Prediction of the long term accumulation and leaching of zinc in Dutch agricultural soils: a risk assessment study

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A dynamic model was used to predict future soil Zn concentrations at ongoing present Zn inputs until steady state is reached (Predicted Effect Concentrations at steady state or PEC steady state) in comparison to the Predicted No Effect Concentration (PNEC) of Zn. The main aim of this report is to evaluate whether the current load of zinc to soils in different forms of land use (arable land, pasture) and soil types leads to an exceedance of the PNECs, and if so at what time scale. Results show that at present there is hardly any exceedance of the PNEC of zinc in the Netherlands. The percentage of plots where PEC steady state will exceed the PNEC is estimated at approximately 50% when using current (year 2000) inputs and this number appears to be very robust. The predicted time period to reach the PNEC for zinc is on average approximately 250 years for grassland and 650 years for arable land when using current inputs. This number is however very uncertain. When respecting the N legislation, this time period increases to approximately 600 years for grassland and 700 years for arable land.

Keywords: agro-ecosystems, heavy metals, balances, critical loads, dynamic models, soil accumulation, leaching, critical limits, target values, transfer functions

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Preface

Recently, a Risk Assessment report (RAR) has been written for Zinc in which the risk of Zn is based on the so-called added risk principle. This implies that the critical or Predicted No Effect Concentration (PNEC) of Zn is equal to a background concentration (here defined as ambient concentration excluding historically polluted sites) and a given Predicted No Effect Concentration of added zinc ($PNEC_{add}$). Using this approach, it is relevant to know whether there will be an exceedance of the PNEC of Zn in rural (agricultural areas) in the future at ongoing Zn inputs, and if so how large the exceedance will become and at what time in future the PNEC is exceeded.

In this context, the International Zinc Association Europe requested Alterra to assess zinc balances for Dutch agricultural soils and make a prediction of future soil Zn concentrations at ongoing present Zn inputs (Predicted Effect Concentrations at steady state or $PEC_{steady\ state}$) in comparison to a critical or Predicted No Effect Concentration (PNEC) of Zn. The main aim of this report is to evaluate whether or not the current load of zinc to soils in different forms of land use (arable land, pasture) and soil types leads to an exceedance of the PNECs, and if so at what time scale.

The Zn input was based on the estimated input by animal manure, fertiliser, atmospheric deposition and other inputs, such as compost and pesticides, at more than 4500 plots in the year 2000. Impacts of expected reduced manure application rates were also calculated. The PNEC of Zn was derived from a calculated ambient Zn concentration excluding historically polluted sites and a given Predicted No effect Concentration of added zinc ($PNEC_{add}$). The future soil Zn concentration was based on a modelled net Zn accumulation or release over several hundreds of years in agricultural top soils until a new steady-state situation was reached. The project focused on Zn concentrations in the upper topsoil and does not include an estimate of the concentrations of zinc in surface waters via run-off or leaching from the agricultural soils, although this item is important for the risk management phase on zinc, since the PNEC in the RAR focused on soils.

The Netherlands was chosen as a 'guide' country, not only because regional data on manure loads, atmospheric deposition and crop removal were available but also because the manure inputs in Dutch agriculture are among the highest in Europe. Available information on zinc mass balances in other EU regions has been used to put the results for Dutch agricultural soils into perspective, while taking into account the representativity of the Dutch climatological conditions and land use–soil type combinations for the EU.

The preliminary results were presented at a workshop organised on June 29th, 2004 in which experts involved in the development of the RAR, member states, industry and academic institutes were invited. Using the comments made at this workshop, the model scenarios were slightly adapted and more emphasis was given to the uncertainties of the results obtained.

The authors like to acknowledge the participants at the workshop for their constructive criticism, especially Dr Wim van Tilborg, Dr. Frank van Assche (IZA) and Dr. Dick Sijm (RIVM) for useful comments on the manuscript. Furthermore, we like to thank Prof. Dr. Eric Smolders for sending us data to calculate soil sensitivity factors on the basis of CEC (for plants and invertebrates), and ambient Zn backgrounds (for microbial processes) to account for the differences observed in zinc toxicity on different soils, upon zinc addition in the laboratory. Finally we acknowledge Prof. Dr. Steve Mc Grath who supplied some valuable field data that were used to compare with model calculations.

Summary

Due to import of animal food (and subsequently the production of manure), atmospheric deposition and use of inorganic fertiliser the supply of zinc to soils often exceeds the removal of zinc from soil by crops and by leaching. Accumulation in soil due to the net input of heavy metals in arable systems can lead to unacceptable levels of metals in crops and the soil itself. Apart from crop uptake also leaching of zinc to lower soil horizons and ground- or surface water can be considered as an unwanted effect.

To assess whether or not current forms of agricultural land use lead to accumulation of Zn and, with time, to an exceedance of Predicted No Effect Concentrations (PNEC) for Zn in soils, a model study was performed for Dutch agricultural soils. In this study an evaluation of long-term effects of current day agricultural land use on the zinc content in soils is made on a national scale. The outcome of the study, i.e. does accumulation lead to an exceedance of critical limits (PNECs), strongly depends on *which critical limits* are considered and *which risk assessment approach* is used.

In this study the PNEC for zinc in soils is based on ecotoxicological criteria, using the added risk approach in line with the Zinc Risk Assessment Report (RAR-Zinc). This implies that the PNEC of Zn in soil is equal to a background concentration (here defined as ambient concentration excluding historically polluted sites) and a given Predicted No effect Concentration of added zinc ($PNEC_{add}$). The value of $PNEC_{add}$ for soil was set at 26 $mg.kg^{-1}$, based on laboratory studies, multiplied by a generic factor of 3 to correct for lab-to-field differences in zinc toxicity and a soil type dependent soil sensitivity factor accounting for the differences in zinc bioavailability observed between different soil types (1.0 for (agricultural) sandy soils, 1.2 for "marine" clay, 1.5 for "river" clay and 1.4 for peat as contained in the RAR of 9 February 2004). Other types of risk assessment, e.g. based on a critical concentration in the soil solution, or based on crop quality criteria undoubtedly will yield different results. However an evaluation of the different risk assessment approaches is beyond the scope of this report.

A zinc mass balance model was applied to the whole of the Netherlands using 4647 so-called STONE plots, limiting ourselves to agricultural land use. These plots consist of one or more 500m x 500m grid cells with a unique combination of land use, soil type and ground water table class. Land use was clustered to grassland (pasture) and arable land (including maize land) and soil type was clustered in sand, clay, loess and peat soils.

Geo-referenced data on annual zinc inputs were derived for all individual STONE plots. Total inputs were divided among several important contributors including animal manure, inorganic fertiliser, atmospheric deposition, compost and pesticides. Major sources of Zn inputs varied only slightly between different land uses and soil types. In grassland animal manure contributes most (more than 90%) to the input of

Zn. Fertilisers are a comparatively small source of Zn, whereas atmospheric deposition is also limited but still roughly twice as high as the input from fertilisers. Other sources, mainly compost and pesticides are a significant source in arable land (approximately 15%).

The model simulations for the Dutch agro-ecosystems showed that

- Present Zn inputs of metals exceed the uptake and present leaching at 81% of the plots. This is an indication that present loads to agro-ecosystems in industrialised countries, such as the Netherlands, generally cause an increase in soil Zn concentrations. Zinc accumulation rates are highest in calcareous clay soils due to low leaching- and uptake rates of Zn.
- Present Zn inputs lead to changes in Zn accumulation and leaching rates over a period of several hundreds or even thousands of years, depending on land use type and soil type considered. In general steady state is reached within 100-1000 years for Zn, but it can last up to more than 4000 years Those time scales are an indication for the transition times in fertilised agro-ecosystems.
- The steady-state soil Zn concentrations that ultimately will be reached differ strongly from the present Zn concentrations in soil. On average, steady state levels are five times higher than current day levels of zinc in soils. Consequently, at steady state the Predicted No Effect Concentration (PNEC) of Zn is predicted to be exceeded at 53% of the plots whereas the present exceedance is less than 1%. Time periods to reach those values are however long (100 - > 4000 years).

Relevant conclusions for the RAR Zink that can be drawn from this model study include:

- In the Netherlands, there is hardly any exceedance today of the PNEC of zinc. Plots where at present PNECs are exceeded only include historically polluted sites, such as the "Toemaakdekken" or floodplain soils.
- The percentage of plots where the predicted steady state zinc content will exceed the PNEC is estimated at 53% when using current (year 2000) inputs and at 47% when the legislation for nitrogen will be respected.
- The predicted time period to reach the PNEC for zinc is on average approximately 250 years for grassland and 650 years for arable land when using current inputs. When respecting the N legislation, this time period increases to approximately 600 years for grassland and 700 years for arable land.

The reliability or plausibility of the results was assessed by comparing model outputs from this study with available Zn accumulation data. Both data from long-term monitoring sites (Rothamsted experimental station) as well as data from regular monitoring networks (Dutch and Swiss sites) were used. Modelled metal balances for arable cropping and dairy farms were in close agreement to field data despite a considerable degree of uncertainty (both in model results and field data). Regionally averaged values of the model results and the data were also in close agreement although the data from Swiss farms showed that local input levels can be extremely high. The use of a model concept such as presented here therefore is useful for regional or national applications but cannot reproduce obvious extremes at the plot level.

The approach (scale, inputs) and focus of this study was based on data from Dutch agro-ecosystems and as such representative for the Netherlands. Nevertheless, the results are likely to be representative for agro-ecosystems in most industrialised countries, that have comparable climatic conditions and soil types (i.e. large parts of north western Europe) as well. Comparison of the modelled values with data on input, output and annual changes in the soil zinc content from the UK, Switzerland and the Netherlands resulted in a good match between data and modelled values.

The outcome of various uncertainty analyses indicated that the area *where* the PNEC for Zinc will be exceeded at steady state can be located with a high degree of confidence. Differences between various scenarios and model assumptions (based on different zinc background levels, Zn inputs, Zn uptake and soil properties) are usually less than 10%. This would imply that at 45 to 55% of all plots the PNEC for Zn will be exceeded at steady state.

In contrast to the certainty with which we can predict *where* PNECs can be exceeded, much more uncertainty exists about *when* this PNEC will be exceeded. Clearly differences in soil type (soil acidity, organic matter content etc.) either speed up or retard the process of accumulation as is the case with the level of input (levels of zinc in manure, atmospheric deposition). This is of importance since the urgency to take measures partly depends on the time frame involved. Despite the fact that the current approach allows for a more or less accurate allocation of sites where the PNEC will be exceeded, its capacity to predict when this will happen seems to be hampered by a lack of accuracy of input data. This clearly stresses the need for reliable input data (soil data, data on input levels in manure and fertiliser) as well as validated model concepts.

1 Inleiding

Background

Recently, a Risk Assessment report (RAR) has been written for Zinc in which the risk of Zinc is based on the so-called added risk principle. This implies that the critical Zn concentration (also defined as Predicted No effect Concentration or PNEC) is equal to a background concentration (defined in this report as ambient concentration excluding historically polluted sites) and a Predicted No effect Concentration of added zinc ($PNEC_{add}$). The main aim of this report is to evaluate whether or not the current load of zinc to soils in different forms of land use (arable land, pasture) and soil types leads to an exceedance of this critical limit, and if so at what time scale. Issues to address and/or clarify included the assessment of:

- Zinc background concentrations in the Netherlands for use in the risk characterisation.
- Present zinc mass balance in different land use and soil types of agricultural soils, subject to different patterns of agricultural practice.
- Zinc mass balances towards the future for the different land use and soil types, using a dynamic model, and integrating the effects of current legislation and policy measures.
- Present and predicted steady state zinc concentrations against the critical limit (Predicted No effect Concentration or PNEC as defined above) for soil.

The study focused on a prediction of the net Zn accumulation or release rate over several hundreds of years in the plough layer (0-30 cm) of arable land and in the top 0 - 10 cm layer in grassland soils) to define whether or not the steady-state Zn concentration will exceed a given no-effect value, and if so, when this will happen. Furthermore, the study focused on the derivation of the zinc background level and calculation of zinc mass balances of agricultural soils in the Netherlands, which has been considered to be a model region for the zinc risk assessment. The Netherlands is proven to be a realistic worst-case region for intensity of agricultural practice in the EU. Available information on zinc mass balances in other EU regions will be used to put the results for Dutch agricultural soils in an EU perspective, while taking into account the representativity of the Dutch climatological conditions and land use – soil type combinations for the EU.

Problems related to an excess of heavy metals

In the Netherlands, there is a concern about the excessive inputs of heavy metals in agriculture, specifically Cd, Cu and Zn (e.g. Moolenaar & Lexmond, 1998). An excess of those heavy metals in agro-ecosystems may result in agricultural products with unacceptable levels, violating food quality criteria, and even reduced crop production (Alloway, 1990; Fergusson, 1990). Apart from adverse impacts on food quality and crop growth, elevated metal concentrations may affect soil organisms, including micro-organisms (Bååth, 1989), nematodes (Bengtsson & Tranvik, 1989) and earthworms (Ma & van der Voet, 1993). Protection of these organisms is relevant to sustain so-called "Life Support Functions", such as decomposition processes, which control the nutrient cycle of elements. Finally, elevated inputs may cause an increase in leaching losses of metals to ground water and surface water, thus affecting drinking water quality and aquatic organisms, respectively (Crommentuijn et al., 1997).

A simplified overview of major pathways of heavy metals in agro-ecosystems, including the most relevant receptors in view of ecotoxicological effects (thus excluding humans and animals) is given in Figure 1. Major pathways are soil to solution transfer (mobilisation) followed by plant uptake and leaching to groundwater and surface water (De Vries et al., 2002).

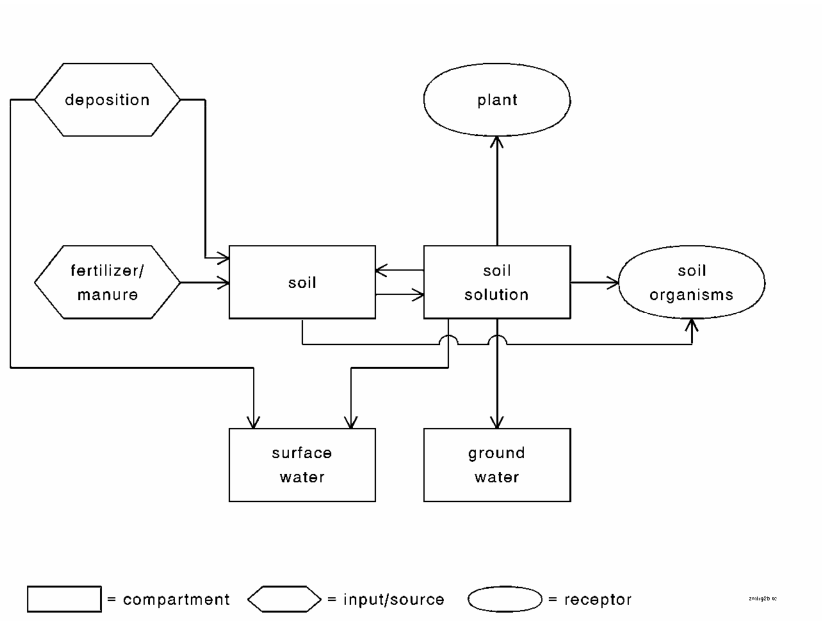

Figure 1 Overview of major pathways of heavy metals in agro-ecosystems

Metal balances
Insight into present metal accumulation and leaching rates in agricultural systems can be derived by balances describing all inputs to the soil, by both fertilisers/animal manure and atmospheric deposition, and all outputs in terms of plant uptake and leaching. Such metal balances can be derived for the field scale and the farm scale. A field scale balance refers to the inputs and outputs to and from the soil compartment (the plough layer) of individual fields, thus allowing the calculation of accumulation in those fields. Field scale balances enable a direct link with criteria for the protection of soil and other relevant environmental receptors. A farm scale balance refers to the inputs and outputs as determined at the farm gate, thus showing the characteristic metal flows onto the farm as a whole and allowing the fine-tuning of metal management at the farm level (Moolenaar, 1998).

The aim of sustainable metal management in agro-ecosystems is to ensure that the soil continues to fulfil its functions in agricultural production, by not restricting nutrient cycling or limiting soil biodiversity. In this context, sustainability can be defined as the situation where (i) no further net accumulation of heavy metals occurs or (ii) accumulation of heavy metals is below critical limits in defined compartments (e.g. soil/soil solution, plants or animal organs). Critical limits or PNECs for heavy metals are generally derived from chronic toxicity data, such as no observed effect concentrations or NOEC's (OECD, 1992). Test organisms in terrestrial systems are microbe-mediated processes, earthworms or arthropods and plants.

In order to get insight in future metal accumulation and leaching rates, use has to be made of models that include the dynamics of uptake and leaching, by relating those outputs to the concentrations in the soil. Such models allow the prediction of metal concentrations in soil, soil solution and plants in time at a given input. They also allow the calculation of time periods before a critical metal concentration or PNEC in soil, soil solution or plants (if ever) is exceeded and time periods that are needed to arrive at steady-state considering the present metal inputs and metal status of the soil.

Aim of the report

Up to now, several papers have been written describing present metal inputs and outputs at the farm or field scale (e.g. Reiner et al., 1996) or the dynamics in metal fluxes at the field scale (e.g. Moolenaar & Beltrami, 1998). An integrated approach, which (i) includes metal balances at the farm scale while making use of field information and (ii) illustrates the use of critical limits in calculating long-term acceptable metal inputs and the time period in which those limits are violated, was presented by De Vries et al., (2002) using data from approximately 100 farms in the Netherlands.

In this report we focus on the fate of Zn input in Dutch agricultural soils by using estimated inputs and outputs of Zn and present Zn concentrations for all Dutch agricultural soils. Use was made of an approach described in De Vries et al. (2002). The application aims to answer the following questions:

- What is the spatial variation in the critical limit or PNEC for Zn in soil, defined as the sum of a spatially variable ambient Zn concentration (excluding historically polluted sites) and a given Predicted No effect Concentration of added Zn?
- To what extend do the present Zn inputs by fertilisers, animal manure atmospheric deposition, compost and pesticides exceed the field outputs by plant uptake and leaching and how large is the net soil release or soil accumulation in response to this input?
- What is the change in accumulation or net release in time and what are the steady-state soil zinc concentrations that will ultimately be reached?
- What is the percentage of plots where the critical limit or PNEC for Zn in soil is exceeded at present and will be exceeded in the future when the zinc input continues at its present load?
- What are the time periods in which steady-state soil zinc concentrations are reached and critical soil zinc concentrations (if ever) are exceeded?

We first describe the methods that were used to assess present, critical and future pools and fluxes, focusing on uptake, leaching and accumulation rates (Chapter 2). This Chapter is followed by a description of all the input data that are needed to make the calculations (Chapter 3). A summary of calculated zinc concentrations and balances (present, critical and future concentrations and fluxes) at 4647 agricultural plots in the Netherlands, using the tools and methods described before, is given in Chapter 4. An overview of various uncertainties and their impacts on the results is presented in Chapter 5. The report finishes with a discussion and conclusions related to the research questions posed (Chapter 6).

2 Methodological approaches to estimate zinc behaviour in Dutch agricultural soils

This chapter describes the methods that were used to calculate balances for Zn at the field scale for agricultural soils in the Netherlands and the time period in which critical limits are exceeded (if ever). The methods are applied for all agricultural soils in the Netherlands using a schematisation of a total of 6405 so-called STONE plots of which 4647 plots occur in agricultural areas. More information on this schematisation is given in Section 3.1.

First a description is given of the approach that was used to calculate zinc background concentrations in the Netherlands, and the assessment of the critical limit (the background concentration and a Predicted No Effect Concentration of added zinc) for Zn in soil, which is used in the risk characterisation (Section 2.1). Then the approach is described to calculate Zn accumulation or release on the basis of a continuing Zn input at present day (year 2000) rates in different types of land use and soil types in Dutch agriculture using a dynamic model (Section 2.2). An assessment of future and of steady-state zinc concentrations and of time periods to reach critical and steady-state concentrations is described in Section 2.3.

2.1 Calculation of background zinc concentrations and critical limits

Terminology

The Added Risk Approach, which has been selected for development of the environmental quality standards (EQS) for Zn, implies the use of a Maximum Permissible Addition, (MPA), being the maximum amount of metal that may be added to the local background concentration (BC) of this metal without adversely affecting the local ecosystem. The critical limit (CL) or environmental quality standard concentration is thus derived as (Crommentuijn et al., 1997):

$$CL = BC + MPA \qquad (1a)$$

This approach assumes that biota: (i) are adapted to the concentrations in local ecosystems due to natural conditions and (ii) may resist a small additional pressure.
The critical Zn concentration can be compared with the present Zn concentration to calculate how large the area is (in % of total) where the present concentration already exceeds the critical concentration. This gives an impression of the pollution status at present. Furthermore, a comparison can be made between the predicted Zn concentration in the future and the critical Zn concentration to calculate the area where the future (steady-state) concentration exceeds the critical concentration.

