but the resulting critical limits are virtually identical (MTR-NL, 9.4  $\mu\text{g l}^{-1}$ ; EU-RAR, 8.8  $\mu\text{g l}^{-1}$ ).

### 3 Results

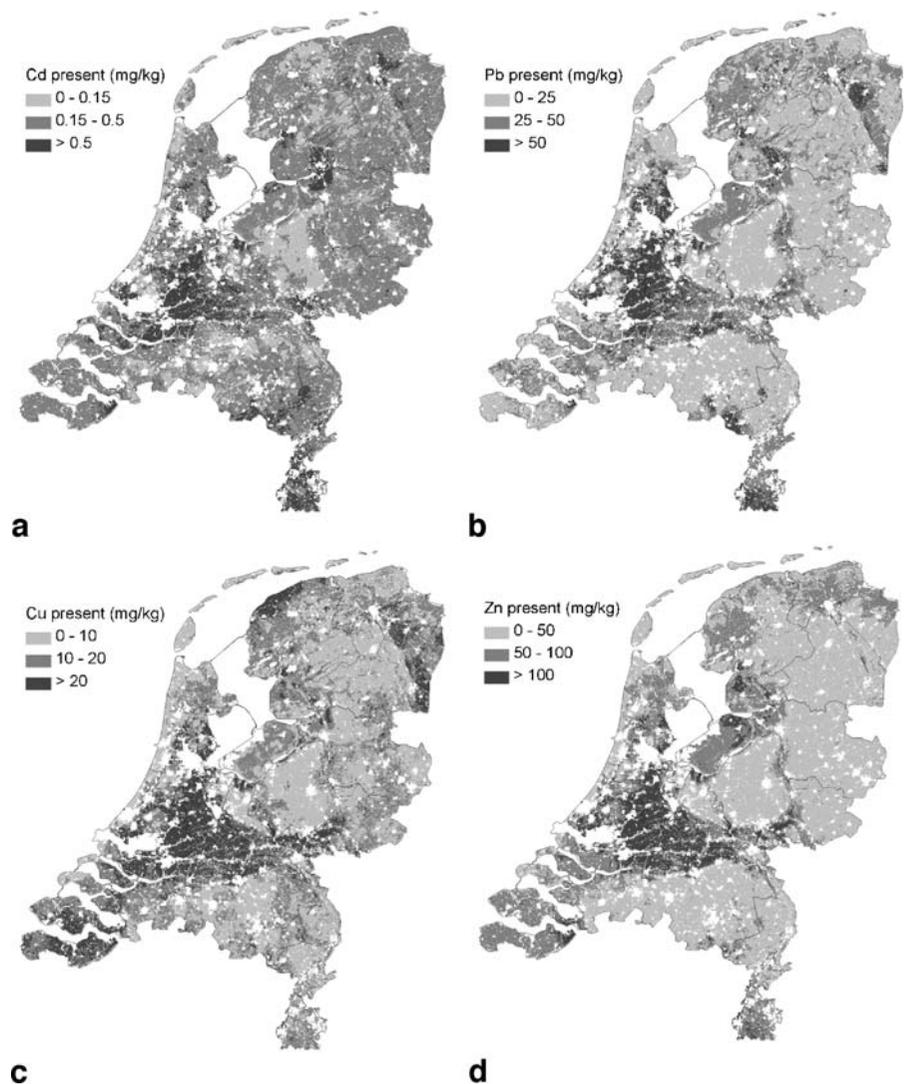
*Present Soil Metal Concentrations* The geographic variation in present soil metal concentrations is shown in Fig. 3. The concentrations are highly correlated with the soil type. Concentrations are consistently

highest in peat soils in the Western part of The Netherlands, which is due to the large capacity of these soils to retain metals. Furthermore, household waste has been applied as fertilizer during the Middle Ages which resulted in elevated copper and lead concentrations in peat soils. Furthermore, concentrations are higher in clay soils compared to sandy soil due to the larger metal retention capacity of these soils. For most metals, concentrations in agricultural areas are higher than those in nature areas, which is related to the use of manure (Cu, Zn) and P-fertilizer (Cd). Also higher pH levels in arable soils ranging from 5.5 to 7 cause a higher retention of metals compared to nature soils where pH levels as low as 3.5 can be found. At near neutral pH, metals added to the soil are retained much more efficient than at pH levels below 5.0.

For lead, historical atmospheric deposition from traffic is the most important source of soil surface loads, which is demonstrated by the fact that lead concentrations in agriculture and nature areas are comparable. Also, lead is less susceptible to leaching at lower pH levels compared to cadmium or zinc, which explains the retention in nature soils as well. Apart from the peat soils, cadmium, lead and to a lesser extent zinc levels are high in the Kempen area (see Fig. 2) on the border of Belgium and The Netherlands. This is related to historic emission from cadmium and zinc smelters in the area. At present, emission rates are strongly reduced due to the shift from a thermal ore treatment to an electrochemical procedure. The elevated cadmium levels in the southern part of The Netherlands are partly of geological origin (different parent material: loess soils) and partly due to elevated atmospheric deposition from nearby industrial zones in Germany (Ruhrgebiet) and Belgium (Liège area).

*Impacts on Agriculture* Agricultural impacts were only derived for Cd, because soil-plant relationships were not significant for Pb and Cu and critical limits for Zn in plants or animal organs are much higher than maximum present Zn concentrations (see Section 2.2). Present soil concentrations of Cd remained below the critical limit for wheat but exceeded critical soil Cd concentrations based on food quality criteria for cows on 7% of the peat soils in the most contaminated western part of The Netherlands (data not shown).

**Fig. 3** Geographic variation in the present concentration of cadmium (a), lead (b), copper (c) and zinc (d) in soils(0–30 cm) throughout The Netherlands



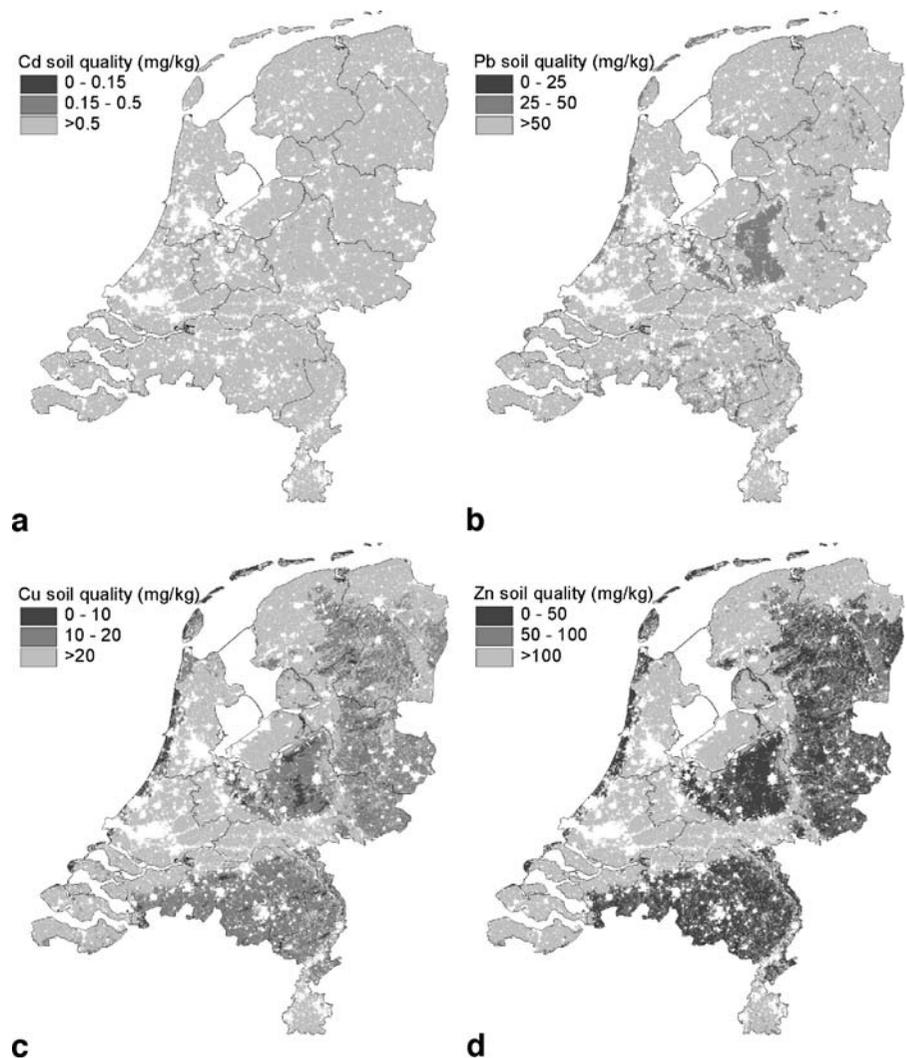
*Impacts on Ecology* The geographic variation in calculated critical soil metal concentrations for Cd, Pb, Cu and Zn in view of ecological impacts on soil organisms and plants is shown in Fig. 4. To enable the comparison with the present concentrations, we used the same legend. However, we reversed the colour code from dark gray (low) to light gray (high), since high critical concentrations imply less risk than low critical concentrations. Results show that the highest critical concentrations for all metals are calculated for soils with high binding capacities, i.e. clay and peat soils.