In the risk assessment report (RAR) on zinc, a slightly different terminology is used for the same approach. For Maximum Permissible Addition, the term $PNEC_{add}$ is used, being the Predicted No effect Concentration of added metal to the soil. The sum of background concentration plus $PNEC_{add}$ is defined as the Predicted No effect Concentration (PNEC), i.e.:

$$PNEC = BC + PNEC_{add} \qquad (1b)$$

The risk of metal (Zn) contamination is assessed by comparing a Predicted Effect Concentration (PEC) at present and in the future (above defined as present or future Zn concentration). This is generally done in terms of a ratio (PEC/PNEC) but can also be done in terms of its difference (PEC-PNEC). In this report, the RAR terminology is further used as much as possible. We further used the term critical limit (as a commonly used alternative to environmental quality standard) for the sum of BC and $PNEC_{add}$ to avoid clumsy wording in the description of the results.

The following analogies do exist and are partly used in the report:
Predicted No effect Concentration (PNEC) = Critical limit (CL). The latter term is mainly used as critical Zn concentration.
Predicted No effect Concentration of added metal = Maximum Permissible Addition. The latter term is not used any more.
Predicted Effect Concentration = Present Zn concentration ($PEC_{present}$) and steady state Zn concentrations ($PEC_{steady\ state}$)

The approaches used to calculate zinc background concentrations (BC) and Predicted No effect Concentration of added zinc ($PNEC_{add}$) are given below.

Assessment of the zinc background concentrations
The added risk approach requires that background concentrations for zinc be established by an appropriate methodology in all selected STONE plots. The background metal concentration can be defined as "the concentration in the present or past corresponding to low anthropogenic pressure". Since the $PNEC_{add}$ is based on No Observed Effect Concentrations, determined by additions ($NOEC_{add}$) to ambient Zinc concentrations (see below), it was decided that ambient Zinc concentrations should be used as background concentrations, excluding historically polluted sites. In this context, an estimate of ambient Zn concentrations was made as a function of clay content, using present Zn concentration data at a depth of 0-30 cm in a representative data set (LSK data base) for the Netherlands, excluding sites that were historically contaminated (notably peat soils in the western parts of the Netherlands, floodplain soils along major rivers and sandy soils in the vicinity of a Cd and Zn smelter). Results are presented in Table 1, including results at depths of 30-60 cm and 60-100 cm. As stated above, the reason for using the data at 0-30 cm is that the experiments from which the $PNEC_{add}$ is derived are generally carried out with top soils with concentrations comparable to those in the topsoil of the LSK data base. To evaluate the effect of the chosen background levels, alternative model simulations were made, using data from a depth of 60-100 cm. Model runs were also made with present Zn concentrations for the whole of the Netherlands, including historically polluted sites (see Chapter 3.2 for the source of those data). This aspect is further discussed in Section 5.1.

Table 1 Average concentrations for Zn at different soil depths as derived from LSK. Values in brackets represent the range from minimum to maximum

Clay	Nr of observations			Zn content ($mg.kg^{-1}$)		
(%)	0-30 cm	30-60 cm	>60 cm	0-30 cm	30-60 cm	>60 cm
0-2	12	14	23	16 (3.5-34)	10 (2.8-36)	8.0 (1.9-26)
2-10	9	9	6	24 (8-45)	11 (2.4-19)	6.3 (3.6-8.3)
10-20	12	12	15	37 (13-116)	18 (5.3-45)	13 (4.6-21)
20-30	11	14	13	56 (31-101)	34 (6.3-119)	32 (3.9-122)
> 30	18	12	7	62 (16-122)	48 (22-70)	23 (3.1-35)

The data in Table 1 originate from the LSK database (Finke et al., 2001). The LSK database contains a selection of soil profiles from major representative soil types in the Netherlands. These profiles were selected based on groundwater level, soil type and special features. Typical for these selected profiles is that each pedogenetic soil horizon was sampled (instead of fixed depth intervals). The data in Table 1 are restructured and clustered based clay content and soil depth. In each class (combination of clay content and depth) at least 6 but often between 10 and 15 samples were available. The criterion used to attribute a soil layer to one of the depth intervals chosen here is simply the middle depth (depth top of horizon + depth bottom divided by 2). The topsoil Zn concentration at 0-30 cm depth, being a surrogate for the background Zn concentration, was mapped as shown in Figure 2. For the sake of comparison, the subsoil Zn concentration at approximately 1m depth is also presented.

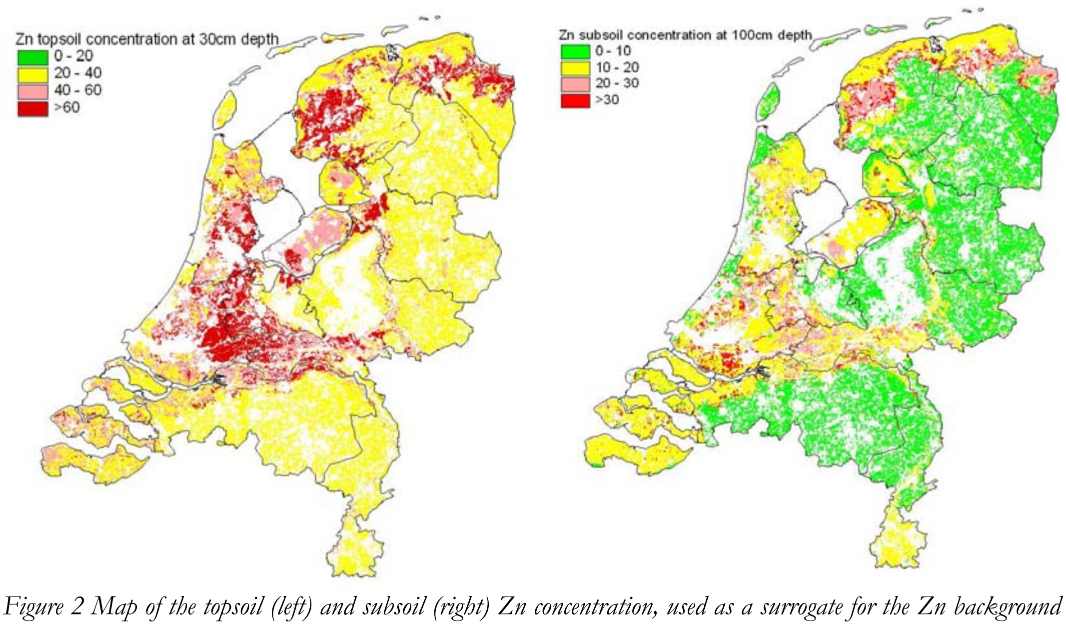

Figure 2 Map of the topsoil (left) and subsoil (right) Zn concentration, used as a surrogate for the Zn background concentration

Assessment of the Predicted No effect Concentration of added Zinc

The Predicted No effect Concentration of added zinc ($PNEC_{add}$) is derived from toxicological data (only No Observed Effect Concentrations, NOECs), using the 5% of these data (95% protection level, using the Aldenberg and Slob method. The value used is the $PNEC_{add}$ from the risk assessment report (RAR) on zinc, equivalent to 26 mg.kg^{-1}. To convert the NOEC thus obtained from laboratory conditions to field (availability correction), a generic correction factor of 3 was applied, based on empirical relationships between toxicity observed under field conditions at long-term Zn exposure on one hand and the short-term toxicity observed in the same soil spiked with Zn under laboratory conditions. This value of 78 mg.kg^{-1} was further multiplied by a "soil sensitivity factor" or "bioavailability factor" to account for the differences in zinc bioavailability observed between different soil types (Risk Assessment report (RAR) for Zinc).

These factors have been calculated on the basis of CEC (for plants and invertebrates), and ambient Zn backgrounds (for microbial processes). This factor explains the difference observed in zinc toxicity on different soils, upon zinc addition in the laboratory. The soil sensitivity factors have been calculated for a range of abiotic conditions (Table 2). Soil pH was kept constant at pH 6 for the corrections of plants and invertebrates because soil pH has a weaker effect on the toxicity than CEC.

Table 2 Soil sensitivity factors (SSF) predicted from the mean and 95% confidence intervals of the slopes. Predictions for plants and invertebrates assumed soil pH of 6.0 throughout all CEC values

Factor	Microbial processes		
Background Zn (mg.kg^{-1})	SSF_{Zn} Lowest slope	SSF_{Zn} Mean slope	SSF_{Zn} Largest slope
10	0.86	0.40	0.12
25	1.02	0.81	0.40
50	1.17	1.37	1.01
100	1.33	2.33	2.54
170	1.47	3.48	5.14
	Plants & invertebrates		
CEC (cmol.kg^{-1})	SSF_{CEC} Lowest slope	SSF_{CEC} Mean slope	SSF_{CEC} Largest slope
5	0.82	0.61	0.39
9	1.11	1.02	0.81
16.5	1.49	1.71	1.69
24	1.71	2.34	2.64
33	1.94	3.04	3.85

Using data from table 2, standard "soil sensitivity factors" for sand, peat, and clay soils are given in the zinc RAR (version of February 9th, 2004) for 4 soils as listed in Table 3 (see also table 3.3.3.1.1.9a of the RAR). These SSF values are based on estimated CEC and Zn concentration values, application of a formula fitting the SSF_{Zn} and SSF_{CEC} data for the lowest slope (see below) and taking the minimum of both SSF values. This approach leads to 1.0 for sandy soils, 1.2 for marine clay, 1.5 for river clay and 1.4 for peat. Ultimately, calculated $PNEC_{add}$ values range from 78 mg.kg^{-1} for sand, 93.6 mg.kg^{-1} for marine clay, 117 mg.kg^{-1} for river clay to 109.2 mg.kg^{-1} for peat. For this calculation, the loess soils were set equal to marine clay (93.6 mg.kg^{-1}). The classification of soils in the STONE plots into those 4 categories was used to apply these $PNEC_{add}$ values.

Table 3 The "soil sensitivity factor" (SSF) for 4 typical soils used in the RAR based on either soil microbial processes or on the plant and invertebrate dataset, using the lowest confidence intervals of slopes

Soil type	Microbial processes		Plants/invertebrates	
	HC5	SSF	HC5	SSF
Generic HC5: selected NOEC's with data on abiotic factors	26	1.0	49	1.0
Sandy soil (Cattle farms, 1994)	27.5	1.1	50.3	1.0
Peaty soil (Cattle farms 1995)	35.8	1.4	100.1	2.0
Marine clay soil (Arable farms 1996)	32.0	1.2	87.0	1.8
River clay soils (Cattle farms, 1996)	38.1	1.5	96.3	2.0

In an alternative approach, that has been used to assess the sensitivity of the results, the SSF was calculated for each plot according to the following formulas for SSF_{Zn} and SSF_{CEC}, based on the data for the lowest slope in Table 2:

$$SSF_{Zn} = 0.81 + 0.00775 \cdot Zn - 2.3179 \cdot 10^{-05} \cdot Zn^2 \qquad (2)$$

$$SSF_{CEC} = 0.49 + 0.0757 \cdot CEC - 9.700 \cdot 10^{-04} \cdot CEC^2 \qquad (3)$$

Zn: Zinc content soil (mg kg^{-1})
CEC: Cation Exchange Capacity (meq 100 gr^{-1})

The CEC at each plot was calculated from the organic matter and clay content and the pH-KCl value according to (Helling et al., 1964):

$$CEC = ((3.0 + 0.44 \cdot pH - KCl) \cdot Clay + (-5.9 + 5.1 \cdot pH - KCl) \cdot OM/2)/10 \qquad (4)$$

Actually, the pH in the data used by Helling et al. (1964) was related to a solution saturated with 0.5 N $BaCl_2$/BaTEA, being comparable in strength to 1M KCl. The ultimate SSF applied was the minimum of both SSF values.

2.2 Calculation of zinc accumulation or release

Zinc accumulation or release

The zinc accumulation (or release in case of negative accumulation) in the mineral topsoil was calculated from the net input to the field (zinc inputs by animal manure, fertiliser, atmospheric deposition and other sources including Zn in compost and pesticides) minus crop uptake and leaching from the soil according to:

$$Zn_{ac} = Zn_{in} - Zn_{up} - Zn_{le} \qquad (5)$$

where:
Zn_{in} = total Zn input to the field ($g.ha^{-1}.yr^{-1}$)
Zn_{up} = total Zn uptake in crops ($g.ha^{-1}.yr^{-1}$)
Zn_{le} = total Zn leaching from the mineral topsoil ($g.ha^{-1}.yr^{-1}$)

The following assumptions apply to the model:

(i) The soil system is homogeneously mixed which implies that both soil properties such as organic matter content and concentrations of the pollutant do not show vertical variation within the observed soil compartment.

(ii) The soil is in an oxidised state and metal partitioning can be described with equilibrium adsorption.

(iii) Transport of water and heavy metals only takes places in vertical direction (no seepage flow, surface runoff and bypass flow).

(iv) Impacts of soil erosion and Zn weathering are neglected

(v) Zn input equals constant input by animal manure, fertiliser and deposition. Inputs due to Zn recycling (crop residues) are not included.

(vi) The time step of the model is annual. Impacts of periodic events, such as manure application, are not included (e.g. short term effects on soil pH direct after manure application)

The inherent limitations caused by the various assumptions are given below:

(i) The assumption of homogeneous mixing implies that the critical load can only be calculated for a distinctive homogeneous layer and not for e.g. the whole rooting zone or a soil profile until ground water level. This is the case in the present application.

(ii) Since the method is developed for the top soil the assumption of an oxidised state is valid in most situations. The model can, however, not be applied to very poorly drained soils, with ground water levels near the surface in the winter period. The major reason is that the anaerobic circumstances violate the equilibrium-partitioning concept due to precipitation of metal sulphides.

(iii) Neglecting surface runoff, bypass flow and seepage will not hold for very poorly drained soils (seepage) and for heavily cracking clay soils (bypass flow). It generally holds for moderately to well drained sandy to loamy soils. However, even on cracking clay soils, Zn application by manure and fertiliser generally takes place in a period before cracking.

(iv) The potential impact of soil erosion was neglected since all sites are located in flat areas. Soil erosion may, however, occur in the loess area in the southern part of the Netherlands. This process will, nevertheless, not affect the Zn concentration significantly as it only removes soil material with Zn included.

(v) Recycling of Zn may have some effect when the Zn is partly leached below the rooting zone. However, considering that most Zn is taken up in the topsoil, the effect of recycling is small

(vi) Periodic events, such as manure application, may lead to high dissolved Zn concentrations, but this will be the case in a period when the downward water flux is low since manure application is only allowed in the growing period (between April-September) in the Netherlands. The effect on the annual water flux is thus expected to be small

In summary, despite the various assumptions, the model seems acceptable for large scale application, when focusing on an adequate description of the major processes, i.e. uptake and leaching. A description of the calculation procedures for uptake and leaching is given below.

Calculation of zinc uptake

The net zinc uptake rate was derived by multiplying the yield of the crop considered by the zinc content in that crop according to:

$$Zn_{up} = Y \cdot Zn_p / 1000 \qquad (6)$$

where:

Zn_{up} = Zn uptake rate (g ha^{-1} yr^{-1})
Y = crop yield ($kg.ha^{-1}.yr^{-1}$)
Zn_p = Zn content in the plant or crop ($mg.kg^{-1}$)

Yields rates are directly related to land use (in our study grass, maize and arable land using a mixture of wheat, other cereals, potatoes, sugarbeet and other crops), soil type (sand, loess, clay and peat) and ground water table (dry, moist and wet). Data are presented in Section 3.4. For the assessment of Zn concentrations in plants, two different approaches were used:

- Application of a relation between the Zn concentration in the plant and the Zn concentration in the soil ("soil-plant relationship"). This relationship was derived from a dataset containing soil and crop data for the crops considered (the standard approach). This approach is described below. Only for the category "all other crops", the median value of Zn in the complete dataset of all crops was used.
- Use of a fixed Zn concentration, using the median value for each crop based on the same dataset for which the soil-plant relationship has been derived (alternative approach). These data are presented in Section 3.4.

The soil-plant relationship mentioned previously relates the soil Zn content to that of the plant according to:

$$Zn_p = K_{sp} \cdot Zn_{soil,tot}^{\ n} \qquad (7)$$

where
Zn_p = Zinc concentration in plant ($mg.kg^{-1}$ dry matter)
$Zn_{soil,tot}$ = Total zinc concentration in soil ($mg.kg^{-1}$)
K_{sp} = Soil plant transfer constant ($[mg^{1-n} \cdot kg^{n-1}]$)
n = coefficient

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

$$\text{Log } K_{sp} = \alpha_0 + \alpha_1 \cdot \text{pH - KCl} + \alpha_2 \cdot \log(\text{OM}) + \alpha_3 \cdot \log(\text{clay}) \qquad (8)$$

Combination of Eq. (7) and (8) gives

$$\log Zn_p = \alpha_0 + \alpha_1 \cdot pH\text{-}KCl + \alpha_2 \cdot \log(OM) + \alpha_3 \cdot \log(clay) + n \cdot \log Zn_{soil,tot} \qquad (9)$$

Values for the various coefficients were derived for Zn in the crops considered, being grass, maize and crops considered representative for arable land (wheat, potatoes and sugar beet). The relationships were based on a data set with combined soil and plant data on Zn for contaminated soils in the flood plains of the river Meuse (Römkens et al., 2004a). In annex 1 an overview of the data underlying these equations is given, including a short discussion on the use and application range of the equations that were derived.

The results for the soil to plant transfer relationship for Zn in soil are presented in Table 4. Results for wheat were also used for other cereals. In general, the relationships were good but it should be mentioned here that the relationships were only based on the "Meuse" dataset. This dataset contains both soil and crop data but originate from river flood plains, some of which contain high amounts of heavy metals. Also the range in soil types was limited, with clay soils dominating the samples in the database. The degree of contamination affects the soil to plant relationship, which is due to differences in the degree of bioavailability of metals in polluted versus non-polluted soils. Also in many floodplain soils, a strong cross correlation exists between organic matter and the metal content which affects the coefficients listed in Table 4. In general, different relationships can be found for polluted and unpolluted soils. Especially data from literature based on soils spiked with Zn show much higher transfer rates from soil to crop. The relationships used here are based on field samples without further spiking with zinc. Use of the relationships for sand and peat soils without checking the predicted values is, however, risky since it implies the application outside the range of derivation. To overcome this limitation we also used median Zn concentrations as presented in Table 15 in Section 3.4.

Table 4 Values for the coefficients a_0, a_1, a_2, a_3 and n in the relationship relating total concentration of Zn in different plants and in soil according to Eq. (9)

Crop	α_0	α_1	α_2	α_3	n	R^2	se-y_{est}
Grass	2.29	-0.13	-0.06	-0.35	0.33	0.20	0.14
Maize	0.90	-0.10	0.28	-0.62	0.90	0.64	0.09
Wheat-grain[1]	1.2	-0.06	0	0	0.37	0.73	0.06
Potatoes	1.11	-0.08	0.12	-0.38	0.45	0.50	0.07
Sugar beet	2.61	-0.38	-0.46	-0.6	1.17	0.63	0.15

[1] relationships for wheat were also used for other cereals

The accuracy of the predictions is illustrated in Figure 3, showing the predicted Zn contents, according to the model fit given above, to the measured Zn contents in sugar beet and maize. Results show that on average the comparison is good although significant deviations may occur at specific sites.

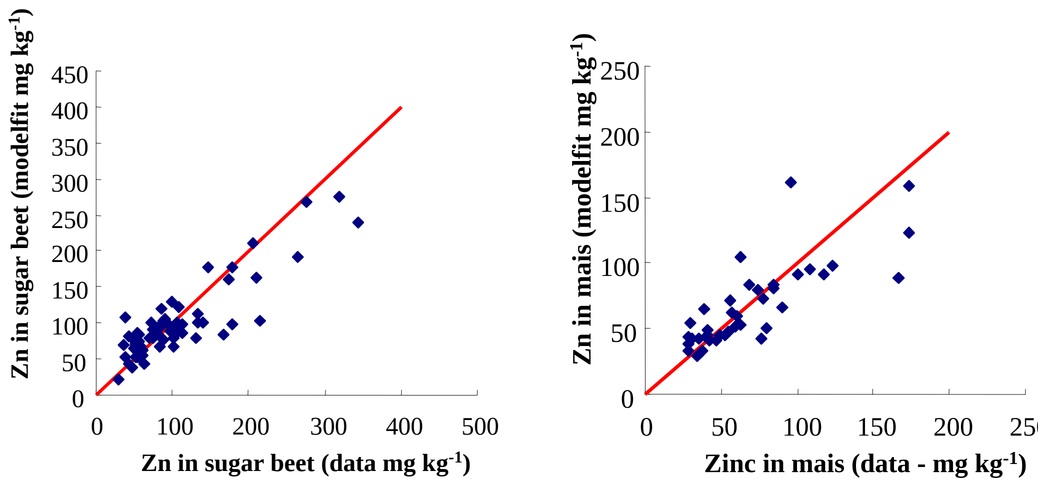

Figure 3 Comparison of predicted plant Zn contents, according to the model fit given in Table 4, to the measured Zn contents in sugar beet (left) and maize (right)

Calculation of zinc leaching

The Zn leaching rate from the topsoil was derived by multiplying the precipitation excess with a dissolved Zn concentration, according to:

$$Zn_{le} = PE \cdot [Zn]_{ss} / 1000 \qquad (10)$$

where:
Zn_{le} = Zn leaching rate from the topsoil ($g.ha^{-1}.yr^{-1}$)
PE = Precipitation excess ($m^3.ha^{-1}.yr^{-1}$)
$[Zn]_{ss}$ = Zn concentration in soil solution ($mg.m^{-3}$)
Information on the derivation of the precipitation excess is given in Chapter 3.