In Table 4 the average present concentrations of Cd, Pb, Cu and Zn are compared with the average critical concentrations for the ecological impacts on

soil organisms and plants. Results indicate that present concentrations of Cd, Pb, Cu and Zn exceed the critical concentrations only in a very small area. Critical limits are exceeded in all soil types, but the total area where critical limits exceed present metal levels remains below 1 to 2% (Table 4). Critical limits in sandy soils are exceeded mainly in the Kempen area (see Fig. 3), whereas exceedances in peat soils are confined to the Western part of The Netherlands.

*Impacts on Surface Water and Groundwater Quality* The geographic variation in calculated present dissolved concentrations in surface water is shown in Fig. 5. Areas where dissolved concentrations exceed the EU

**Fig. 4** Geographic variation in the critical concentrations of cadmium (a), lead (b), copper (c) and zinc (d) in view of ecological impacts on soil organisms and plants (soil quality) in The Netherlands



RAR values are shown in middle gray, those that exceed the Dutch MTR values are shown in dark gray. For copper shades are reversed because the EU RAR exceeds the Dutch MTR value. Cadmium levels in water bodies hardly ever exceed either the EU RAR or the Dutch MTR guidelines. For lead, EU RAR values are exceeded in most parts of The Netherlands, while Dutch MTR values are exceeded only in a small area. For copper, EU RAR values are exceeded in a small part in the peat area in the Western part of The Netherlands, while Dutch MTR values are exceeded in a significantly larger area. For zinc, both guidelines are exceeded on a large scale across The Netherlands. Leaching losses are especially high in peat soils with superficial groundwater levels. In these soils, leaching to groundwater

predominantly takes place from the upper soil layers, which generally contain the highest metal concentrations.

Results for the average present dissolved metal concentrations and the exceedance of the critical limits for Cd, Pb, Cu and Zn in view of groundwater (drinking water) and surface water quality are summarized in Table 5. Results show that a substantial exceedance of ground water critical limits only occurs for Pb in view of the drinking water limit (17% of the area). An exceedance of critical limits for surface water is consistently low for Cd and Pb (<3%), high for Zn (41–43%) but for Cu it strongly varies from a low (5.3%) to a considerable exceedance (39%) depending upon the criterion used.

**Table 4** Average present concentrations and critical concentrations for cadmium, lead, copper and zinc and the area (in % of total) where actual concentrations exceed the critical concentrations considering ecological effects (values between brackets are equal to the 5 and 95 percentile levels)

| Metal | Soil type | Average present concentrations (mg kg <sup>-1</sup> ) |             | Average critical concentrations (mg kg <sup>-1</sup> ) |           | % Exceedance |
|-------|-----------|---|-------------|--|-----------|--------------|
| Cd    | Sand      | 0.19  | (0.08–0.33) | 1.4  | (0.6–2.2) | 0.05         |
|       | Clay      | 0.32  | (0.15–0.60) | 5.2  | (2.5–7.2) | 0            |
|       | Peat      | 0.44  | (0.18–0.86) | 7.1  | (4.0–11)  | 0.05         |
| Pb    | Sand      | 16  | (9.0–23)    | 57   | (32–75)   | 0.30         |
|       | Clay      | 31  | (18–50)     | 106  | (76–136)  | 0.04         |
|       | Peat      | 52  | (20–120)    | 182  | (105–275) | 0.65         |
| Cu    | Sand      | 6.8   | (1.8–13)    | 16   | (8.6–21)  | 0.57         |
|       | Clay      | 16  | (6.9–28)    | 35   | (22–54)   | 1.7          |
|       | Peat      | 21  | (6.7–45)    | 69   | (31–119)  | 1.5          |
| Zn    | Sand      | 19  | (6.5–36)    | 48   | (28–67)   | 0.6          |
|       | Clay      | 72  | (39–123)    | 166  | (106–230) | 1.1          |
|       | Peat      | 69  | (20–149)    | 200  | (67–348)  | 0.78         |