For the topsoil of 0-10 cm (grassland) or 0-30 cm (arable land; plough layer), the annual average dissolved concentration was estimated from the measured total metal concentrations and soil properties, using so-called transfer functions. First a transfer function is used relating the total dissolved Zn concentration to the reactive soil Zn concentration and vice versa according to (Römkens et al., 2004b):

$$Zn_{soil,re} = K_f \cdot [Zn]_{ss}^{\,n} \qquad (11a)$$

or

$$[Zn]_{ss} = (Zn_{soil,re} / K_f)^{1/n} \qquad (11b)$$

where:
$[Zn]_{ss}$ = concentration of Zn in the soil solution ($mmol.l^{-1}$)
$Zn_{soil,re}$ = reactive concentration of Zn in the soil, in this case the 0.43 M HNO_3 extractable concentration ($mol.kg^{-1}$)
K_f = Freundlich coefficient ($mol^{1-n} \cdot kg^{-1} \cdot l^{n}$)

The value of K_f is calculated as a function of the content of organic matter, clay and pH-$CaCl_2$ according to:

$$\log K_f = \beta_0 + \beta_1 \cdot \log(\%OM) + \beta_2 \cdot \log(\%\,clay) + \beta_3 \cdot (pH - CaCl_2) \quad (12)$$

where:
$\beta_0 \ldots \beta_3$ = model coefficients
%OM: = percentage organic matter
%clay: = percentage clay (< 2µm or lutum)
$pH\text{-}CaCl_2$ = pH in dilute salt solution (or soil solution)

Data for $pH\text{-}CaCl_2$ were derived from pH-KCl data by a linear regression based on several of hundreds of both pH values. Values for the various regression coefficients were derived from laboratory experiments with approximately 1400 soil samples from Dutch locations (Römkens et al., 2004b), as shown in Table 5.

Table 5 Values for the coefficients β_0, β_1, β_2, β_3 and n in the relationships relating dissolved total concentrations and reactive soil concentrations of Zn, according to Eq. (11) and (12) after Römkens et al. (2004b)

Metal	β_0	β_1	β_2	β_3	n	R^2	se(Y)
Zn	-4.51	0.39	0.35	0.45	0.74	0.82	0.40

The reliability of the predictions is shown in Figure 4, presenting the predicted dissolved Zn concentrations, according to the model given above to the measured dissolved Zn concentrations. Results show that on average the comparison is good although significant deviations may occur at specific sites.

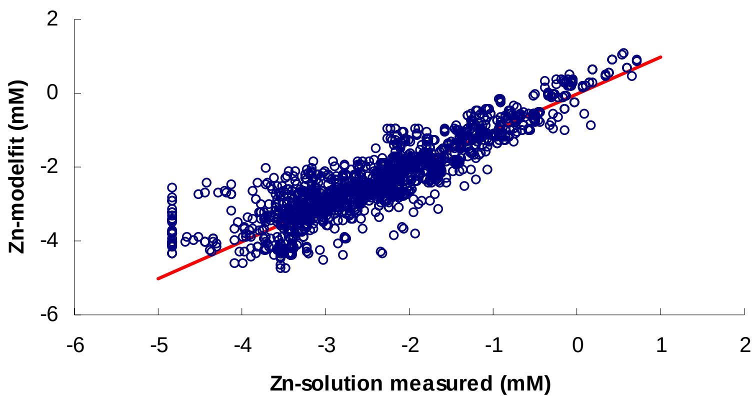

Figure 4 Comparison of predicted dissolved Zn concentrations, according to the model fit given in Table 5, to the measured dissolved Zn concentrations (Römkens et al., 2004b)

Since the data on present Zn contents in soil refer to *total* concentrations, the reactive concentrations were derived from total concentrations, since part of the Zn in soil is not reactive (total = reactive + not reactive). The reactive Zn concentration was derived from the total Zn concentration and the content of organic matter and clay according to:

$$\log Zn_{soil,re} = \gamma_0 + \gamma_1 \cdot \log Zn_{soil,tot} + \gamma_2 \cdot \log(\%OM) + \gamma_3 \cdot \log(\%clay) \quad (13a)$$

or

$$\log \mathrm{Zn}_{\mathrm{soil,tot}} = (\log \mathrm{Zn}_{\mathrm{soil,re}} - (\gamma_0 + \gamma_2 \cdot \log(\%\mathrm{OM}) + \gamma_3 \cdot \log(\%\mathrm{clay})))/\gamma_1 \qquad (13b)$$

Values for the various coefficients relating reactive and total soil concentrations of Zn were from a database of 300 to 600 samples in which both the reactive and total soil concentrations were measured together with soil properties. Results thus obtained are also described in Römkens et al. (2004b) and presented in Table 6.

Table 6 Values for the coefficients γ_0- γ_3 in the relation between reactive and total concentration of Zn in the soil according to Eq. (13) after Römkens et al. (2004b)

Metal	γ_0	γ_1	γ_2	γ_3	R^2	se-y_{est} [1)]
Zn	0.428	1.235	0.183	-0.298	0.96	0.16

[1)] On a logarithmic basis

2.3 Prediction of future zinc concentrations and of time periods to reach critical and steady-state concentrations

Because of accumulation or release, the soil Zn concentrations changes in time, thus influencing both leaching and uptake. Changes in soil Zn concentrations were calculated according to:

$$M_{soil}(t) = M_{soil}(t-1) + \frac{M_{ac}(t-1)}{\rho \cdot T \cdot 10} \qquad (14)$$

where:
$M_{soil}(t)$ = soil metal concentration at time t (in mg kg^{-1})
$M_{soil}(t\text{-}1)$ = soil metal concentration at time t-1 (in mg kg^{-1})
$M_{ac}(t\text{-}1)$ = total metal accumulation during time step from (t-1) to (t) in g ha^{-1}
ρ = bulk density of the soil ($kg.m^{-3}$)
T = soil thickness (m)

Bulk density was derived by relationships with the organic matter and clay content for mineral soils (Hoekstra & Poelman, 1982) and peat soils (Van Wallenburg, 1988). Changes in Zn leaching, due to a change in the soil Zn concentration were derived from Eq. (11) and (12).

Because of changes in leaching and outflow, the estimates of Zn accumulation (Eq. 5) changed over time. Time periods to reach steady state were calculated iteratively by requiring that the change in Zn concentration was less that 0.01% in one year. Practically, Zn accumulation was negligible when using this criterion. The procedure to calculate those time periods is further illustrated in Figure 5.

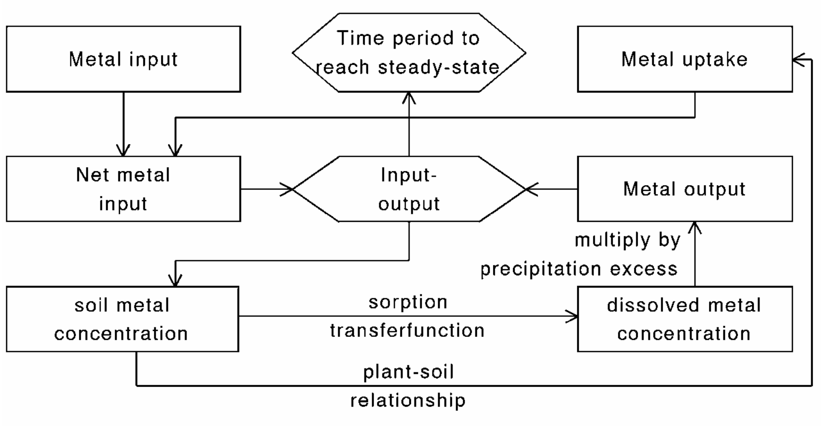

Figure 5 Diagram illustrating the calculation of time periods to reach steady-state

In this context, a simple steady-state model was also applied to calculate and map the steady-state Zn concentration. At steady-state, the Zn accumulation or release is negligible, leading to a steady-state dissolved Zn concentration according to (see Eq. (5) and Eq. (10) with $Zn_{ac} = 0$) :

$$[Zn]_{ss} = (Zn_{in} - Zn_{up})/(PE/1000) \quad (15)$$

The steady-state soil Zn concentration was derived by combining Eq. (11a), (12) and (13b) with Eq. (15). This steady state concentration was also compared with:
- The critical Zn concentration to calculate how large the area is (in % of total) where the steady-state concentration exceeds the critical concentration and
- The present concentration to indicate the area where accumulation or release takes place and calculate the area (in % of total) where the steady-state Zn concentration exceeds the present Zn concentration.

Regarding the dynamic behaviour of zinc, there are six possible options depending on the present concentration (P), the critical concentration (C) and the steady-state concentration at present inputs (SS):
1. P<C<SS: in this case, during the run the Zn concentration will exceed the critical Zn concentration and *the (damage delay) time can be calculated.*
2. P>C>SS: in this case, during the run the Zn concentration will drop below the critical Zn concentration and *the (recovery delay) time* can be calculated.
3. P<SS<C: in this case, during the run the model will calculate an increase in Zn concentration but it will never exceed the critical Zn concentration and the (damage delay) time is infinite.
4. P>SS>C: in this case, during the run the model will calculate a decrease in Zn concentration but it will not drop below the critical Zn concentration and the (recovery delay) time is infinite.
5. C>P>SS: in this case, during the run the model will calculate a decrease in Zn concentration but it is already at the start below the critical Zn concentration.
6. C<P<SS: in this case, during the run the model will calculate an increase in Zn concentration but it is already at the start above the critical Zn concentration.

The number of plots occurring in each of these six situations and the time periods to reach the critical level (option 1 and 2) was calculated.

3 Assessment of input data

3.1 Study area

The Zn mass balance model was applied to the whole of the Netherlands in which land use was clustered to grassland (pasture) and arable land (including maize land) and soil type was clustered in sand, clay and peat soils. Geo-referenced data on annual zinc inputs, divided in animal manure, fertiliser and atmospheric deposition were used for 4647 so-called STONE plots, limiting ourselves to agricultural land use. These plots consist of one or more 500m x 500m grid cells with a unique combination of land use, soil type and ground water table class.

The reason for using the STONE plots is that each plot has a detailed profile description (including data on organic matter, clay, pH, Fe and Al-hydroxides) down to 13 meters below the soil surface in combination with a detailed hydrological schematisation (Kroon et al., 2001). Hydrological data are available for individual plots for the time period between 1971 and 2000 for each consecutive period of 10 days (Kroes et al., 2001). However, to reduce the amount of calculations, data were summed to yearly values and for the applications presented here data for an 'average' year have been used. Alternatively runs with extreme conditions (either dry or wet) can be performed. For each distinguished layer, both vertical and lateral water fluxes are distinguished and quantified in mm water $year^{-1}$. For this application, only data from the topsoil were used. Heavy metals are not included in the STONE schematisation. Based on the 500x500 grid map for Zn, an overlay of the STONE plots and the Zn map resulted in an estimate of the average Zn level in each STONE plot.

Land use in the STONE plots is divided in 4 classes: arable land, pasture, maize and nature. For this application, maize and arable land are combined. Nature has not been considered here. This resulted in a total of 4647 plots (out of 6405). To simplify the overview of data, all plots (after the calculation for all plots) were clustered into 3 major soil types: clay, sand or peat. Specific soil types, such as the loess soils, were included in the clay soils. In total 5 soil types were distinguished: sand and clay (calcareous and non-calcareous for both sand and clay) and peat. The further division in calcareous and non-calcareous sandy soils and clay soils was made since pH strongly affects both Zn uptake and Zn leaching, both being decreased at high pH values. Calcareous soils are thus prone to accumulation. In combination with two types of land use (arable land or pasture) this results in 10 combinations.

Information on areas of those land use–soil type combinations is given in Table 7. Results show that arable land and grassland each cover approximately 50% of the total Dutch agricultural area. Grassland is mainly located on non-calcareous sand followed by peat and calcareous clay, whereas arable land is mainly located on calcareous clay followed by non-calcareous sand and peat.

Table 7 Area of the included combinations of major land use and soil type (values in brackets refer to the percentage of the total area)

Soil type	Area (ha)		
	Grassland	Arable land	Total
Sand	387836 (20)	303965 (16)	691801 (35)
Sand calcareous	656 (0.03)	19732 (1.0)	20388 (1.1)
Clay	84653 (4.3)	34552 (1.8)	119205 (6.1)
Clay calcareous	220485 (11.3)	455966 (23)	676451 (35)
Loess	12081 (0.62)	18754 (1.0)	30835 (1.6)
Peat	277832 (14.2)	133852 (6.9)	411684 (21)
Total	983543 (50)	966821 (50)	1950364 (100)

An overview of the geographic distribution of the major distinguished soil types, which largely influences the pattern of Zn uptake and leaching and thus Zn accumulation is presented in Figure 6. The map shows that the non-calcareous sandy soils are mainly located in the eastern part of the Netherlands. The calcareous sandy soils only occur near the sea (the dune area) in the north-western part of the Netherlands. The non-calcareous clay soils are mainly river clays occurring in the central part of the Netherlands. The calcareous clay soils are mainly marine clays in the western part of the Netherlands, whereas the peat areas occur both in the central-western and northern part of the Netherlands (Figure 6).

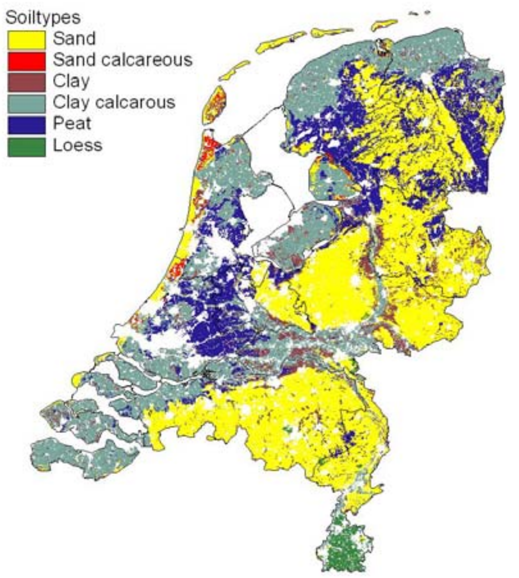

Figure 6 Geographic distribution of the major distinguished soil types

To apply the model, most recent available data (year 2000) on the zinc inputs through deposition, manure and fertiliser application. The calculation of outputs via crop removal and leaching (lateral and vertical) was based on recently measured Zn contents. By using the year 2000 the effects of quite recent legislation and policy measures were included.

3.2 Soil properties and present zinc concentrations

The dissolved zinc concentrations are calculated using a transfer function that describes the relationship between dissolved and adsorbed concentrations of Zn while accounting for the effect of organic matter, clay content and pH. These soil properties all influence the metal availability, thus having impacts on concentrations and behaviour of metals in soil, soil solution and crops. Data on organic matter content, clay content and pH-KCl are based on the Dutch Soil Information System. The interpolation of those data to the considered STONE plots was derived by a geostatistical method called "Simple indicator kriging with local prior means" (Brus et al., 2002). Using this approach, Brus et al. (2002) calculated values for organic matter content, clay content and pH-KCl for 500m x 500 m grid cells. These data were used to calculate mean area values for each STONE plot. Ranges in those soil properties are given in Table 8.

Table 8 Average values and ranges of organic matter and clay contents and pH in the combinations of major land use and soil type. Values in brackets give the range between 5% and 95%

Land use	Soil type	Org. Matter (%)		Clay (%)		$pH-H_2O$		pH-KCl	
Grass land	sand	8.2	(5.3-13)	6.8	(4.7-11)	5.3	(5.0-5.5)	5.0	(4.7-5.3)
	clay	9	(5.6-14)	31	(14-47)	6.9	(6.2-7.7)	6.1	(5.3-7.2)
	peat	32	(11-55)	39	(7.3-65)	5.6	(5.2-6.1)	5.3	(4.7-5.8)
Arable land	sand	7.8	(4.1-13)	6.6	(4.5-11)	5.3	(5.0-6.5)	5.0	(4.7-6.5)
	clay	5.9	(3.5-10)	27	(17-41)	7.4	(6.3-7.8)	6.8	(5.4-7.2)
	peat	22	(4.9-38)	16	(4-43)	5.6	(5.2-6.8)	5.3	(4.7-6.8)

Apart from this geostatistical approach, a second schematization exists that is, among others, used to predict phosphate leaching from soil on a national scale. In this approach, all soils in the Netherlands are classified among 21 different soil types, where each soil type has a pre-described (fixed) profile description (containing data on texture, organic matter, pH, and Fe-Al oxides and depth of each diagnostic horizon). Each STONE plot is subsequently linked to one single soil type. Regional (geochemical) differences between similar soil types (sandy soils in the southern sandy regions vs. the north eastern parts) are therefore not considered in this approach. In the remainder of the text we will use the term 'generic assignment' for this approach.

A comparison of soil properties obtained with generic assignment compared to the geostatistical interpolation method, used in this study is shown in Figure 7. Apart from the large scatter, results obtained by geostatistical interpolation are systematically higher than those derived by generic assignment. This is illustrated in Table 9, which presents the results of a linear regression on both data according to: $y_{assigned} = a + b.y_{interpolated}$. The results show that values of b are always below 1 implying that the generically assigned values are generally lower than the interpolated values. The only exception is the assignment of pH-KCl in arable land (Table 9). The systematic difference between both methods is further illustrated by cumulative frequency distributions of these soil properties using both approaches (Figure 8). The impact of these differences has been investigated to gain insight in the influence of uncertainties in soil properties on the results.

Table 9 Comparison of soil properties generically assigned for each soil type or geostatistically interpolated according to $y_{assigned} = a+b\ y_{interpolated}$

Soil property	Arable land			Grass land		
	α	β	R^2_{adj}	α	β	R^2_{adj}
Organic matter content	-1.34	0.87	0.61	1.15	0.59	0.71
Clay content	-0.5	0.81	0.83	-0.63	0.83	0.80
pH-KCl	-0.5	1.05	0.76	1.28	0.71	0.65

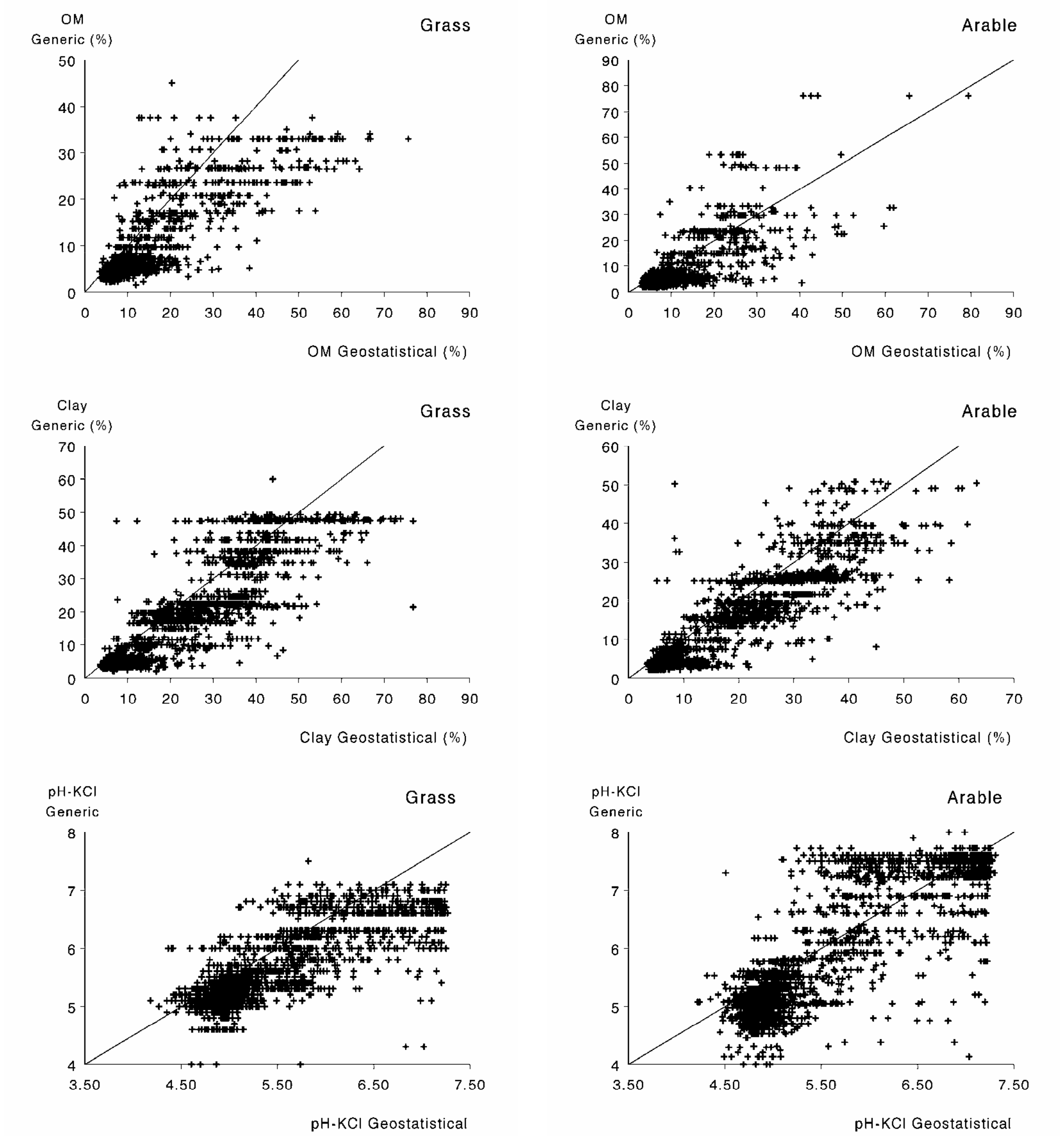

Figure 7 Scatter plots of generically assigned values of the organic matter content, clay content and pH-KCl compared to geostatistically interpolated values (standard approach)

The data on the Zn content of the soil (present state) originate from a large database that contains analyses of 2865 individual soil samples for zinc (Brus et al., 2002). This database contains data from Provincial monitoring Networks, the National Soil Monitoring Network of the RIVM and data from the former Institute for Soil

Fertility in Haren. The Zn content reported in this database is the 'total' zinc content, usually determined with Aqua Regia. The word 'total' is put between quotation marks since it is not really a total destruction like a destruction using HF. As such, the database gives a good overview of the soil zinc content in non-polluted soils. The locations for all samples were selected in such a way that specific (point)sources of pollution were excluded. The value for the Zn content in each 500 x 500 m grid cell was also derived with "Simple indicator kriging with local prior means" (Brus et al., 2002). The Zn content for each STONE plot was obtained by calculation of the mean value of the Zn content in all 500 x 500 grid cells within that specific STONE plot.

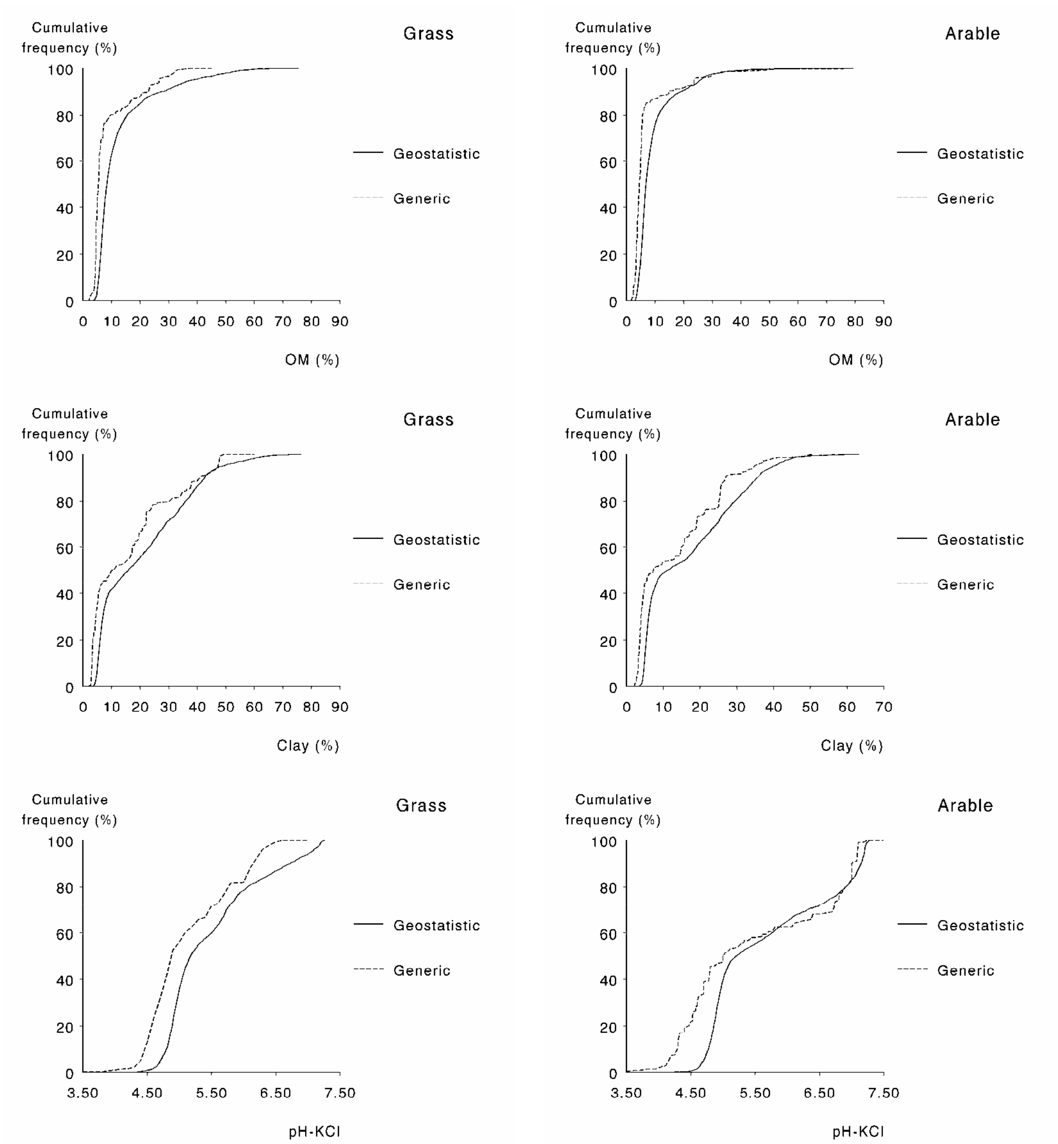

Figure 8 Cumulative frequency distributions of generically assigned values and geostatistically interpolated values of the organic matter content, clay content and pH-KCl

The average Zn concentrations in soil as well as their ranges are quite comparable for grass land and arable land, with the exception of grassland (cattle farms) and arable land on peat (Table 10). The average Zn concentrations in soil generally increase going from sand < clay < peat due to the increase in organic matter and clay content. An exception is arable land on peat where the Zn concentrations are generally lower than on clay soils (Table 10).

Table 10 Average values and ranges of the soil Zn concentrations (in mg kg⁻¹) in various combinations of major land use and soil type. Values in brackets give the range between 5% and 95%

Land use	Sand		Clay		Peat		Total	
Grass land	40	(32-53)	82	(58-115)	103	(50-158)	72	(34-143)
Arable land	41	(32-55)	81	(58-108)	61	(40-107)	65	(34-104)
Total	40	(32-54)	81	(58-111)	90	(43-154)	68	(34-124)

3.3 Zinc input

Geo-referenced data on annual zinc inputs, divided in animal manure, fertiliser, atmospheric deposition and other sources (compost and pesticides) were derived for 4647 so-called STONE plots, consisting of one or more 500m x 500m grid cells with a unique combination of land use, soil type and ground water table class, limiting ourselves to agricultural land use.

Data for the zinc input via animal manure were based on results from the CLEAN model of RIVM, using data statistics at farm and municipal level for the year 2000. This model does give the N inputs by animal manure for each of the 4647 agricultural STONE plots. The results for manure were scaled by multiplying the amounts with an annual average Zn/N ratio in the various types of manure (cows, pig, poultry etc) according to:

$$Zn_{in,am} = N_{in,am} \cdot ctZn_{am} / ctN_{am} \qquad (16)$$

$N_{in,am}$ = N in animal manure (kg ha^{-1} yr^{-1})
$ctZn_{am}$ = Zinc in animal manure (mg kg^{-1})

Most recent available data on Zn and N concentrations in animal manure are given in Table 11.

Table 11 Median values (in mg kg⁻¹ dry matter) of Zn and N in animal manure (Driessen & Roos, 1996) and the resulting ratios in both 1996 and those scaled to 2000

Animal manure	Zn	N	Zn/N	
			1996	2000
Cattle	156	53000	0.0029	0.0021
Pig	712	76000	0.0094	0.0066
Poultry	343	55000	0.0062	0.0044

For the zinc content in different types of animal manure the values are based on data from Driessen & Roos (1996). The resulting Zn input by animal manure on agricultural land in the Netherlands, using those data, is 2056 ton. This is exactly in line with input data by Zn for the year 1996 given by CBS (CBS, 2003). Recent data for the year 2000, however, are much lower, which is partly due to a reduction of the N input but also because the Zn suppletion to animal forage has decreased. Delahaye et al. (2003) thus estimated an annual Zn input by animal manure in 2000 of 1452 ton. To account for this decrease the Zn/N ratio for 1996 was multiplied by a factor 0.7 (being equal to 1452/2056) to obtain the corrected Zn/N ratio for 2000. By doing so, the estimated total Zn input in 2000 equals the input by Delahaye et al. (2003). The calculated N input at each plot determines the spatial variation in the zinc input.

Data for the zinc input via fertilisers were also based on results form the CLEAN model of RIVM by allocating the known annual national input of Zn in fertilisers (country statistics) to STONE plots with the N fertiliser application rate, according to:

$$Zn_{in,f,STONEplot} = N_{in,f,STONEplot} \cdot Zn_{in,f,country} / N_{in,f,country} \qquad (17)$$

The national values used were 423 $kton.yr^{-1}$ for N and 55.4 $ton.yr^{-1}$ for Zn, based on a compilation of national data from Delahaye et al. (2003).

Zn deposition data were based on modelled Zn deposition data by TNO at a 10 km x 10 km grid scale for the year 2000, using the model OPS (Bleeker, 2004). For the agricultural plots an overlay of those data with the plot area was made. Atmospheric deposition data were based on model calculations including emission estimates for the various metals and the emission-deposition model OPS (Van Jaarsveld & Onderdelinden, 1993), describing the transport and chemical transformations in the atmosphere (Van Jaarsveld, 1994).

Data on the zinc input by compost and pesticides were based on a national value of 158.4 $ton.yr^{-1}$, based on a compilation of national data from Delahaye et al. (2003). It is known that especially compost is not used on all soils and the distribution of the load of compost is quite heterogeneous. However, since detailed information on regional loads of compost to soil is not available the total amount of compost (and pesticides) has been applied equally on the total area of arable land.
The contribution of various sources of farm inputs to the total input of metals depends on the land use (Table 12). It is clear, however, that animal manure (due to feed concentrates) contributes most to the input of Zn to livestock systems (grasslands) and arable land, whereas fertilisers are the smallest source of Zn, being even less than atmospheric deposition of Zn (Table 12). The results show that the overall average Zn input is close to 900 $g.ha^{-1}.yr^{-1}$ with the average input on grassland and arable land being close to each other. The lower Zn input by manure in arable land compared to grassland is compensated for by the input with compost and pesticides. The Zn input on arable land on sand is relatively high. More than 90 % of the Zn input in grassland is due to animal manure; the remainder of the input comes from fertiliser and deposition. In general, input from atmospheric deposition is roughly twice as high as inputs from fertiliser use. The deposition values are slightly lower than previously published Zn deposition values which are in the range of 70 - 200 $g.ha^{-1}.yr^{-1}$, possibly indicating the decrease in Zn emission, mainly by industrial

sources. In arable land, approximately 75 % of the Zn input is due to animal manure with the remaining 25% divided over fertiliser, deposition and compost/pesticides (other sources; see Table 12).

A further distinction could be made based on the total N-load that legally can be applied to the land. A distinction between areas below and above the target values (250 $kg.ha^{-1}.yr^{-1}$ for grassland and 170 $kg.ha^{-1}.yr^{-1}$ for arable land) can be made. This would distinguish land uses with relatively high and low inputs since the Zn input is mainly due to animal manure and thus related to the N input by animal manure. Results showed, however, that the differences are relatively small and furthermore, the accumulation appeared to be more influenced by the difference between calcareous and non-calcareous soil, because of the large impact of pH on uptake and leaching. Therefore, these differences have not been presented.

Table 12 Average inputs of Zn in fertiliser, manure and deposition to all STONE plots on agriculture

Land use	Soil type	Zn flux ($g.ha^{-1}.yr^{-1}$)				
		Manure	Fertiliser	Deposition	Other sources	Total
Gras	Sand	828	38	72	0	938
	Sand calcareous	738	37	78	0	853
	Clay	853	38	78	0	969
	Clay calcareous	777	41	67	0	885
	Loess	773	38	77	0	889
	Peat	885	43	85	0	1013
Arable	Sand	785	16	74	164	1039
	Sand calcareous	631	13	60	164	868
	Clay	652	19	76	164	911
	Clay calcareous	646	19	70	164	899
	Loess	592	21	58	164	836
	Peat	733	11	84	164	993
Total	All	744	28	71	81	926

The overall ranges (5%-95%; not shown in Table 12) are 300-1152 $g.ha^{-1}.yr^{-1}$ for the input by animal manure, 8-45 $g.ha^{-1}.yr^{-1}$ for the fertiliser input and 43-101 $g.ha^{-1}.yr^{-1}$ for the input by deposition. The overall range for all inputs is 531-1415 $g.ha^{-1}.yr^{-1}$. A comparison with (measured) data from farms in other EU countries is given in Annex 2. Results show that the average Zn inputs by animal manure in other countries are generally in the same order of magnitude as in the Netherlands.

3.4 Zinc uptake by arable crops and grassland

Geo-referenced data on annual zinc outputs by net uptake were estimated by assessing yields and Zn concentrations as a function of land use, soil type and ground water table class, thus allocating them to combinations occurring in distinct plots. In the agricultural STONE plots, a distinction is made between grassland, maize and arable land (various rotations with potatoes, sugar beet, cereals, and vegetables) whereas soils are divided in sand, loess, clay and peat. Furthermore, a distinction is made in different hydrological regimes (wetness classes), using ground water table classes (Gt) from the 1: 50 000 soil map used in the plots, according to:

- wet (poorly drained): Gt I, II, II*, III, III*, V, V*; mean highest water level <40cm
- moist (moderately drained): Gt IV, VI; mean highest water level 40-80cm
- dry (well drained): Gt VII, VII*; mean highest water level >80cm

For arable land, data were used of the area of each considered crop within each STONE plot to assess the yield and Zn content (and thus the uptake) by those crops. The resulting uptake from arable land was calculated by an area averaged uptake of all the considered crops in the STONE plot. The used average yields in ton dry matter per hectare are presented in Table 13. Apart from grass and maize all yield data were derived by multiplication of available data on the average yield in fresh weight with the dry matter percentage as presented in Table 14. The data for potatoes, wheat and sugar beet were taken from Schröder et al. (2004) Yields for vegetables "category other" and "other cereals" were based on data in CBS statline.

Table 13 Yield data in ton dry matter per hectare for the considered crops in the calculation

Soil	Drainage	Yield (ton dry matter ha^{-1})						
		Grass	Maize	Potato	Wheat	Sugar beet	Other cereals	Other crops
Sand	Dry	10	13	10	6.4	12.2	5.1	7.5
	Moist	12	16	10	6.4	12.2	5.1	7.5
	Wet	12	16	10	6.4	12.2	5.1	7.5
Loess &	Dry/Moist	12	16	11.5	7.4	13.8	5.5	7.5
Clay	Wet	10	13	11.5	7.4	13.8	5.5	7.5
Peat	Dry/Moist	11	11	10	6.4	12.2	5.1	7.5
	Wet	10	10	10	6.4	12.2	5.1	7.5

Table 14 Yield data in ton fresh weight per hectare and the dry matter percentage of arable crops

Soil	Drainage	Yield (ton fresh weight/ha)				
		Potato	Wheat	Sugar beet	Other cereals	Other crops
Sand	Dry	43.6	7.5	53	6	15
	Moist	43.6	7.5	53	6	15
	Wet	43.6	7.5	53	6	15
Loess &	Dry/Moist	50	8.7	60	6.5	15
Clay	Wet	50	8.7	60	6.5	15
Peat	Dry/Moist	43.6	7.5	53	6	15
	Wet	43.6	7.5	53	6	15
		Dry matter percentage				
		23	85	23	85	50

As stated before the zinc content in each crop was calculated by the soil to plant transfer relationships using soil properties from each plot. Alternative to the use of soil-plant relationships, median (default) Zn concentrations for the various combinations of land use and soil type were also used in the simulation, as presented in Table 15.

Table 15 Median concentrations of heavy metal in crops used to calculate the total metal uptake in the alternative approach

Soil	Lime status	Median Zn concentration ($mg.kg^{-1}$ dry matter)				
		Grass	Maize	Wheat	Potato	Sugar beet
Sand	Non-Calcareous	71	40	31	18	53
	Calcareous	38	25	25	12	11
Clay	Non-calcareous	34	22	35	11	15
	Calcareous	28	17	30	8.9	8.5
Loess	-	50	29	34	14	32
Peat	-	56	58	38	19	32
All	-	58	34	32	16	37
Data		71 (49-126)	59 (29-168)	50 (36-78)	16 (12-22)	87 (39-257)

The median zinc levels reported in Table 15 were obtained using the soil to plant relationship for all 4647 plots, grouping the calculated values per soil type and taking the median value. For comparison, data from the floodplain soils are shown as well ("Data"). Clearly, the zinc levels in the floodplain soils exceed the calculated values for non-polluted soils, with the exception of potatoes. This confirms our previous hypothesis that using these measured data would result in an overestimation of crop uptake.

The use of default median crop zinc levels instead of plot specific calculated values was made to gain insight in the impact of the uncertainties in Zn uptake on the resulting steady-state concentrations (see Section 5.1). The use of median default values also is an alternative approach to avoid the possible calculation of outliers by applying the Zn soil to plant transfer relationship (far) outside its range of application. More information on the validity and range of the applicability of the soil to plant transfer relationship is given in Annex 1.

3.5 Precipitation excess

Geo-referenced data on annual zinc outputs by leaching were estimated by a multiplication of water leaching fluxes and dissolved metal concentrations. Water leaching fluxes were calculated by subtracting actual interception, soil evaporation and transpiration fluxes from the precipitation. The water leaching fluxes (precipitation excess) were thus calculated as:

$$PE = (1 - fr_{int}) \cdot P - E_s - E_t \quad (18)$$

with

$$E_t = E_{t,ref} + fr_{tr} \cdot (P - 780) \quad (19)$$

where:
PE = precipitation excess ($mm.yr^{-1}$)
P = precipitation ($mm.yr^{-1}$)

E_s = soil evaporation ($mm.yr^{-1}$)
E_t = transpiration ($mm.yr^{-1}$)
$E_{t,ref}$ = reference transpiration at a precipitation of 780 $mm.yr^{-1}$ ($mm.yr^{-1}$)
fr_{int} = interception fraction (-)
fr_{tr} = transpiration fraction (-)

Precipitation data for the STONE plots in agriculture were based on an overlay of interpolated precipitation normals from 280 stations over the period 1950-1980 at 10 x 10 km grid cells. Interception evaporation is described as a fraction of the precipitation. Interception fractions were set at 0.05 for grassland and 0.1 for maize and arable land (De Visser & de Vries, 1989). Soil evaporation and transpiration fluxes were based on calculations using a water flux model. The sum of evaporation and transpiration was estimated as a function of land use and soil type as presented in Table 16. Average values were 448 mm for grassland, 361 $mm.yr^{-1}$ for maize and 349 $mm.yr^{-1}$ for arable land.