#### 4 Discussion and Conclusions

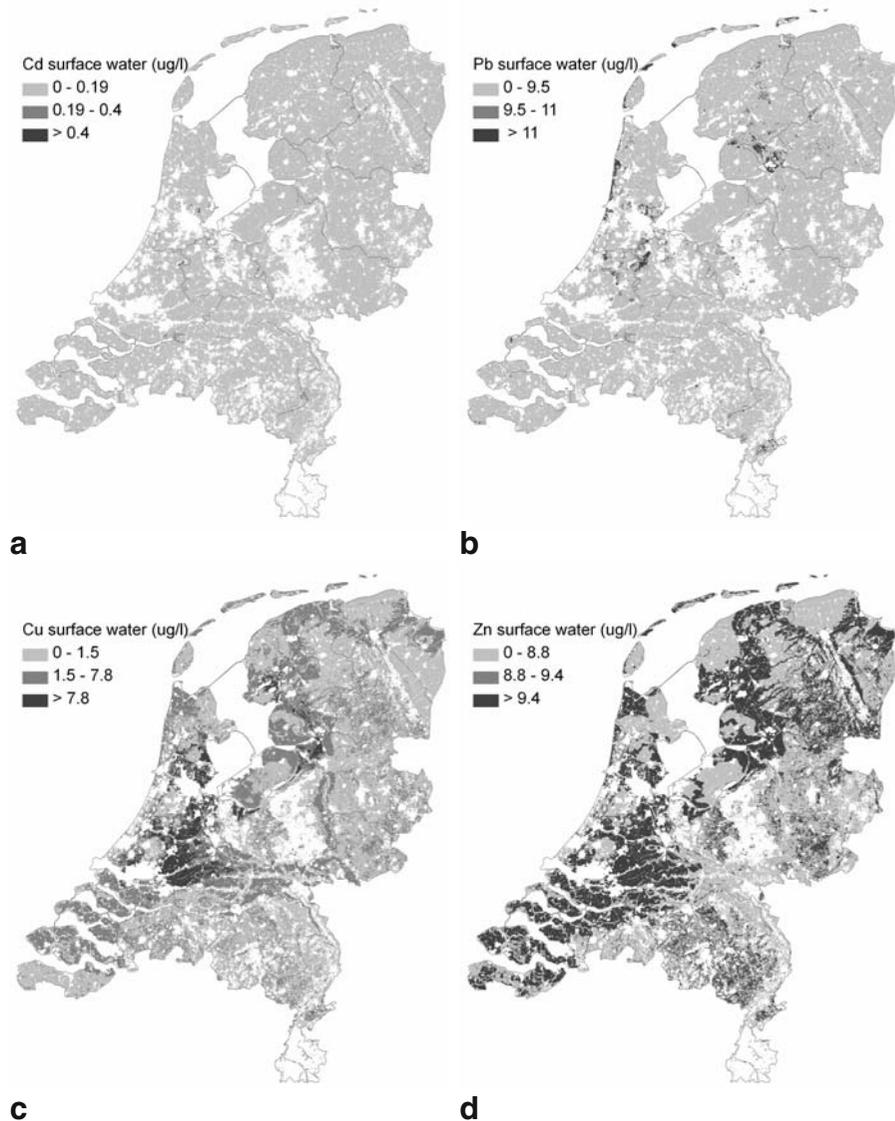
The methodology and results presented in this paper illustrate the applicability of an integrated risk assessment of present soil metal concentrations on a regional scale. The approach allows for an allocation of areas where adverse effects of heavy metal contamination can be expected. For The Netherlands, risks of present soil metal concentrations related to agriculture and ecosystems appear to be low, but risks in view of surface water quality can be large, depending on the critical limit used. An issue left untouched in the calculations is the effect of uncertainty in (input) data, critical limits and model approaches on the calculated size of the areas affected. Below we discuss the most important factors in the presented approach influencing the reliability of the results.

*Reliability of the Approach* The results of this study are subject to uncertainties in the models/concepts, input data and critical limits. With respect to the *model*, the approach is based on empirical relationships of which the validity and reliability is highly determined by the uncertainty in the regression coefficients. This involves the partitioning relations that describe the metal transfer from soil to plants, reactive to total soil and transfer from soil to soil solution. An indication of the uncertainty of these transfer functions is given by the value for  $R^2$  and by the standard error of the  $y$ -estimate, as presented for all the functions in the [Annex](#). These tables show that

the reliability of the relationship between reactive and total metal concentrations, relevant for the ecological risk assessment is high, whereas there is more uncertainty in the soil–plant relationships, relevant for the ecological risk assessment, and in the soil–solution relationships, that are most relevant for assessing risks on water quality.

Regarding the *data*, uncertainties in soil properties and hydrological characteristics influence the reliability of this risk assessment approach on a national or regional scale. Uncertainties in soil properties affect both the calculated critical and present soil metal concentrations in view of agricultural and ecological impacts. Fortunately, the soil properties have a similar effect on both present and critical concentrations in the soil (e.g. an overestimation of the organic matter content will lead to an overestimation of both the present and the critical concentrations). However, uncertainties still can lead to different outcomes regarding the difference between critical and present concentrations, as illustrated in [Fig. 6](#). Here we performed a Monte-Carlo simulation on a sandy soil sample (OM=3%, clay=1%, pH-KCl=5.5). We calculated critical and present concentrations of Cu, assuming a maximum uncertainty of 30% for both OM and clay content and 0.5 units for pH-KCl. The figure shows that when using the average original values (large circles) no exceedance of the critical limit was calculated. However, for the Monte-Carlo simulation, in approximately 20% of the cases present concentrations exceed critical concentrations. Even though the averages of the

**Fig. 5** Geographic variation in the present dissolved concentrations of Cd (**a**), Pb (**b**), Cu (**c**) and Zn (**d**) in surface water in The Netherlands



present and critical Cu concentrations of all calculations were very close to the values that are derived when using the average data for the soil properties, there can thus be an impact on the area exceeding critical limits. The results show that the impacts of uncertainties are generally larger on the critical concentrations than on the present concentrations, implying that the eventual effects on the difference between present and critical concentrations can not be neglected, especially when the difference is small. Fortunately, for most areas critical concentrations are much larger than present concentrations and this holds even more for the other metals.

Uncertainties in soil properties used partly arise by the use of geographically average values. Averaging data on a certain spatial resolution, such as the STONE plots used in this study, will neglect the variation in soil properties within each geographical unit and therefore will neglect possible exceedances of critical concentrations for some parts of a geographical unit.

Ideally, both the range and the uncertainty in soil properties within each geographical unit should be taken into account.

For groundwater and surface waters, critical concentrations are fixed values and not related to soil properties. Uncertainties in calculated present con-

**Table 5** Ranges (5–95%) in present dissolved metal concentrations, critical dissolved concentrations in view of ground water quality and surface water quality (fixed values) and the area (in % of total) where critical concentrations are exceeded

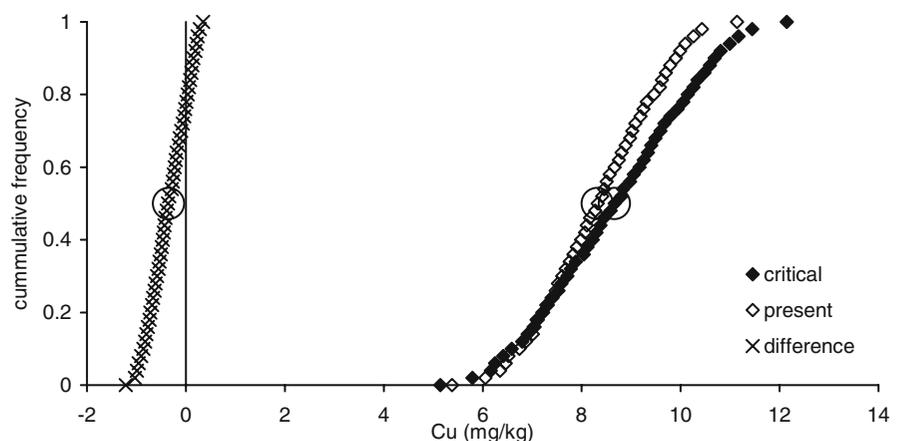
| Metal | Compartment   | Limit          | Present concentration ( $\mu\text{g l}^{-1}$ ) | Critical concentration. ( $\mu\text{g l}^{-1}$ ) | % Exceeded (area) |
|-------|---------------|----------------|--|--|-------------------|
| Cd    | Groundwater   | Drinking water | 0.0018–0.15                                    | 3  | 0                 |
|       |               | Target value   | 0.0018–0.15                                    | 0.4  | 0.72              |
|       | Surface water | EU RAR         | 0.0044–0.086                                   | 0.19   | 0.32              |
|       |               | MTR NL         | 0.0044–0.086                                   | 0.4  | 0.03              |
| Pb    | Groundwater   | Drinking water | 1.9–14.7                                       | 10   | 17                |
|       |               | Target value   | 1.9–14.7                                       | 15   | 4.7               |
|       | Surface water | EU RAR         | 1.8–9.1  | 9.5  | 3.0               |
|       |               | MTR NL         | 1.8–9.1  | 11   | 1.6               |
| Cu    | Groundwater   | Drinking water | 0.090–9.7                                      | 2,000  | 0                 |
|       |               | Target value   | 0.090–9.7                                      | 15   | 0.60              |
|       | Surface water | EU RAR         | 0.18–8.4                                       | 7.8  | 5.3               |
|       |               | MTR NL         | 0.18–8.4                                       | 1.5  | 39.1              |
| Zn    | Groundwater   | Drinking water | 0.46–132                                       | 3,000  | 0                 |
|       |               | Target value   | 0.46–132                                       | 65   | 7.4               |
|       | Surface water | EU RAR         | 0.79–55  | 8.8  | 43.0              |
|       |               | MTR NL         | 0.79–55  | 9.4  | 41.0              |