Table 16 Sum of evaporation and transpiration data in the considered land uses in the calculation

Soil type	Drainage	Sum of evaporation and transpiration ($mm.yr^{-1}$)		
		Grass land	Maize land	Arable land
Sand	Dry	435	379	356
	Moist	461	380	362
	Wet	463	347	345
Clay	Dry	456	376	362
	Moist	452	353	349
	Wet	443	318	335
Peat	Dry	449	363	356
	Moist	455	360	346
	Wet	437	309	319
Loess	Dry	450	385	368
	Moist	476	386	371
	Wet	462	396	373

4 Zinc concentrations and zinc fluxes at agricultural sites in the Netherlands

4.1 Present, critical and steady state zinc concentrations

Present, critical and steady state concentrations and their exceedances

The range in present ($PEC_{present}$), critical (PNEC) and steady state ($PEC_{steady\ state}$) Zn concentrations is given in Table 17. Results show that the present Zn concentration in grassland increases going from non-calcareous sand < calcareous sand < loess and clay < peat. In arable land the average concentrations in clay soils are higher than those in peat soils. The critical Zn concentrations, defined as the sum of ambient concentration and Predicted No effect Concentration of added zinc, increase going from sand < loess < clay and peat. The average present Zn concentration is always less than the critical Zn concentration, with a relatively small variation between the soil types (mostly between -40 and -80 $mg.kg^{-1}$).

In general, the steady-state Zn concentration increases going from non-calcareous sand < calcareous sand, loess and peat< non-calcareous clay < calcareous clay. This illustrates the impact of organic matter content clay content and pH on Zn accumulation. Apart from the non-calcareous sandy soils, the steady-state Zn concentrations are much higher than the present concentrations. In loess soils and in peat soils below arable land, the difference is also relatively small. On average, the steady state Zn content does not exceed the critical Zn content for these soil types. Differences in steady-state soil Zn concentrations and present metal concentrations were highest for calcareous clay soils, especially under arable land (Table 17).

Table 17 Average present, critical and steady state soil Zn concentrations

Land use	Soil type	Zn concentration ($mg.kg^{-1}$)					
		Present	Critical	Steady state	Present-Critical	Steady state-Critical	Steady state-Present
Grass	Sand	40	102	42	-62	-60	2
	Sand calc.	60	102	121	-42	19	61
	Clay	79	163	334	-84	171	254
	Clay calc.	83	154	456	-71	302	373
	Loess	77	130	126	-53	-4	49
	Peat	103	162	217	-59	55	113
Arable	Sand	40	102	56	-62	-46	16
	Sand calc.	48	103	162	-54	60	114
	Clay	81	154	354	-72	200	272
	Clay calc.	81	145	551	-64	407	470
	Loess	77	130	127	-53	-3	50
	Peat	61	144	127	-83	-17	66
All	All	68	133	262	-65	128	194

In Figure 9, cumulative frequency distributions are given of critical, present and steady state Zn contents and of the differences between the present and critical content, steady state and critical content and steady state and present content.

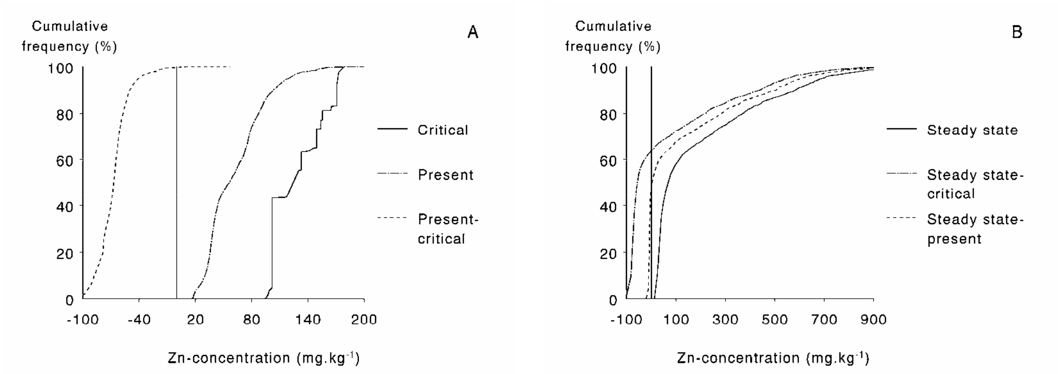

Figure 9 Cumulative frequency distributions of critical, present and present-critical Zn contents (A) and the steady state content, the steady state-critical content and steady state-present content (B)

Results show that current Zinc levels in soils at the moment hardly exceed the critical limit. However at steady state, more than 50% of all plots will exceed the critical limit. The percentage of plots in which the steady-state Zn content exceeds the present Zn content, implying that accumulation does occur, is given in Table 18. This table also presents the percentage of plots exceeding critical limits for zinc at present and at steady-state.

Table 18 Percentage of plots at which the steady-state Zn content exceeds the present Zn content (accumulation does occur) and at which the critical Zn content is exceeded at present or steady-state

Land use	Soil type	% of plots with Zn accumulation	% of plots exceeding critical Zn limit	
			Present	Steady-state
Grass	Sand	42	0	1.9
	Sand calcareous	100	0	100
	Clay	100	0	80
	Clay calcareous	100	0.11	100
	Loess	100	0	20
	Peat	93	2.4	72
Arable	Sand	75	0	3.1
	Sand calcareous	100	0	63
	Clay	100	0	66
	Clay calcareous	100	0.23	98
	Loess	99	0	76
	Peat	71	0.33	23
All	All	81	0.43	53

Results show that Zn accumulation takes place in 81% of the plots, implying that the present (year 2000) input of Zn exceeds the uptake and leaching at those plots. The number of plots where release occurs thus equals 19% for all the plots considered. This phenomenon occurs mainly in non-calcareous sandy soils. The Zn accumulation induced by the Zn loads in 2000 cause a large increase in the number of sites exceeding the critical limits values for Zn. The overall increase is from 0.43-53%, the largest changes taking place in calcareous sand below grassland (from 0-100%) and the smallest changes taking place in non-calcareous sandy soils (from 0-3%), followed by grassland on loess and arable land on peat soils (from 0- 20-25 %).

The impact of soil type and land use reflects the degree to which the critical limit will be exceeded. Especially soil pH has a huge impact on the net accumulation rate and the percentage of plots that exceed the critical limit. In non-calcareous sandy soils less than 10% of the plots will ultimately exceed the critical limit, whereas in calcareous clay soils almost all plots will eventually exceed the critical limit. This is entirely due to the fact that in slightly acid to acid soils, the retention of metals is much lower, resulting in larger leaching fluxes. It should be mentioned here that the risk assessment approach followed here is a rather 'one-dimensional' approach since only accumulation risks are considered. The risk of large leaching losses in sandy soils, which can lead to an increase in the dissolved metal concentration in the upper groundwater or, in wet sandy soils, in surface waters is not accounted for in the considered critical Zn limit. The fact that most metals are retained in soils with pH values higher than 6.5 to 7 means that accumulation occurs even under rather low input scenarios. In Section 4.4 an evaluation of the time scale involved to reach steady state (or exceedance of critical limits) is presented.

Spatial distribution of present, critical and steady state concentrations and their exceedances

The geographic variation of the present, critical and steady state Zn concentrations and their exceedances are mapped as shown in Figure 10. In Figure 10A present zinc levels in soil are presented. The Zn concentrations in the range of 0 to 50 $mg.kg^{-1}$ refer mainly to sandy soils in the Eastern part of the Netherlands, whereas the Zn concentrations in the range of 50 and 150 $mg.kg^{-1}$ mainly refer clay soils and peat soils occurring in western part of the Netherlands (compare also Figure 6). Values above 150 $mg.kg^{-1}$ occur in a few regions in the Netherlands:

1. Soils in the central western part. In this area peat lands are present (mainly grassland) that have been used since the Middle Ages by people from major cities (Amsterdam, Utrecht, the Hague) to dispose their city waste material. These soils, the topsoil of which is called "Toemaakdekken" ('Toemaak' meaning covering) are usually enriched in Zn, Cu, and Pb.
2. Flood plain soils along major rivers (Rhine, Meuse, Schelde) that are affected by deposition of polluted sediments. Strong local variation exists in the degree of contamination.
3. Soils in the eastern sandy district along the Belgian Dutch border (Kempen area). Here long term industrial activities, namely Zn smelting, has resulted in elevated Zn levels in soils. Due to the acidity of the soils, levels usually are below those found in other European areas affected by smelting activities and range between 50 and 300 $mg.kg^{-1}$.

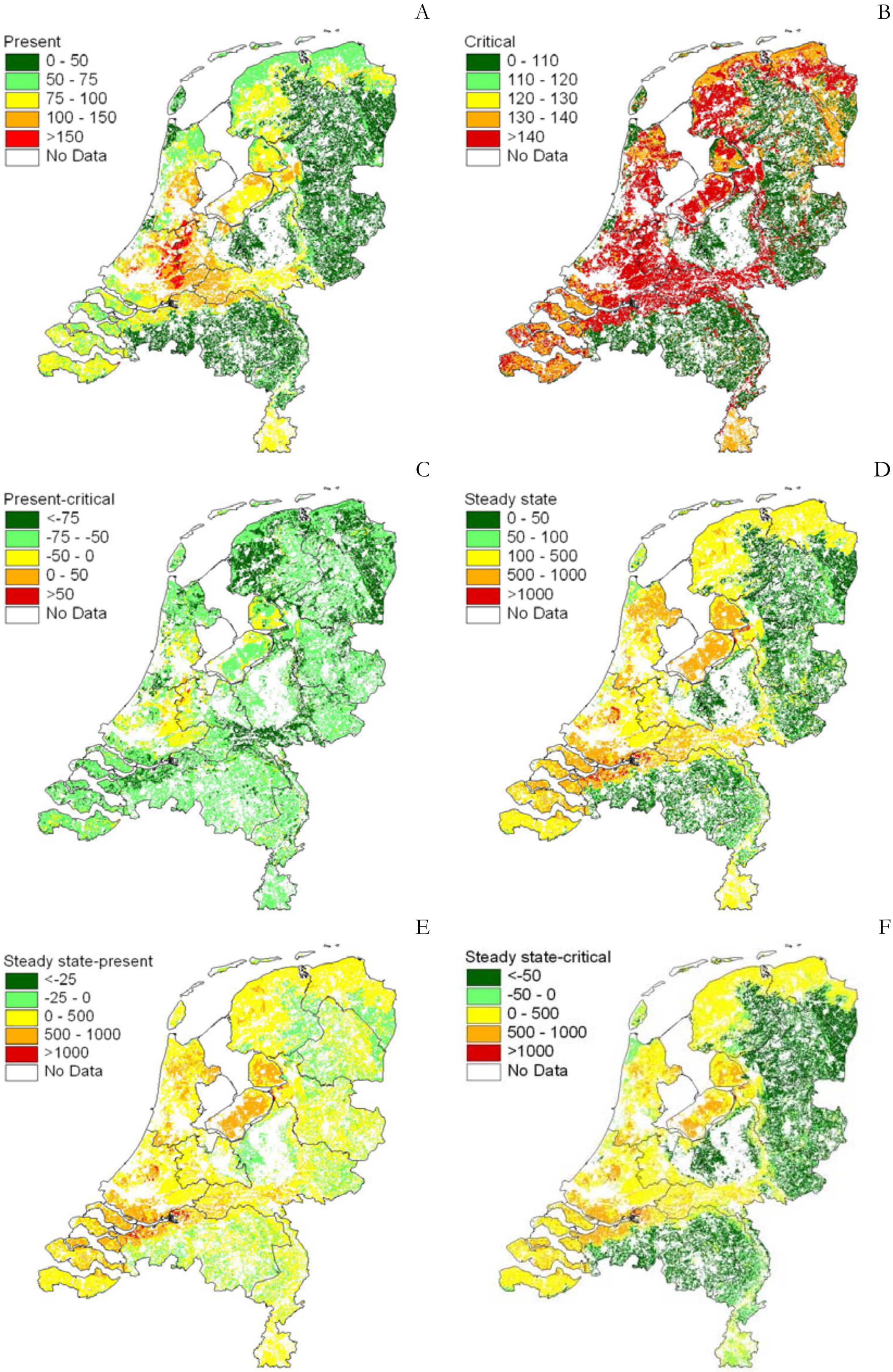

Figure 10Maps of present (A), critical (B), and steady state Zn contents (D) and the differences of the present-critical content (C), steady state- present content (E) and steady state – critical content (F)

The soils in the first category (peat soils in the Western areas) can be detected quite easily, but both the floodplain soils and the elevated zinc levels in the Kempen soils do not appear very pronounced on the maps (Figure 10A). This is partly due to the fact that relatively few measuring points are included in the database of both categories (an exception are the floodplain soils along the Meuse, where an intensive measuring campaign has been carried out during the 80's).

In general the critical zinc levels are higher than the present levels as illustrated in Figure 10B. Compared to the present Zn concentration, the variation is much smaller, but also here values are higher for the clay and peat soil in the Western part of the Netherlands than for the sandy soils in the Eastern part. To evaluate whether critical zinc levels are exceeded at this moment, Figure 10C was constructed. In this figure the critical limit was subtracted from the actual zinc content. Negative (green to yellow) colours indicate areas where critical limits have not been exceeded yet. The data in figure 10C show that current exceedance of the critical limit is restricted to a few contaminated peat soils mentioned before ("toemaakdekken").

In Figure 10D steady state concentrations are shown. Not surprisingly, the levels observed are much higher (in most plots) than actual levels. Nevertheless Figure 10D shows that in certain areas (e.g. the Northeast) steady state levels are in the same order of magnitude or even lower than present day levels. This is illustrated in Figure 10E where steady state levels are compared to actual levels. The areas where actual zinc levels exceed steady state levels are restricted to areas with acid sandy soils.

The most important figure for this purpose is Figure 10F showing areas where the PNEC (critical limit) will be exceeded due to accumulation. As stated before and summarised in Table 18, exceedance of the PNEC is common in clay and peat soils in the Western part of the country and hardly in the loess soils and sandy soils in the eastern part of the Netherlands.

4.2 Present zinc balances

A comparison of the average metal balances for the various types of land use and soil type shows that the zinc input is highest on grassland on sandy soils, whereas Zn input is lowest on arable land on peat (Table 19). On average Zn uptake is clearly higher in grassland than in arable land, leading to lower accumulation rates considering that the average input is comparable. On average, there is never a net loss (negative accumulation) of Zn from the topsoil. Accumulation is generally lowest in grassland on non-calcareous sandy soils, where both uptake and leaching is high. Average accumulation is highest on the clay soils, especially the calcareous clay soils below arable land, where leaching is very low. Below calcareous sandy soil, leaching is also low, while uptake is also reduced leading to relative large accumulation rates (Table 19).

Table 19 Average fluxes of Zn for the various land use and soil types in 2000. Both leaching and accumulation refer to the plough layer (0-10cm for grassland and 0-30 cm for arable land)

Land use	Soil type	Zn flux ($g.ha^{-1}.yr^{-1}$)			
		Input	Uptake	Leaching	Accumulation
Grass	Sand	938	700	228	10
	Sand calcareous	853	510	66	277
	Clay	969	474	34	460
	Clay calcareous	885	390	16	479
	Loess	1013	636	117	260
	Peat	889	455	126	308
Arable	Sand	1039	392	377	271
	Sand calcareous	868	319	86	463
	Clay	911	347	43	521
	Clay calcareous	899	238	19	642
	Loess	993	405	178	410
	Peat	836	317	271	248
All		926	425	152	349

The ranges in Zn input, uptake, leaching and accumulation from the topsoil are shown in Figure 11.

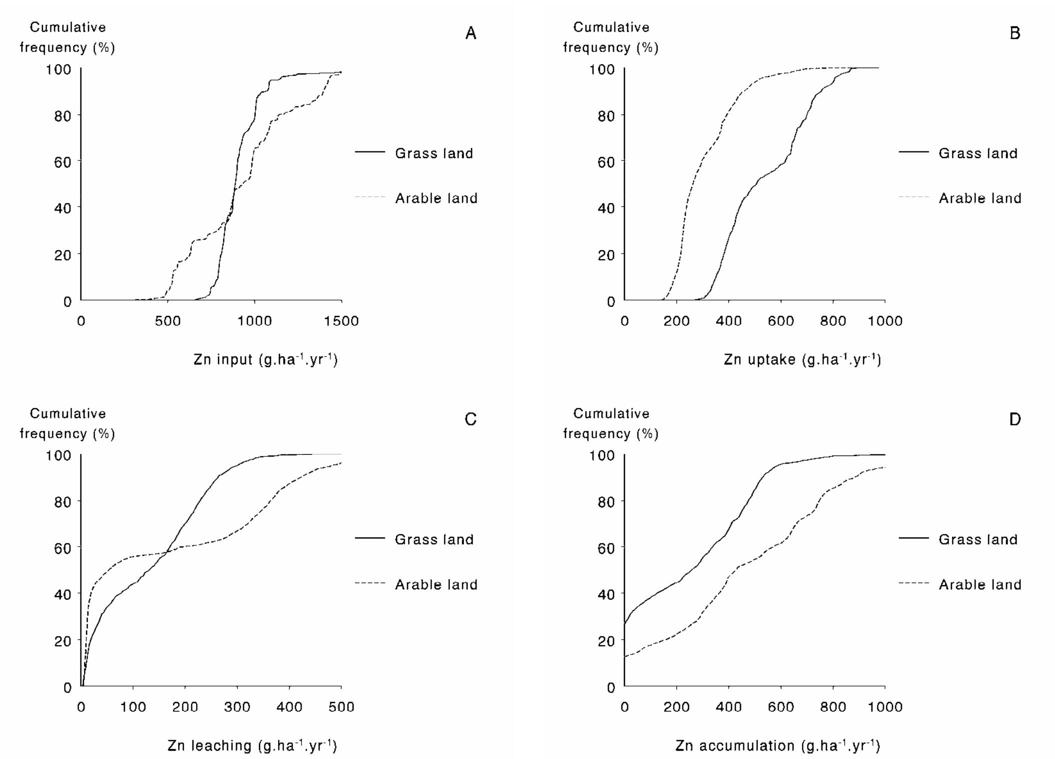

Figure 11 Ranges in the input (A), uptake(B), leaching (C) and accumulation flux (D) of Zn on grassland and arable land in the year 2000

In general the variation in Zn inputs to grassland is less than those to arable land but the median value of both types of land use are close (around 900 $g.ha^{-1}.yr^{-1}$, Figure 11A). Zinc uptake by grass on the other hand is higher than uptake by arable crops (Figure 11B). This is mainly due to the higher zinc content of grass compared to crops like potato or wheat. Zinc levels in sugar beet or maize are in the same order as those for grass (see Annex 1). In contrast to uptake, differences in leaching losses between arable land and grassland are smaller (Figure 11C). This is mainly due to the fact that leaching is not so much related to land use but to soil acidity (in combination with the zinc levels in soils of course). The highest leaching losses occur on non-calcareous arable land (peat) where the combination of a low (less than 5) pH and high zinc levels in soil result in large leaching losses. The resulting net accumulation rate is larger in arable land, reflecting the difference in uptake (Figure 11D). Figure 11D also shows that in arable land net depletion occurs in approximately 10% of the plots (intercept with Y-axis). Net depletion in grassland occurs in approximately 30% of the plots.

4.3 Changes in zinc fluxes and concentrations in time

Changes in zinc fluxes in time

Soil zinc concentrations change over time, thus influencing Zn leaching and crop uptake. Ultimately, a steady state was reached where soil Zn accumulation is negligible and the excess soil Zn input (Zn input minus Zn crop uptake) is equal to the amount lost by leaching. Those changes are illustrated in Table 20.

Results show that on average the accumulation decreases from near 250 and 450 $g.ha^{-1}.yr^{-1}$ in grassland and arable land, respectively, in 2000 to zero accumulation at steady state. At steady state the average uptake is more than 2 times higher compared to leaching in grass land (656 versus 260 $g.ha^{-1}.yr^{-1}$), whereas average values are of equal magnitude in arable land (475 versus 460 $g.ha^{-1}.yr^{-1}$). The relative increase in uptake, due to increasing Zn contents in the soil, is much smaller (approximately 40-60%) than the relative increase in leaching (approximately 200-275%)

Table 20 Average input, uptake, leaching and accumulation fluxes of Zn in the topsoil at different time periods and at steady state

Land use	Situation	Zn flux ($g.ha^{-1}.yr^{-1}$)			
		Input	Uptake	Leaching	Accumulation
Grass land	2000	916	541	133	241
	2100	916	573	155	188
	2500	916	619	205	92
	Steady-state	916	656	260	0
Arable land	2000	936	306	172	458
	2100	936	324	209	403
	2500	936	359	271	306
	Steady-state	936	475	460	0

Changes in zinc concentrations in time

Trends in soil Zn concentrations in time in accumulation and release plots are illustrated in Figure 12 by graphs of the 5%, 50% and 95% values for the period 2000-2500. The results illustrate that the accumulation rate in the plots with a high increase (especially the clay soils) is relatively constant during the first 500 years (compare the lines of the 50 and 95% of Fig. 12A). The release rate in the non-calcareous sandy soils decreases relatively fast within a 100 year period (Fig 12B).

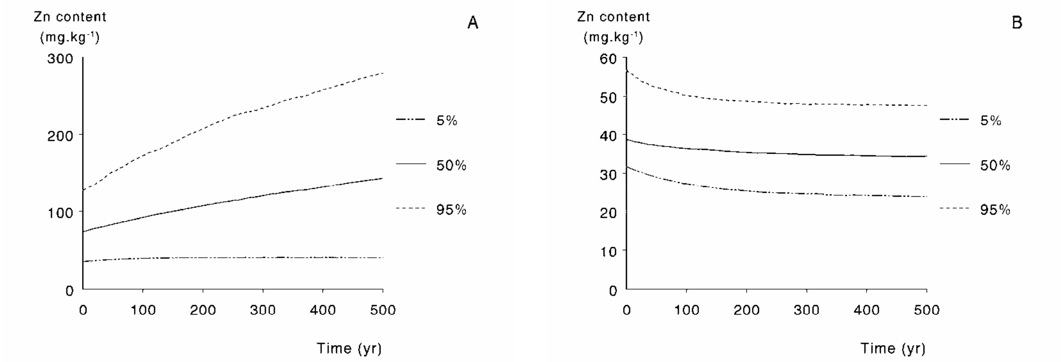

Figure 12 Graphs of the 5%, 50% and 95% of trends in soil Zn concentrations in accumulation (A) and release plots (B) in the period 2000-2500.

An indication of the differences in trends in accumulation plots for the various distinguished soil types is presented in Figure 13. In each graph also the line with the critical limit for the considered soil type is included. The results show that the time period in which a critical limit is reached (if ever) varies strongly between different soil types. In the non-calcareous sandy soils and loess soils, even the 95% does not reach the critical limit within 500 years (Fig. 13A, E). In calcareous sandy soils and clay soils, the median crosses the critical limit near or within 500 year (Fig. 13B, C and D) and for peat soils this is even within 200 year (Fig. 13 F). Here the 95% already exceeds the critical limit at the beginning (polluted "toemaakdekken").

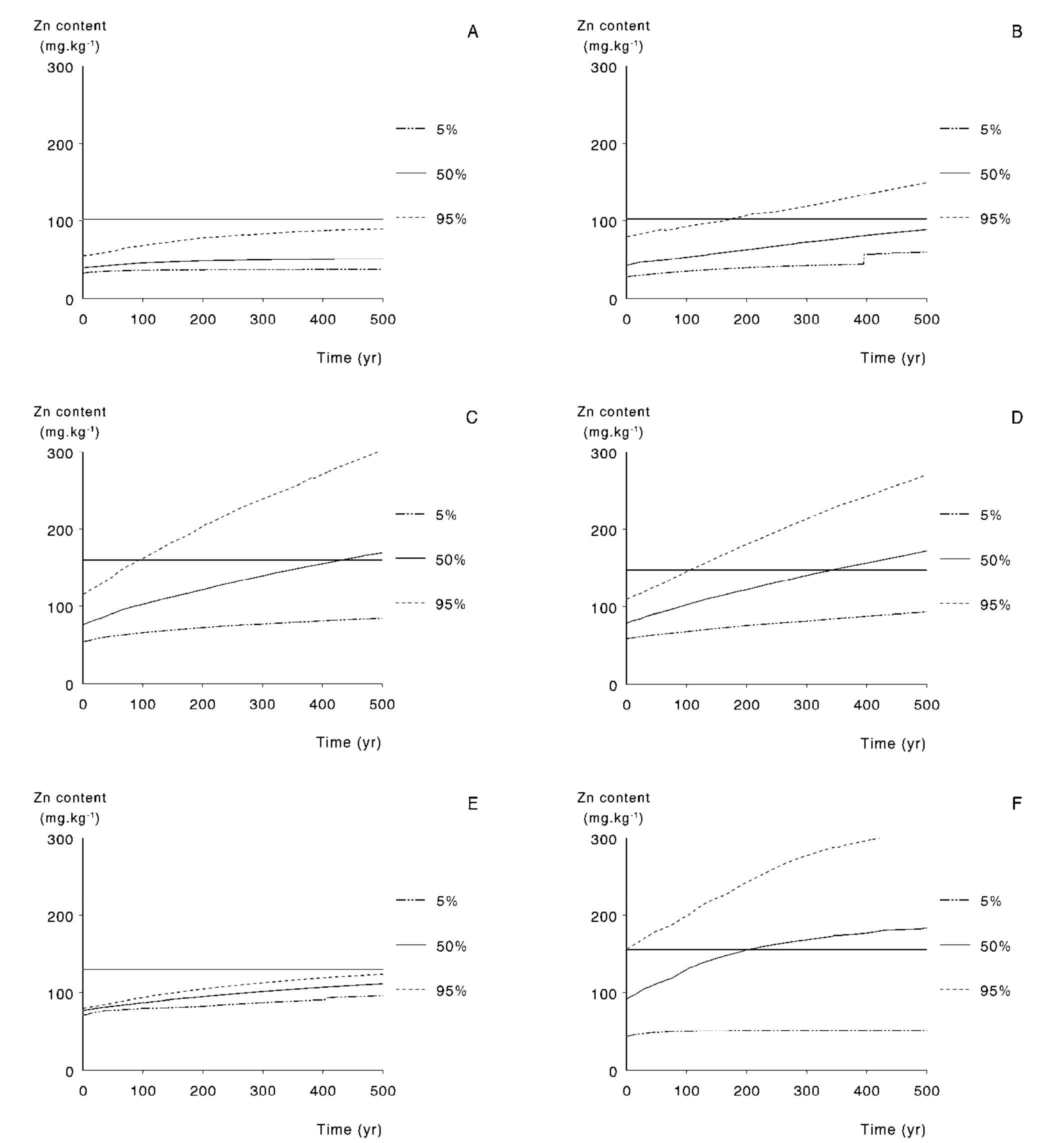

Figure 13 Graphs of the 5%, 50% and 95% of trends in Zn concentrations in accumulation plots of non-calcareous sandy soils (A), calcareous sandy soils (B), non-calcareous clay soils (C) calcareous clay soils (D), loess soils (E) and peat soils (F).

Time periods to reach steady state soil zinc concentrations

More information on the time periods to reach steady state is given in Table 21. Results show that the overall average time period is approximately 1500 year. The time periods increase in the order non-calcareous sandy soils (near 300-400 years) < loess and peat soils (near 600-1000 years) < calcareous sandy soils (near 900-1800 years) < non-calcareous clay soils (near 1500-2300 years) < calcareous clay soils (near 2000-4000 years). The results clearly illustrate that the time period to reach steady state is very large in soils where Zn accumulation ultimately leads to problems, i.e. clay soils and calcareous sandy soils.

Table 21 Averages of time periods to reach steady-state for Zn on all considered land use types and soil types. Values in brackets give the range between 5% and 95% (90 percentile ranges)

Soil type	Time period to reach steady state (yr)					
	Grass		Arable		Total	
Sand	297	(84-491)	457	(163-796)	369	(96-656)
Sand calcareous	896	(896-896)	1859	(865-2677)	1828	(865-2675)
Clay	1582	(904-2515)	2319	(634-4100)	1794	(854-3708)
Clay calcareous	2151	(1493-3036)	3713	(2009-4608)	3204	(1622-4503)
Loess	678	(592-888)	1066	(821-1125)	913	(623-1111)
Peat	642	(151-1246)	776	(151-2659)	686	(151-2021)
All	943	(121-2565)	2159	(211-4359)	1551	(151-4242)

4.4 Temporal changes in soil zinc concentrations in view of critical limits

The comparison of present and steady-state zinc concentration to the critical

As stated before, regarding the dynamic behaviour of zinc, there are four major possible options depending on the present concentration (P), the critical concentration (C) and the steady-state concentration at present inputs (SS):

1. The soil zinc concentration always stays above the critical zinc concentrations, with a further subdivision:
   - C<SS<P: in this case, the model predicts a decrease in the soil Zn concentration but this decrease is insufficient to drop below the critical soil Zn concentration which results in an infinite recovery delay time.
   - C<P<SS: in this case, already at the beginning of the model the model predicts an increase in the soil Zn concentration but it is already at the start above the critical Zn concentration.
2. The soil zinc concentration always remains below the critical zinc concentrations, again with two different scenarios:
   - P<SS<C: in this case, the model will calculate an increase in the soil Zn concentration but it will never exceed the critical soil Zn concentration and consequently, the (damage delay) time is infinite.
   - C>P>SS: in this case, the soil Zn concentration at the beginning of the simulation is below the critical soil Zn concentration and the model predicts a further a decrease in the soil Zn concentration
3. P<C<SS: in this case, the soil Zn concentration will exceed the critical Zn concentration during the simulation and the (damage delay) time can be calculated.
4. P>C>SS: in this case, the soil Zn concentration will drop below the critical Zn concentration during the simulation and the (recovery delay) time can be calculated.

The percentage of plots from the options listed above are given in Table 22. The results show that the number of plots where either: (i) the zinc concentration stays always above the critical zinc concentration (case 1) or (ii) drops below the critical Zn concentration during the simulation (case 4) are negligible. The plots either stay always below the critical limit (case 2) or the Zn concentration increases such that it will exceed the critical Zn concentration during the simulation (case 3). Both cases represent approximately half of the plots (Table 22).

Table 22 Percentage of plots with zinc concentrations above or below critical limit

Land use	Percentage of plots with zinc concentrations above or below critical limit			
	Always above	Always below	Decrease to critical limit	Increase to critical limit
Grass land	0.33	25	0.02	25
Arable land	0.08	22	-	27
Total	0.41	47	0.02	53

The geographic variation of the plots over the four options is illustrated in Figure 14. Results are in accordance with the spatial pattern of soil types in the Netherlands (Figure 6). Only in the polluted peat area in the central part of the Netherlands, values are always exceeding critical limits. There is only one plot where the Zn concentration decreases below the critical limit. The areas increasing to critical limits are located in the western part of the Netherlands where both clay and peat soils occur. Areas where the soil Zn content always remain below the defined critical limit occur in the eastern part where non-calcareous sandy soils predominate.

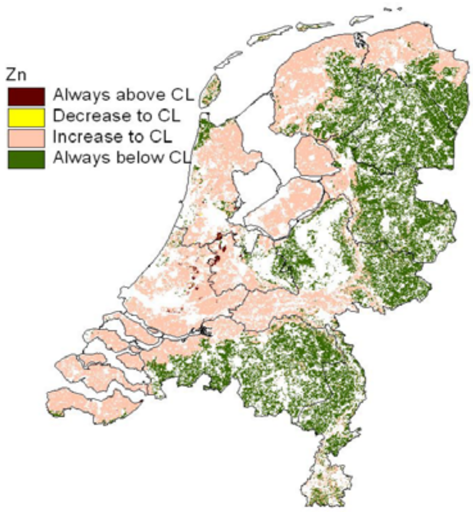

Figure 14 Geographic distribution of plots with zinc concentrations always above or always below critical limit and decreasing or increasing to critical limit

Time periods to reach critical soil zinc concentrations

During the period to steady-state, the increase in soil Zn concentrations at 53% of the plots was such that the critical values were exceeded. Time periods to reach critical soil Zn concentrations at sites where they are ultimately reached are given in Table 23. Results show that, unlike the time period to reach steady-state, the time periods to reach critical limits are not so strongly influenced by the different land uses and soil types, although the influences are significant. On average, critical Zn concentrations are reached within 300 years for grassland and within 650 years for arable land. Especially on arable land, and specifically on clay soils, the time period can be very long and can last more than 3000 years.

Table 23 Averages of time periods to reach the critical limits for Zn on those types of land use soil type where exceedance did occur in the course of time. Values in brackets give the range between 5% and 95% (90 percentile ranges)

Soil type	Time period to reach critical Zn limits (yr)					
	Grass		Arable		Total	
Sand	291	(26-495)	444	(81-1180)	377	(80-1152)
Sand calcareous	373	(372-372)	577	(67-1108)	566	(82-1050)
Clay	589	(92-2741)	885	(204-2978)	664	(102-3765)
Clay calcareous	262	(92-457)	594	(205-1352)	484	(136-1268)
Loess	435	(80-681)	1704	(848-1960)	1516	(264-1952)
Peat	161	(29-391)	773	(111-2509)	244	(29-778)
All	268	(34-506)	643	(194-1747)	463	(63-1353)

The geographic variation of the time periods to reach critical limits, limiting ourselves to the plots at which the Zn concentrations increases until the critical limit is exceeded, is given in Figure 15. Results show that the time periods are relatively small in the areas where the present Zn concentrations are already close to the critical Zn concentration.

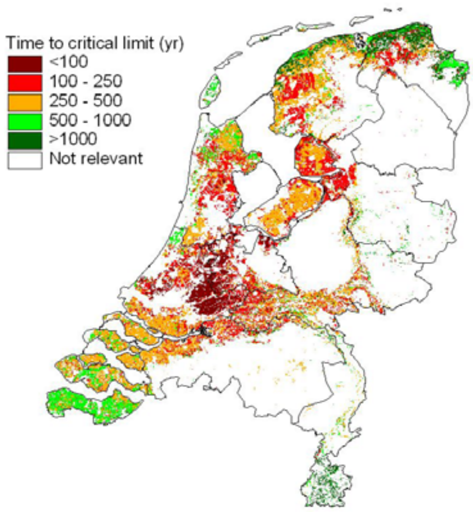

Figure 15 Geographic distribution of the time periods to reach critical limits

5 Plausibility and representativity of the results

The validity of model results, like the ones presented here, largely depends on the adequacy of the model used (leaching and plant uptake model). In addition to the model performance boundary conditions like uncertainties in critical limits and data will affect model inputs and model outputs (see Chapter 6). An impression of the validity of the overall model results can be obtained from a comparison of model outputs on measured data. This does however require measured information on both model inputs (in this study specifically zinc inputs to the soil) and model outputs (in this study specifically net zinc uptake by crops and zinc leaching from the soil). The availability of these data at the desired scale level is usually limited. To evaluate the dynamic behaviour of the model, it is even needed to have information on the changes with time, preferably during a period of various decades. The availability of such data is even more limited.

There are, however, a few well documented cases that can be used for comparison of model results with field data on the plot or regional scale. A strict model validation was not carried out as this would require an application of the model on those plots to compare model outputs with the measured data. Instead we compared the results for the Netherlands obtained in our study with available Zn accumulation data in time (Rothamsted experimental station) and in space (data from Dutch and Swiss monitoring networks that include sites with measurements at a fixed point in time) to get an impression of the plausibility of the model results (paragraph 5.1). Also Europe-wide data on farm gate balances were used to assess whether or not the modelled range in Zinc accumulation rates are representative for Europe (paragraph 5.2)

5.1 Plausibility of the model results

The plausibility of the model results was assessed from a comparison of the results with data from site specific and regional studies, as described in detail below.

Data on zinc accumulation in time at Rothamsted experimental station

Long term studies are needed to validate model studies such as the one presented here. One of the very few well documented cases where both land use, input levels and output have been quantified are the field trials at Rothamsted experimental station. Here, annual inputs and outputs have been monitored since 1843 (Jones et al., 1987) at various sites in both control plots and farmyard manure (FYM) treated soils. In Table 24, the present soil zinc contents in two clay soils are shown for a control plot and a FYM treated soil. The original zinc content was approximately 35 $mg.kg^{-1}$. Using this value, the annual change at the Rothamsted experimental fields treated with farmyard manure was found to range from 0.37 to 0.54 $mg.kg^{-1}.yr^{-1}$. These changes were compared with the predicted yearly accumulation rate in the clay soils presented in Table 19. Using Eq. 14, we calculated that based on a net accumulation input rate of 521 (non calcareous clay) to 642 (calcareous clay) $g.ha^{-1}.yr^{-1}$, the annual change in the soil zinc content ranges from 0.16 to 0.20 $mg.kg^{-1}.yr^{-1}$. These value indicate that the model calculated changes in the soil zinc content are not an overestimation of actual (measured) accumulation rates at the field scale.

Table 24 Overview of Zn content in two experimental fields at Rothamsted experimental station (data kindly supplied by S. McGrath)

Soil	Zn content (mg kg^{-1})
Broadbalk (150 yrs)	
Control	62
FYM treated soil	91
Barnfield (130 yrs)	
Control	70
FYM treated soil	105

One reason why the observed changes at Rothamsted exceed the (average) calculated values is that inputs due to atmospheric deposition are rather high (estimated at 600 $g.ha^{-1}.yr^{-1}$, Jones et al., 1987). Based on these data, it was estimated that the annual change due to atmospheric inputs alone already ranged from 0.18 to 0.27 $mg.kg^{-1}.yr^{-1}$. After correction of the total change for atmospheric deposition, the contribution of other sources (mainly manure) ranged from 0.19 to 0.27 $mg.kg^{-1}.yr^{-1}$. These values are in close agreement with model calculated changes presented here. The total input due to manure was estimated at 1470 $g.ha^{-1}.yr^{-1}$ which is also a bit higher than the average input rate in the model study (approx. 900 $g.ha^{-1}.yr^{-1}$) which could further explain the somewhat higher observed accumulation rates.

Dutch data on zinc accumulation at different sites at a specific point in time

Data on Zn (and Cu) supply and removal (farm level Zn metal balances) on 17 dairy farms have recently been presented by Boer and Hin (2003). The farms are located throughout the Netherlands on different soil types comparable to the ones used in the model study presented here (sand, loess, clay and peat). The average net zinc accumulation rate (i.e. inputs minus outputs) on all farms equalled 507 g ha^{-1} yr^{-1} but data from individual farms (in 2001) ranged from -29 g ha^{-1} yr^{-1} to +1187 $g.ha^{-1}.yr^{-1}$. These data are in close agreement with those reported in Table 19 (although slightly higher) but data from individual farms confirm that the range can be quite substantial and site-specific information is needed to predict changes for individual farms (soil properties, crop type, yield etc.).

In the report from Boer and Hin (2003) also data on the zinc content in grass and maize are given. For grass and maize measured zinc levels ranged from 30 to 68 $mg.kg^{-1}$ dm (average 42 $mg.kg^{-1}$) and from 24 to 49 $mg.kg^{-1}$ (average 36 $mg.kg^{-1}$), respectively. These data are in agreement with model predictions presented in table 15 showing a modelled range for zinc of 28 to 71 $mg.kg^{-1}$ for grass and 17 to 58 $mg.kg^{-1}$ for maize.

Swiss data on zinc accumulation at different sites at a specific point in time

One of the countries with a high measuring point density and (partly)comparable climate is Switzerland. In a study by Keller (2000) an extensive model analysis was presented on Zinc input and output fluxes on 201 farms. The net zinc flux (accumulation) was found to be close to 600 $g.ha^{-1}.yr^{-1}$ with extremes ranging from values close to 100 to almost 40000 $g.ha^{-1}.yr^{-1}$. For 'normal' dairy farms values between 349 and 614 $g.ha^{-1}.yr^{-1}$ were obtained which are quite comparable with the data presented in Figure 11 and Table 19, although again slightly higher. The individual components of the metal balance (deposition, leaching, uptake etc.) were found to be quite close although atmospheric deposition levels in Switzerland appear to be higher than those in the Netherlands. In the Swiss study zinc uptake by grass in dairy farms was predicted to be much higher (approximately twice as high) than that of arable crops (compare Table 19). This was observed in the Dutch model results as well. An uncertainty analysis showed that up to 70% of the total observed variance in the model results was explained by variation of the zinc content in manure (approx. 30%), uptake by crops (20%) and a combination of soil pH and CEC (20%). The remainder of the variance was distributed among a.o. the soil zinc content of the soil and regression errors.

Apart from the model study also data were compiled from a large number of agricultural farms. Measured zinc input levels for dairy farms again are comparable to the data presented here. For dairy and mixed farms the total input equalled approx. 900 ± 265 $g.ha^{-1}.yr^{-1}$ whereas output (crops and leaching) equalled approx. 530 ± 200 $g.ha^{-1}.yr^{-1}$. For arable farms input levels were lower (approx. 530 $g.ha^{-1}.yr^{-1}$) mainly due to the fact that no manure was used (which is the case in the Netherlands). These data show that the values obtained from the model study presented here are realistic although the extreme fluxes observed in some Swiss farms (input due to manure application up to 40000 $g\ ha^{-1}\ yr^{-1}$ in an intensive pig breeding farm, Keller 2000) shows that real input levels in high intensity animal breeding farms are probably much higher than the average values used in our study

The comparison of modelled results with measured field data suggests that the order of magnitude in predicted current zinc accumulation rates as well the changes in zinc accumulation and in soil zinc concentrations is realistic. Of course, predictions for specific sites in regions will deviate from average values, but in general the predicted levels of inputs, outputs (crops) and changes in the soil zinc content were found to be close to measured values at certain sites.