centrations in groundwater and surface water are only partly due to uncertainties in soil properties. Although, considering the limited soil data in the subsoil, there is a special need for more detailed information here. However, the uncertainties are more determined by the hydrological fluxes and groundwater tables. For example, a higher groundwater table results in an increased drainage from more superficial soil layers. These superficial soil layers contain higher levels of metals which leads to higher calculated pore water concentrations and, ultimately, also in higher lateral outflow fluxes.

The uncertainty in *critical limits* in view of ecological impacts is specifically influenced by differences in metal toxicity of laboratory spiked soil and

field-contaminated soils. In laboratory spiked soil the availability of added metals is higher than that in field-contaminated soils due to: (1) metal-induced acidification due to hydrolysis of the metal in solution and displacement of protons from the solid phase, (2) higher ionic strength of the soil solution, reducing the sorption of cationic metals in soil and (3) the assumed slow ageing reactions which metals undergo in the field (McLaughlin et al. 2004). Comparison of field and laboratory NOEC soil data in the EU Risk Assessment Reports for Cu, Pb and Zn indeed showed that critical limits derived from field data were consistently higher than those derived from laboratory experiments. Consequently, laboratory to field conversion factors were derived to correct the

**Fig. 6** Monte-Carlo simulations of present and critical Cu concentrations using uncertainties in organic matter content, clay content and pH. Large circles show the average values for OM (=3%), clay (=1%) and pH (=5.5). Difference is present minus critical



laboratory-based critical limit to relevant limits for field conditions. These factors range from 4 for Pb, 3 for Zn, 2 for Cu and 1 for Cd.

In our study, critical limits are based on laboratory spiked soils, assuming that the amount of metals added to the soil is reactive. The conversion of the reactive fraction to a total level of metals in soils, including an inert fraction, accounts for the assumed slow ageing reactions which metals undergo in the field. The calculated average ratio between the total and reactive metal concentration, which ranges from 1.2 for Cd, 1.5 for Pb, 2.2 for Cu to 4.0 for Zn (Table 6) is quite comparable to the laboratory to field factors used in the EU Risk Assessment Reports. This again implies that a correction for ageing could be an important aspect for Zn and to a lesser extent also for Cu. The slightly higher values found in our approach for Cd, Cu and Zn imply that we may slightly overestimate the critical concentration of these metals, possibly by neglecting the laboratory artefacts in the approach. Such artefacts include metal-induced acidification and differences in ionic strength. The much lower correction factor for Pb, which can be related to an overestimation of the reactive fraction for lead in the dilute nitric acid extraction (Weng et al. 2002; Bonten et al. 2007, submitted), implies that we may slightly underestimate the critical concentration of this metal.

Another aspect that affects the reliability of the critical limits in view of ecological impacts is the uncertainty in background metal concentrations to be added. The NOEC data used are based upon toxicity test data in which the critical concentrations of the metal are expressed as a dose of metal added to the soil. Metals naturally present in the test soil are not considered. This means that the critical metal concentrations in the field, calculated by the critical

limit functions, represent the critical increase in excess of the natural background concentration. In this approach, the critical limit is expressed by adding a background field concentration, but it would be more appropriate to include the background metal in the toxicity test soils. By collating the background soil metal concentrations available for the toxicity test soils or assess methods for their estimation, the critical limit functions as described in Eq. 3 can be updated to derive critical limits for reactive cadmium, lead, copper and zinc.

*Applicability of the Approach* In past, critical limits derived from NOEC data for metals have not been used in The Netherlands since the limits (MPCs being the 5 percentile values of NOEC data) thus derived appeared to be lower than present concentrations of heavy metals in unpolluted areas. Instead, target values were based on actual metal concentrations from non-polluted areas considering a correction for organic matter and clay content (Edelman and de Bruin 1986). A similar approach is used in most other European countries. This implies that risks related to metal transfer from soil to plants, water and organisms are not considered as such although it is reasonable to assume that levels of metals in non-polluted natural areas pose no significant threat to the target receptors addressed in this study. Furthermore, these levels were not meant to serve as risk levels in the first place but rather as target levels. Recently, the Dutch government decided to use new monitoring data on present metal concentrations from selected non-polluted areas (Lamé et al. 2004) as a basis for target values of heavy metals. One of the reasons of using these fixed levels instead of risk based (ecological) threshold values was that the latter were simply the 5 percentile values of NOEC data, being far below current background levels, giving the appearance that the whole country is at risk. By accounting for: (1) the impact of soil properties, (2) the occurrence of immobile metal and (3) the addition of a geogenic background concentration, this paper, however, indicates that risk based critical limits for impact on ecosystems, are nearly always higher than current levels of metals in soils. Based on the calculations, there is hardly an exceedance of critical soil metal concentrations in view of impacts on soil