An additional remark refers to some of the fluxes (input as well as output). Although in both studies data were used to obtain most fluxes, some in- and outputs were obtained from estimates or literature. In the Dutch study, leaching was kept constant at 207 $g.ha^{-1}.yr^{-1}$ whereas atmospheric deposition was estimated at 164 $g.ha^{-1}.yr^{-1}$ In the Swiss study, leaching fluxes were not constant but were calculated using a similar approach as was used in this study (Freundlich model based on soil properties). In a strict sense, these balances are therefore not entirely based on local data but do contain either default values or estimates based on expert judgement or models.

Assessment of validity of model predictions of dissolved zinc concentrations
One of the most important outputs presented in this study is the leaching flux. In this report leaching fluxes are based on model predictions of water leaving the soil at 10 cm (grassland) and 30 cm depth (arable land). However, little or no data -other than measured soil solution concentrations that were used to calibrate and validate the model- exist on soil solution concentrations in the upper soil horizon and a direct comparison between model predictions and data is thus not possible. Therefore, it was decided to compare the predicted soil solution concentrations with measured values from monitoring networks in both upper groundwater (Fraters et al., 2001) and in surface water (Bonten et al., 2004). For upper groundwater, the individual measured concentrations of zinc were used and clustered according to soil type and land use. The data from the surface water monitoring network were allocated to STONE plots and average values within each STONE plot were calculated to derive frequency distributions for each soil type considered. Beware that data were only available for approximately 600 STONE plots, however with an even distribution among sand, clay and peat soils.

The plausibility of the predicted concentrations in the soil solution can thus be tested by requiring that they should be (at least) equal or higher than measured concentrations in upper groundwater and surface water since Zn concentrations will decrease with depth in the soil profile. This is mainly due to the decrease in the total Zn content in soil with depth which causes Zn retention. Furthermore, changes in soil properties can cause a significant decrease, for example in a calcareous subsoil below a non-calcareous topsoil. Similarly, surface water concentrations are likely to be lower, because of reasons described above and because of further metal retention in surface waters.

In general, the modelled soil solution concentrations indeed are higher than those measured in upper groundwater and surface water (Table 25). The concentrations decrease going from soil solution> upper groundwater > surface water, with the exception of clay soils where the concentration in upper groundwater is lower than in surface water. In sandy soils and peat soils, the median modelled values in the soil solution exceed the median data for ground water and surface water by a factor of 3 to 9, respectively (Table 25). In clay soils, however, the match between modelled values in soil solution and measured data in upper groundwater and surface water is much closer, thus indicating that further metal retention at lower soil depths and in surface waters is very limited in clay soils. A striking difference, however, exists in the upper concentration range (90% and maximum value) where model predictions in clay and peat soils clearly exceed measured values.

It should be noted however that model predictions listed here summarise more than 6000 soil profiles, whereas measurements in upper groundwater and surface water are limited to approximately 250 to 600 sites, respectively. The range in soil properties present in the model database therefore exceeds that of the data and invariably leads to a larger range in predicted concentrations. In addition to this, averaging of measured values of surface water data within STONE plots also implies that peak values are not visible anymore.

Table 25 Comparison between modelled Zn concentrations in soil solution and data from upper groundwater and surface water (source: Fraters et al., 2001; Bonten et al., 2004)

Soil Type	Water type	Data type	Dissolved Zn concentrations (ug.l-1)				
			min	5%	50%	90%	max
Sand	Soil solution[1]	Model	6	64	150	210	683
	Upper ground water[2]	Measured	< 5	10	57	190	300
	Surf. Wat. Arable[3]	Measured	6	7	19	56	238
	Surf. Wat Nature[3]	Measured	5	6	15	60	353
Clay	Soil solution	Model	3	5	15	73	169
	Upper ground water	Measured	< 5	< 5	bd[4] - 11[5]	16-20[5]	50
	Surf. Wat. Arable	Measured	1	6	13	41	107
	Surf. Wat Nature	Measured	2	5	13	26	45
Peat	Soil solution	Model	5	16	91	188	540
	Upper ground water	Measured	< 5	10	33	52	80.
	Surf. Wat. Arable	Measured	5	6	11	23	97
	Surf. Wat Nature	Measured	<1	3	13	34	117

[1]: "Soil solution" refers to the calculated concentrations in the 0-10 (grassland) or 0-30 cm (arable land) layer in the topsoil

[2]: Data from Fraters et al. (2001): measured in the upper meter of the groundwater in the field.

[3]: Data from Bonten et al. (2004): measured concentrations in surface waters. The values listed represent the minimum, 5, 50, 90 and 100% percentile for the STONE plot averaged values for each soil type.

[4]: bd below detection

[5]: Range indicates difference between sea clay and river clay

In summary, based on this very crude comparison it seems that predicted soil solution concentrations for Zn are in line with those measured in upper groundwater and surface water.

5.2 Representativity of the results

Insight in the representativity of the results for Europe as a whole was obtained by a comparison of model results with reported European-wide data on zinc inputs and on net zinc inputs in European experimental farms, as described in detail below.

A comparison of Zn inputs by manure in EU countries

The representativity of the results with respect to the Zn inputs used is discussed in detail in Annex 2, based on a comparison of Zn inputs in manure and slurries (but excluding sewage sludge!) in EU countries, using an (unpublished) overview of manure production, use and composition made by ADEME (A. Bispo, C. Schubetzer and I. Feix). The results show that input of manure and slurry in the Netherlands are indeed high compared to other countries but the average Zn input near 1250 $g.ha^{-1}.yr^{-1}$, used in our study for the Netherlands is quite comparable to those reported in the ADEME study for Germany, Denmark, Ireland, Luxembourg, UK and Belgium (see Figure A2.1). However, data in several national reports (e.g. Denmark) from various countries deviate from the data presented in this graph and the absolute values presented in this graph are likely to be rather high. For Denmark, the initial value (even higher than the value in the current graph) was verified and the corrected value (included in the graph in Annex 2) was found to be comparable to those for the Netherlands as reported in this study (not the ones in the graph in Annex 2). The input data used thus represent a worst case, but seemingly not an extreme one and the results can be considered to be representative for large areas in North-Western Europe with similar climatic conditions and soil types.

A comparison of net zinc inputs in European experimental farms

Ultimately, it is not the input but the excess of Zn (input minus uptake) that determines the possible Zn accumulation in soil. Recently, heavy metal balances were compiled for a range of European wide experimental farms within the context of the so-called AROMIS study. These farms include regular farm types but also farms where excessive amounts of organic soil amendments like sludge have been used. In Table 26 an overview of the minimum, mean and maximum net Zn input (input minus uptake) per year is given. To calculate these loads, the same inputs and outputs were considered as has been done for the Dutch sites described in this report.

Table 26 Overview of net Zinc input rates to soils in Europe

Net Zink input ($g.ha^{-1}.yr^{-1}$)					
Animal production farms			Arable Crop farms		
min	med	max	min	med	max
-188	593	6797	-102	289	6939

Again, most fluxes in these balances were measured with the exception of the leaching flux. This flux was calculated based on the (measured!) net water leaching loss (input minus plant uptake and evaporation) and a calculated soil specific concentration in the soil solution. Leaching losses thus calculated were significant in north western parts of Europe (similar to the fluxes presented in this study) but negligible in southern countries due to the fact that water leaching rates were close to zero or even negative (net water shortage).

A difference between both approaches is that the AROMIS balances are based on a farm approach, whereas the balances in our study are based on a field approach. In a farm balance the internal flows on the farms are not included. Crops produced on the farm and used as cattle food for example do not occur on the balance, nor does the manure produced from this food (unless it is being exported from the farm itself). Import of feed additives that are mixed with the food are taken into account as input. Additional important inputs that are not considered in the Dutch balance study include disinfecting solutions (important source of copper). Export on dairy farms includes animals and animal products (milk, beef) instead of grass. One can show, however that the field and farm balance is comparable if similar inputs are used.

The median value of 593 $g.ha^{-1}.yr^{-1}$ for animal production farms, as presented in Table 26, is about equal to the average value for Dutch farms (see Table 12). The median value of 289 $g.ha^{-1}.yr^{-1}$ for arable crop farms, however, is less than half of the average value for Dutch farms. Also the minimum values (-188 and -102 $g.ha^{-1}.yr^{-1}$ in animal production farms and arable crop farms respectively), which indicate a net loss of zinc, are in the same order as the values reported for the Dutch farms (-53

$g.ha^{-1}.yr^{-1}$). It should be stressed though that the net loss is strongly related to the net water loss from the soil. From the AROMIS data it appeared that negative Zn loads (net loss of Zn) only occurred in countries in North Western parts of Europe (data from Norway, Denmark) with low inputs of animal feed additives or manure in combination with high leaching and moderately acid soil pH levels.

In general the magnitude of the net Zn load was correlated quite strongly to the use of manure (import of manure) or the import of feed additives as is shown in Figure 16. Data from individual farms from different countries confirmed that the median values on Zn (as well as other metals) loads do not differ very much between countries. This is especially true for farms under comparable climatic conditions like northern France, the UK, southern Norway, Denmark, Switzerland, Germany and the Netherlands. The ultimate Zn load in all these farms is strongly related to input (and export) of animal feed (or manure when exported). As such the Dutch scenarios as presented in this report are a reasonable reflection of North Western European conditions.

As can be seen in Table 26, the maximum values of the observed net Zn loads (> 5000 $g.ha^{-1}.yr^{-1}$) are much higher than those encountered in the Netherlands. These data however are from experimental farms where excessive amounts of sludge are used to evaluate the impact on soil health. As such they are not representative for 'average' farm types. In intensive animal production farms, the annual zinc balance reached levels of approximately 2000 $g.ha^{-1}.yr^{-1}$ in countries like France, Switzerland and the UK. In 'average' animal production farms where high application rates of manure and/or sludge (UK) were used, annual zinc balances ranged between 500 and 1000 $g.ha^{-1}.yr^{-1}$.

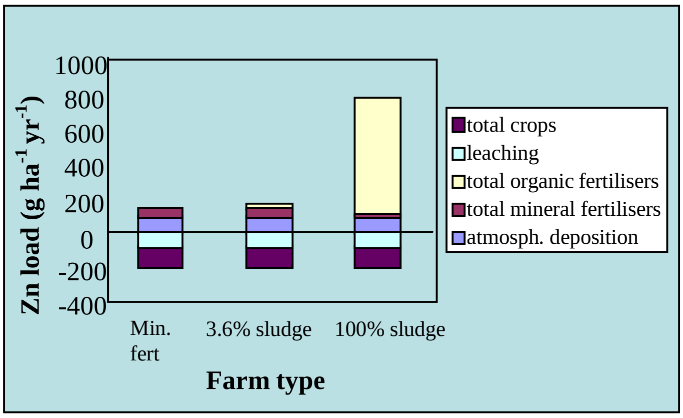

Figure 16Impact of the use of sludge as a source of N on the Zn load in a Danish experimental farm. Outputs include crop uptake and leaching, inputs include atmospheric deposition, organic fertilisers and mineral fertilisers. If the N requirements are met by sludge (100% sludge scenario), the Zn load increases from -61 $g.ha^{-1}.yr^{-1}$ to 749 $g.ha^{-1}.yr^{-1}$

6 Uncertainties in the results

Uncertainties in the areas exceeding critical Zn limits in the new steady state situation are determined by uncertainties in both the critical and the steady state Zn content. Both aspects are discussed below in Section 6.1 and 6.2. Uncertainties are presented by focusing the results on the: (i) percentage of plots exceeding critical Zn limits (PNECs of Zn) and (ii) average time period to reach critical Zn limits, distinguishing between grass land and arable land and between the various soil types. Regarding soil types, however, no results are shown for the calcareous sandy soils and the loess soils because of the (very) limited number of plots. There is only one plot with grass land on calcareous sandy soil. The number of plots with loess plots is larger namely 15 below grassland and 21 below arable land, but only 1 and 2 plots, respectively, do occupy an area of approximately 70%. This does sometimes cause extreme effects but the area for which it applies is hardly relevant. Furthermore, application of e.g. other input or uptake values, do sometimes affect the number of plots for which the calculations are relevant. For example, when the input data change, certain plots that exceeded the critical Zn limit in the standard situation may never exceed this value in the alternative situation (percentage of plots exceeding critical Zn limits is affected). Those plots are thus not included in the average time period to reach critical Zn limits, since the time is infinite. This difference in the number of plots may cause unexpected differences for the calcareous sandy soils and the loess soils because of their limited number and thus those soil types have been excluded from the tables

6.1 Uncertainties in critical limits for zinc

Using the approach according to the RAR for Zn, uncertainties in the critical content are influenced by the values of the used Zn background concentrations and of the Predicted No effect Concentration of added Zn ($PNEC_{add}$). In this study, we investigated the impact of the uncertainties in both values.

Uncertainties resulting from the approach used to derive background concentrations

In the RAR zinc (2004), the $PNEC_{add}$ is calculated from nominal (=added) chronic NOEC values, mostly originating from experiments on soils containing field (=ambient) zinc concentration. For the risk characterisation, this $PNEC_{add}$ can thus also be added to an estimated "ambient concentration", to compare with the actual measured (total) zinc level at a given location. Considering the added risk approach, the same reference background must in principle be considered at both PEC and PNEC side. If the natural background is considered, the fraction of the ambient background (in soils taken from the field) which is not the pristine natural fraction, but added in the past, must be added to the NOEC observed on this soil, since this fraction in terms of the added risk approach now contributes to the observed toxicity. In this project, we used the NOECs as mentioned in the RAR and applied an ambient Zn concentration, using a topsoil Zn content at 0-30 cm in unpolluted areas as being representative.

An alternative approach would be to just use the ambient present concentrations of Zn in all STONE plots as derived by geostatistical interpolation, including historically polluted sites. Inversely a subsoil Zn content at 60-100 cm could be used as a real background. One can argue, however, that the levels of metals found at 60 to 100 cm merely represents a geological background and not so much a soil background level. Even under natural (no input from agriculture or industry) conditions, some degree of accumulation of metals in the topsoil occurs due to cycling of metals (uptake by roots, litter fall) and natural atmospheric deposition. Whether or not these natural processes lead to higher (or lower!) soil background values compared to the true geological background entirely depends on the acidity of the soil in combination with soil properties (organic matter and clay). Both approaches (i.e. current Zn content from all plots in the topsoil and at 60 to 100cm) were applied here and results were compared with those obtained with Zn content data at a depth of 0-30 cm (standard approach), to see what the sensitivity of the model results is for such changes.

Critical Zn contents using present Zn concentrations obtained by geostatistical interpolation as background data are generally higher than the Zn content data at a depth of 0-30 cm (the standard approach) whereas the use of subsoil Zn content at 60-100 cm leads to systematically lower values, as illustrated by the scatter plots given in Figure 17. The impact of an alternative background concentration on the critical limit is on average + 29 $mg.kg^{-1}$ when using present Zn concentrations obtained by geostatistical interpolation (162 instead of 133 $mg.kg^{-1}$) and - 27 $mg.kg^{-1}$ when using a subsoil Zn concentration at 60-100 cm (106 instead of 133 $mg.kg^{-1}$).

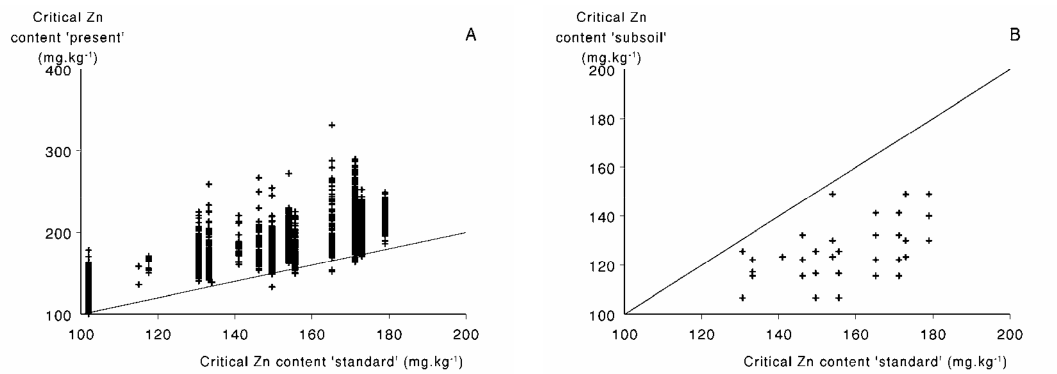

Figure 17 Scatter plots of calculated critical soil Zn concentrations using present Zn concentrations obtained by geostatistical interpolation (A) and a subsoil Zn content at 60-100 cm (B) as compared to Zn content data at a depth of 0-30 cm (standard approach)

Results obtained with the alternative approaches (the geostatistical interpolated present Zn concentrations and a subsoil Zn concentration at 60-100 cm) on the percentage of plots at which the steady-state Zn concentration exceeds the critical Zn concentration are given in Table 27.

Table 27 Percentage of plots at which the steady-state Zn concentration exceeds the critical Zn concentration for an alternative and standard background Zn concentration

Soil type	% of plots exceeding critical Zn limit					
	Grass land			Arable land		
	Present Zn content	Subsoil Zn content	Standard approach	Present Zn content	Subsoil Zn content	Standard approach
Sand	1.3	3.3	1.9	1.7	6.6	3.1
Clay	70	93	80	61	79	66
Clay calcareous	99	100	100	96	99	98
Peat	45	81	72	20	30	23
All	42	56	51	52	59	55

The results show that the effect on the percentage of plots at which the steady-state Zn concentration exceeds the critical Zn concentration is limited (overall 46% and 57% instead of 53%, when using the present Zn concentration and subsoil Zn concentration, respectively).

The impact of the alternative approaches on the average time period before a critical limit is reached is illustrated in Table 28. The results show that the alternative approaches do lead to large differences in the time period needed to exceed the critical soil Zn concentration is exceeded. For grassland the overall difference is approximately plus (present Zn concentration) or minus (subsoil Zn concentration) 150 years. For arable land the overall difference is approximately plus (present Zn concentration) or minus (subsoil Zn concentration) 300 years (Table 28).

Table 28 Averages of time periods to reach critical limits for Zn on the considered land use types and soil types. where exceedance did occur in the course of time for the standard and the alternative approach to calculate Zn background concentrations

Soil type	Average time period to reach critical Zn limits (yr)					
	Grass land			Arable land		
	Present Zn content	Subsoil Zn content	Standard approach	Present Zn content	Subsoil Zn content	Standard approach
Sand	580	545	291	550	372	444
Clay	641	389	589	1205	924	885
Clay calcareous	395	125	262	937	315	594
Peat	348	81	161	937	440	773
All	418	171	268	948	369	643

Uncertainties resulting from differences in the Predicted No effect Concentration of added zinc to the soil

In the RAR zinc (2004), the $PNEC_{add}$ is calculated from standard SSFs, being the standard approach used in this study. As an alternative approach, we calculated the SSF for each plot according to the following formulas for SSF_{Zn} and SSF_{CEC} given in Eq. (2) and (3) using present concentrations of Zn in all STONE plots as derived by (i) a topsoil Zn concentrations at 0-30 cm in a representative Dutch data set (SSF_1) and (ii) geostatistical interpolated topsoil Zn concentrations (SSF_2). Scatter plots of critical Zn contents obtained with the standard SSF and plot specific SSF values are given in Figure 18. The figure shows that the first alternative approach nearly always leads to lower critical Zn contents, whereas the second alternative approach generally leads to higher values for the lower critical limits (the sandy soils and loess soils) and lower values for the higher critical limits (the clay soils and peat soils).

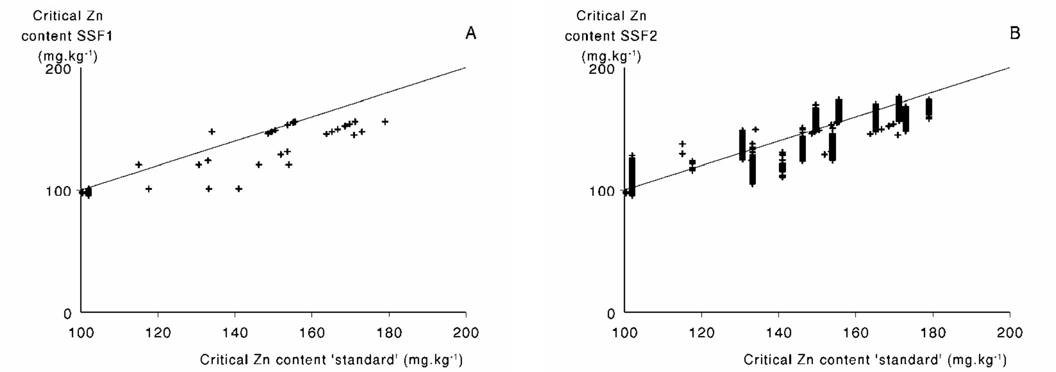

Figure 18 Scatter plots of calculated critical soil Zn concentrations using soil sensitivity factors (SSFs) calculated for each individual plot using the present Zn concentration data for the topsoil based on data in a representative Dutch data set (A) and on geostatistically interpolated data (B) as compared to standard SSF data for each soil type (standard approach)

Results obtained with the alternative approaches (a topsoil Zn concentration at 0-30 cm and geostatistical interpolated present Zn concentrations) on the percentage of plots at which the steady-state Zn content exceeds the critical Zn content are given in Table 29. The results show that the effect on the percentage of plots at which the steady-state Zn concentration exceeds the critical Zn concentration is very small (overall 55% and 53% instead of 53%, when using the subsoil Zn concentration and present Zn concentration, respectively).