**Table 6** Calculated average ratios between total and reactive metal concentrations as a function of soil type in The Netherlands

| Soil | Ratio total/reactive |     |     |     |
|------|----------------------|-----|-----|-----|
|      | Cd                   | Pb  | Cu  | Zn  |
| Sand | 1.2                  | 1.4 | 1.9 | 3.5 |
| Clay | 1.2                  | 1.6 | 2.5 | 5.0 |
| Peat | 1.1                  | 1.4 | 2.1 | 3.3 |
| All  | 1.2                  | 1.5 | 2.2 | 4.0 |

organisms or plants as derived from NOEC data. The same is true for impacts in view of agricultural production. Calculated critical limits as well as target levels in soil based on the approach outlined on this paper can indeed serve as a basis for true risk-based soil quality standards. By including uncertainty analyses, the possible exceedance of a critical limit can be evaluated in a probabilistic manner rather than as a deterministic value, which might provide a stronger basis for future policy evaluation.

**Annex**

Coefficients used in the calculation of metal partitioning relations between plants, soil (total and reactive content) and soil solution.

**Table 7** Values for the coefficients  $a_0$ – $a_3$  and  $n$  in the soil–plant relations for Cd in grass, maize, wheat, potatoes and sugar beet (according to Eq. 1)

| Crop               | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $n$  | $R_2$ | se- $y_{est}$ <sup>a</sup> |
|--------------------|-------|-------|-------|-------|------|-------|----------------------------|
| Grass              | 1.45  | -0.38 | –     | –     | 1.22 | 0.63  | 0.23                       |
| Maize              | 0.90  | -0.21 | –     | -0.32 | 1.08 | 0.62  | 0.26                       |
| Sugar beet         | 1.33  | -0.22 | –     | -0.13 | 0.62 | 0.83  | 0.15                       |
| Wheat <sup>b</sup> | 0.22  | -0.12 | -0.33 | -0.04 | 0.62 | 0.64  | 0.20                       |
| Lettuce            | 2.55  | -0.33 | -0.39 | -0.19 | 0.85 | 0.71  | 0.08                       |

<sup>a</sup>The standard error of the  $y$ -estimate on a logarithmic basis

<sup>b</sup>Relationships for wheat were also used for other cereals

**Table 8** Values for the coefficients  $b_0$ – $b_2$ , in the relations between the critical limit for the reactive soil metal contents of Cd, Pb, Cu and Zn and soil properties (according to Eq. 3)<sup>a</sup>

| Metal | $b_0$ | $b_1$ | $b_2$ |
|-------|-------|-------|-------|
| Cd    | -2.27 | 0.33  | 1.00  |
| Pb    | 0.58  | 0.11  | 0.66  |
| Cu    | 0.26  | 0.02  | 0.68  |
| Zn    | -0.74 | 0.14  | 1.07  |

<sup>a</sup>These results are based on data sets including both NOEC soil data and soil properties from major organisms, drawn from several draft reports on EU Risk Assessment procedures for these metals as presented in De Vries et al. (2007a)

**Table 9** Values for the coefficients  $c_0$ – $c_3$  in the relationship between reactive, (0.43N HNO<sub>3</sub>), and pseudo-total (aqua regia) soil concentrations of Cd, Pb, Cu and Zn (Eq. 4), using a Dutch dataset (Römkens et al. 2004).The relationships hold for both  $M_{tot}$  and  $M_{re}$  in mg kg<sup>-1</sup>

| Metal | $c_0$ | $c_1$ | $c_2$  | $c_3$ | $R_{adj}^2$ | se- $y_{est}$ <sup>a</sup> |
|-------|-------|-------|--------|-------|-------------|----------------------------|
| 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                       |
| Cu    | 0.318 | 0.761 | 0.044  | 0.191 | 0.94        | 0.10                       |
| Zn    | 0.614 | 0.753 | -0.107 | 0.275 | 0.96        | 0.12                       |

<sup>a</sup>Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 Mol l<sup>-1</sup> HNO<sub>3</sub> and Aqua Regia (Römkens et al. 2004). The dataset consists of a large variety of soil types with a relative wide variety in soil properties, such as the organic matter (median of 4% and 95-percentile of 14%) and clay content (median of 13% and 95-percentile of 36%). The dataset comprises both polluted and unpolluted soils

**Table 10** Values for the coefficients  $d_0$ – $d_3$  in the relationship estimating background concentrations of Cd, Pb, Cu and Zn from soil properties (according to Eq. 5)

| Metal | $d_0$  | $d_1$ | $d_2$ | $d_3$ | $R^2$ |
|-------|--------|-------|-------|-------|-------|
| Cd    | -1.919 | 0.418 | 0.186 | 0.059 | 0.30  |
| Pb    | 0.443  | 0.469 | 0.267 | –     | 0.45  |
| Cu    | -0.142 | 0.481 | 0.594 | –     | 0.57  |
| Zn    | 0.330  | 0.402 | 0.425 | 0.076 | 0.65  |

**Table 11** Values for the coefficients  $e_0$ – $e_3$  and  $n$  in the relationships relating dissolved total concentrations and reactive soil concentrations of Cd, Cu, Pb and Zn, according to Eqs. 6 and 7 (after Römkens et al. 2004)<sup>a</sup>

| Metal | $e_0$ | $e_1$ | $e_2$ | $e_3$ | $n$  | $R^2$ | se- $y_{est}$ |
|-------|-------|-------|-------|-------|------|-------|---------------|
| Cd    | -0.91 | 0.58  | 0.28  | 0.27  | 0.54 | 0.79  | 0.33          |
| Pb    | 0.78  | 0.83  | 0.02  | 0.25  | 0.68 | 0.57  | 0.55          |
| Cu    | 0.41  | 0.48  | 0.18  | 0.16  | 0.47 | 0.62  | 0.35          |
| Zn    | -1.04 | 0.39  | 0.35  | 0.45  | 0.74 | 0.82  | 0.40          |

<sup>a</sup>Regression relations were derived from laboratory experiments with approximately 1,400 soil samples from Dutch locations (Römkens et al. 2004). More information on the derivation is given in De Vries et al. (2007b)

**Table 12** Values for the coefficients  $f_0$ – $f_3$  in the relationships relating present total soil concentrations of Cd, Cu, Pb and Zn, and soil properties according to Eq. 8, with  $M_{\text{tot}}$  in  $\text{mg kg}^{-1}$ 

| Metal       | $f_0$  | $f_1$ | $f_2$ | $f_3$ | $R^2$ | se- $y_{\text{est}}$ |
|-------------|--------|-------|-------|-------|-------|----------------------|
| Agriculture |        |       |       |       |       |                      |
| Cd          | -1.152 | 0.380 | 0.138 | 0.033 | 0.20  | 0.36                 |
| Cu          | 0.407  | 0.420 | 0.228 | 0.026 | 0.37  | 0.31                 |
| Pb          | 0.799  | 0.456 | 0.251 | –     | 0.43  | 0.29                 |
| Zn          | 0.757  | 0.327 | 0.366 | 0.056 | 0.54  | 0.25                 |
| Nature      |        |       |       |       |       |                      |
| Cd          | -1.540 | 0.654 | –     | 0.058 | 0.41  | 0.42                 |
| Cu          | -0.359 | 0.647 | 0.271 | 0.073 | 0.67  | 0.33                 |
| Pb          | 0.774  | 0.554 | 0.218 | –     | 0.59  | 0.32                 |
| Zn          | -0.046 | 0.563 | 0.282 | 0.169 | 0.71  | 0.32                 |

**Table 13** Values for the coefficients  $g_0$ – $g_5$  in the relationships relating present total soil concentrations of Cd, Cu, Pb and Zn, at a certain depth with the concentration in the topsoil and soil properties, according to Eq. 9

| Metal | $g_0$  | $g_1$  | $g_2$ | $g_3$ | $g_4$ | $g_5$ | $R^2$ | se- $y_{\text{est}}$ |
|-------|--------|--------|-------|-------|-------|-------|-------|----------------------|
| Cd    | -0.496 | -0.354 | 0.382 | 0.174 | 0.261 | 0.011 | 0.44  | 0.45                 |
| Pb    | 0.364  | -0.351 | 0.102 | 0.372 | 0.650 | 0.009 | 0.64  | 0.43                 |
| Cu    | 1.141  | -0.560 | 0.191 | 0.312 | 0.369 | 0.014 | 0.55  | 0.38                 |
| Zn    | 0.343  | -0.111 | 0.146 | 0.320 | 0.466 | 0.071 | 0.69  | 0.32                 |

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