Table 29 Percentage of plots at which the steady-state Zn content exceeds the critical Zn content for two alternatives correcting the Predicted No effect Concentration of added zinc by soil sensitivity factors and the standard approach

Soil type	% of plots exceeding critical Zn limit					
	Grass land			Arable land		
	SSF specific 1	SSF specific 2	Standard approach	SSF specific 1	SSF specific 2	Standard approach
Sand	2.0	1.4	1.9	3.2	2.6	3.1
Clay	92	90	80	79	73	66
Clay calcareous	100	100	100	99	98	98
Peat	78	73	72	27	25	23
All	53	52	51	57	54	55

The impact of the alternative approaches on the average time period before a critical limit is reached is illustrated in Table 30. The results show that time periods using the subsoil Zn concentration to calculate the $PNEC_{add}$ (SSF_1) do lead to an average decrease in time period of 40-80 years for grassland and arable land, respectively, compared to the use of the topsoil Zn concentration at 0-30 cm (standard approach). Differences are, on average, minor when the geostatistically interpolated present Zn concentrations are used (SSF_2), but deviations between soil types are large (Table 30).

Table 30 Averages of time periods to reach critical for Zn limits on the considered land use types and soil types. where exceedance did occur in the course of time for two alternatives correcting the Predicted No effect Concentration of added zinc by Soil Sensitivity factors and the standard approach

Soil type	Average time period to reach critical Zn limits (yr)					
	Grass land			Arable land		
	SSF specific 1	SSF specific 2	Standard approach	SSF specific 1	SSF specific 2	Standard approach
Sand	376	391	291	503	607	444
Clay	576	645	589	870	988	885
Clay calcareous	203	248	262	516	622	594
Peat	111	148	161	619	690	773
All	229	274	268	561	649	643

6.2 Uncertainties in zinc dynamics and steady state zinc contents

Uncertainties in Zn dynamics and steady state Zn contents are influenced by the uncertainties in: (i) inputs, (ii) uptake: yields and soil-plant relationships for Zn, (iii) precipitation excess: precipitation and evapotranspiration data, (iv) transfer functions from dissolved to reactive and reactive to total and (v) soil parameters in the various transfer functions and (vi) soil mixing depths considered. In this study, we focused on the uncertainties due to inputs, uptake, soil parameters in the various transfer functions and soil mixing depths.

Uncertainties due to variation in values for inputs

In this study we investigated the impact of using present (year 2000) Zn inputs. The present Zn inputs are dominated by the application of animal manure. The uncertainties in the Zn inputs for each plot are thus dominated by the uncertainty in the N application rate and the Zn/N ratio in the manure. To gain insight in the impact of Zn input, also in view of the representativity of the results (see Section 5.3), we used as an alternative the Zn inputs related to an N input by animal manure below or at the targets of 250 $kg.ha^{-1}.yr^{-1}$ for grassland and 170 $kg.ha^{-1}.yr^{-1}$ for arable land, being the current EU standards. Actually, the value of 250 $kg.ha^{-1}.yr^{-1}$ is a request for grassland and we additionally investigated the use of 170 $kg.ha^{-1}.yr^{-1}$ for both grassland and arable land. The Zn/N ratio was assumed to remain constant in this approach. The impacts of these targets on the Zn inputs is very large for grass land but very limited for arable land as shown in Figure 19. The much larger input of Zn in arable land than on grassland when using a target of 170 $kg.ha^{-1}.yr^{-1}$ for the N input by animal manure is due to: (i) the input of compost and pesticides occurring on arable land only and (ii) the larger input of cattle manure (especially by grazing) on grassland than on arable land, with a much lower Zn/N ratio than pig and poultry manure (see Table 11).

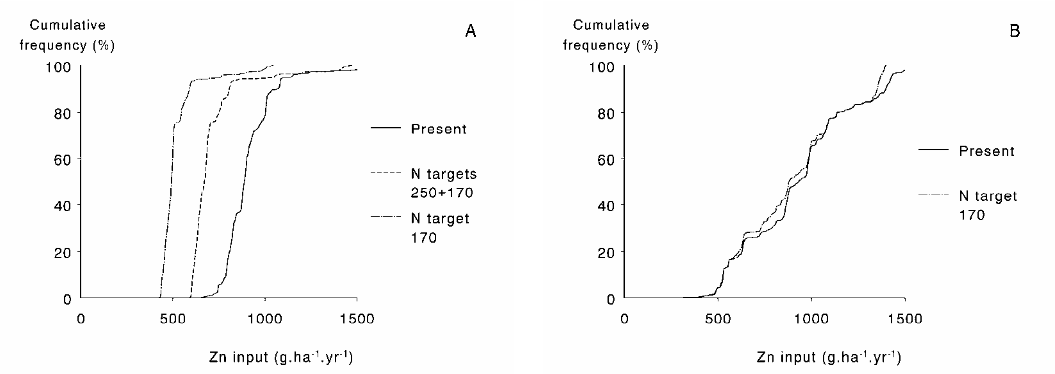

Figure 19 Zn inputs to grassland (A) and arable land (B) using the year 2000 N inputs and applying the N legislation

The impacts of the two alternative inputs on the percentage of plots at which the steady-state Zn content exceeds the critical Zn content is presented in Table 31.

Table 31 Percentage of plots at which the steady-state Zn content exceeds the critical Zn content for two alternative inputs (Zn input related to an N input of 250 kg.ha^{-1}.yr^{-1} for grassland and 170 kg.ha^{-1}.yr^{-1} for arable land or 170 kg.ha^{-1}.yr^{-1} for both land use types) and the standard input, using data for the year 2000

Soil type	% of plots exceeding critical Zn limit				
	Grass land			Arable land	
	N input 170	N input 250	Standard input	N input 170	Standard input
Sand	0.81	1.3	1.9	2.9	3.1
Clay	50	62	80	66	66
Clay calcareous	98	99	100	97	98
Peat	12	40	72	22	23
All	30	40	51	55	55

Results show that the impact of the N target of 170 kg.ha^{-1}.yr^{-1} for arable land is negligible. However, on grassland, the exceedance of plots reduces from 51% to 40% when using a Zn input related to a maximum N input of 250 kg.ha^{-1}.yr^{-1} and it further reduces to 30% when the N target of 170 kg.ha^{-1}.yr^{-1} is used (Table 31).

The impact of the alternative approaches on the average time period before a critical limit is reached is illustrated in Table 32.

Table 32 Averages of time periods to reach critical for Zn limits on the considered land use types and soil types. where exceedance did occur in the course of time for the standard and alternative Zn uptake approach

Soil type	Average time period to reach critical Zn limits (yr)				
	Grass land			Arable land	
	N input 170	N input 250	Standard input	N input 170	Standard input
Sand	3740	2530	291	456	444
Clay	2706	1124	589	1300	885
Clay calcareous	2792	587	262	647	594
Peat	714	341	161	800	773
All	2515	613	268	706	643

The results show that time periods using the subsoil Zn concentration to calculate the MPA do lead to an enormous increase in the time periods before critical loads are reached, from an overall average of 268 years when the Zn inputs for the year 200 are used to 2515 years when the N target of 170 $kg.ha^{-1}.yr^{-1}$ is used (Table 32). Note, however, that the number of plots for which the calculations are relevant differ.

Uncertainties due to variation in calculated crop uptake rates

Uncertainties due to uptake were investigated by comparing results directly using soil-plant relationships for Zn in each STONE plot and results using the calculated median values for Zn in crops based on the application of those relationships. The impacts of the alternative uptake approach (constant uptake using median Zn values for all major combinations of crops and soil type; see Table 15) on the percentage of plots at which the steady-state Zn content exceeds the critical Zn content is presented in Table 33. Overall, the effect of an alternative uptake on the percentage of plots at which the steady-state Zn content exceeds the critical Zn content is small (48% instead of 53%, see Table 33), but for certain soil types it is large (especially peat.

Table 33 Percentage of plots at which the steady-state Zn content exceeds the critical Zn content for an alternative (median Zn values) and standard uptake approach (use of soil-plant relationships)

Soil type	% of plots exceeding critical Zn limit					
	Grass land		Arable land		Total	
	Alternative	Standard	Alternative	Standard	Alternative	Standard
Sand	0.68	1.9	1.8	3.1	1.2	2.4
Clay	87	80	77	66	84	76
Clay calcareous	100	100	98	98	99	98
Peat	48	72	16	23	37	56
All	44	51	53	55	48	53

The impact of the alternative approaches on the average time period before a critical limit is reached is illustrated in Table 34. The use of the alternative uptake approach leads to an average decrease of the time period to reach critical limits of approximately 110 years. For the non-calcareous sandy soils below grassland, the time period is, however, much longer (Table 34).

Table 34 Averages of time periods to reach critical for Zn limits on the considered land use types and soil types. where exceedance did occur in the course of time for the standard and alternative Zn uptake approach

Soil type	Average time period to reach critical Zn limits (yr)					
	Grass land		Arable land		Total	
	Alternative	Standard	Alternative	Standard	Alternative	Standard
Sand	3688	291	232	444	1367	377
Clay	212	589	572	885	307	664
Clay calcareous	174	262	494	594	388	484
Peat	130	161	410	773	171	244
All	189	268	490	643	353	463

Uncertainties due to variation in soil properties

Uncertainties due to soil properties (for a given plot) were quantified by comparing results from two scenarios. One scenario (alternative approach) is based on soil data (organic matter, pH and clay content) from the generic assignment, i.e. the approach with fixed soil profile descriptions for 21 different soil types. All STONE plots were assigned to one of the 21 profiles (see also paragraph 3.2 for a further explanation). The second scenario is the standard approach where soil properties for each plot are based on the geostatistically based soil map. In this approach, the values for organic matter, clay and soil pH were obtained by averaging the values of individual 500 m x 500 m grid cells in one STONE plot. The value in each grid cell was calculated as the average value of the frequency distribution for each soil property, representing the chance distribution for that property (see Brus et al., 2002). In an alternative approach, we also used the median value of this distribution (i.e. the 50-percentile) instead of the average value. A comparison both approaches is given in Annex 3.

The effect of the alternative approach on the steady state Zn concentration is shown in Figure 20. As with the soil properties itself (see Figure 7) results show a large scatter, but in general the steady state soil Zn concentrations calculated with geostatistically interpolated soil properties are systematically higher than those derived by generic assignment, especially in grassland.

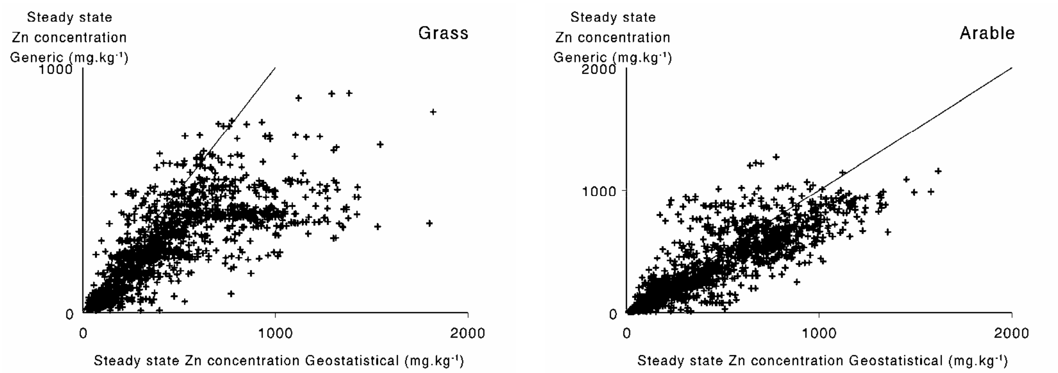

Figure 20 Scatter plots of calculated steady state soil Zn concentrations using generically assigned values of the organic matter content, clay content and pH-KCl as compared to geostatistically interpolated values (standard approach)

The results show that the use of generic soil profiles (alternative approach) leads to much higher leaching rates of Zn (on average more than two times as high) whereas the uptake rate also increases by 15% on average. One of the reasons why the leaching rates increase more pronounced than the plant uptake is that a small decrease in soil pH already leads to a considerable increase in the dissolved Zn concentration, whereas the impact on the Zn concentration in crops is much less pronounced. The range in (measured and modelled) solution concentration within a certain pH is therefore, much larger than the range in Zn contents in crops. This effect (impact of changes in soil properties on solubility versus plant uptake) also holds for other soil properties included in the equations (organic matter and clay) but the effect is less strong.

Both effects (increased leaching and uptake) lead to much lower accumulation rate (Table 35). Despite this large difference, the ultimate effect on the percentage of plots where the critical limit eventually will be exceeded remains small (see Table 36) and decreases from 53% to 46% For grassland, however, the impact is more pronounced (38% exceedance instead of 51%, see Table 36).

Table 35 Average uptake, leaching and accumulation fluxes of Zn for the various land use and soil types in 2000 in the topsoil (0-10cm for grassland and 0-30 cm for arable land) using generically assigned values of the organic matter content, clay content and pH-KCl (alternative approach) and geostatistically interpolated values (standard approach)

Land use	Soil type	Zn flux ($g.ha^{-1}.yr^{-1}$)					
		Uptake		Leaching		Accumulation	
		Generic	Geostat.	Generic	Geostat.	Generic	Geostat.
Grass	Sand	739	700	573	228	-373	10
	Clay	551	474	63	34	355	460
	Clay calcareous	476	390	29	16	380	479
	Peat	541	455	242	126	107	308
Arable	Sand	501	392	1036	377	-498	271
	Clay	389	347	127	43	395	521
	Clay calcareous	245	238	23	19	631	642
	Peat	400	317	650	271	-214	248
All		483	425	372	152	71	349

Table 36 Percentage of plots at which the steady-state Zn content exceeds the critical Zn content using generically assigned values of the organic matter content, clay content and pH-KCl (alternative approach) and geostatistically interpolated values (standard approach)

Soil type	% of plots exceeding critical Zn limit					
	Grass land		Arable land		Total	
	Alternative	Standard	Alternative	Standard	Alternative	Standard
Sand	0	1.9	0.06	3.1	0.03	2.4
Clay	61	80	53	66	58	76
Clay calcareous	100	100	99	98	99	98
Peat	34	72	21	23	30	56
All	38	51	54	55	46	53

The impact of the alternative approach on the average time period before a critical limit is reached is illustrated in Table 37. The results show that time periods using the alternative soil properties do lead to an overall increase in time period of 80 years. For the non-calcareous sandy soils, the time period is, however, much longer, whereas the reverse is true for loess soils (Table 37).

Table 37 Averages of time periods to reach critical limits for Zn in different types of land use and soil types where exceedance did occur in the course of time using generically assigned (alternative) and geostatistically interpolated soil properties (standard)

Soil type	Average time period to reach critical Zn limits (yr)					
	Grass land		Arable land		Total	
	Alternative	Standard	Alternative	Standard	Alternative	Standard
Sand	-	291	584	444	584	377
Clay	529	589	610	885	550	664
Clay calcareous	402	262	654	594	572	484
Peat	233	161	716	773	343	244
All	376	268	665	643	543	463

It should be noted that all the results given above on the differences between Zn behaviour using the generic assignment (the approach with fixed soil profile descriptions for 21 different soil types) and geostatistically interpolated data are based on the use of an average value of the frequency distribution for each soil property, as mentioned above. When using the median (50-percentile) value of this distribution, the difference in results obtained with generic assignment and geostatistically interpolated data is only small (see also Annex 3).

Uncertainties due to the use of different soil mixing depths
Due to the fact that metal inputs to grassland are mixed in the 0 to 10 cm layer (instead of 30 cm for arable land), the average time period to reach critical limits in grassland are shorter than those for arable land (in case of similar inputs and soil properties of course). An effect that could elongate the time period to reach the critical limit is the renewal of grassland every 5 to 15 years. To achieve this, grassland is ploughed, which results in a dilution of the 0 to 10 cm metal content due to mixing with the underlying soil. To evaluate the impact of ploughing of grassland on the time period to reach steady state (or exceedance of the critical limit) we used an alternative scenario assuming a mixing zone of 30 cm instead of 10 cm. Grassland on peat soils with a high organic matter content (we use a lower limit of 75%) were not considered in this approach since these soils are not ploughed. This assumption does not affect the percentage of plots at which the steady-state Zn content exceeds the critical Zn content, but only the time period to reach the critical limit as is illustrated in Table 38 for grassland. As expected the time period increases overall by a factor near 3 (2.64) varying between 2.1 for non-calcareous clay soils to 3 for non-calcareous sandy soils (7).

Table 38 Averages of time periods to reach critical for Zn limits on grassland where exceedance did occur in the course of time using a topsoil of 30 cm (alternative) and 10 cm (standard)

Soil type	Average time period to reach critical Zn limits (yr)	
	Alternative	Standard
Sand	873	291
Clay	1224	589
Clay calcareous	736	262
Peat	482	161
All	709	268

7 Discussion and conclusions

Validity of the model approach used

A strict model validation, which would include a comparison of model outputs with measured data at the individual plot level, was beyond the scope of this study. However to obtain an idea of the validity of the order of magnitude of the model results a comparison of the results with available Zn accumulation data varying in time at Rothamsted experimental station and at a fixed point in time at various Dutch and Swiss sites was made. The results showed that the modelled metal balances for arable cropping and dairy farms are comparable despite a considerable degree of uncertainty (both in data an model output). Regionally averaged values of the model results and the data were in close agreement but the data from Swiss farms showed that locally input levels can be extremely high.

However, both the Swiss and Dutch balances that were used for comparison with modelled data in this study, contained data that were obtained by modelling or expert judgement as well. Leaching losses were either modelled (Swiss data) or kept constant (Dutch data). In general, little or no data exist to calculate accurate leaching fluxes from soils. At best, data from shallow groundwater can be used but these are usually obtained at greater depth than the layer considered in the modelling approach (i.e. 10 or 30 cm below the surface). A useful approach as an alternative for modelling exercises to overcome this limitation could be the use of standardized extraction tests (extraction with dilute salt solutions) that can be used as surrogate soil solutions.

Despite the fact that the balances used for comparison were not entirely based on data, the results still suggest that model approaches such as the ones used here are useful (and valid) for applications on a regional (or national) scale. Application on a specific plot however requires more detailed input (application rates, crop yields and water fluxes) to obtain a representative model result.

In general the model concepts used here are in line with generally accepted approaches. Both the soil solution model and the plant uptake model are similar to published models albeit that model parameters are derived from data from the Netherlands, both for the soil solution model and the plant uptake model. As such these statistical relationships are valid within the boundary conditions of the database from which they are derived. For the soil solution model the database was very large and included the entire range of soil properties and metal content obtained in the model scenarios (no extrapolation beyond the data range in the database) An analysis of the plant uptake model, which was based on less data, showed that extrapolation of the model did not result in extreme values.

Despite the fact that at present the chosen model approach seems applicable, several model assumptions have to be improved in the future. For example, differences in DOC (Dissolved Organic Carbon) between different soils are not considered. It is obvious that DOC from manure and slurries is of a different nature than DOC from stabilised soil organic matter, or on the other end, sewage sludge. Both stability, mobility and the capacity to bind metals has been shown to vary considerable among different types of DOC. This will undoubtedly lead to differences in the amount of metals leached from soils, but the impact of these difference on the leaching fluxes cannot be quantified at present. Also the role of colloidal material in the transport of metals through soils is not included in the model. Contrasting evidence has been put forward in the literature as to whether or not colloidal transport is relevant. For applications on regional or national scale levels existing information is simply not suitable to be incorporated in the model.

Representativity of the results
The results of this study are primarily applicable to Dutch agro-ecosystems. Nevertheless, the results are likely to be close to those in agro-ecosystems in other industrialised countries in North Western parts of Europe. This is based on the similarity in the inputs in other countries as shown by the literature review. The modelled trends are expected to be representative for areas with similar climatic conditions and soil type. Although the model predictions for both plant uptake and solubility of heavy metals are believed to be valid for other areas in Europe as well, large differences in the net water flux through soil will result in markedly lower leaching rates (and consequently higher accumulation rates). Although the comparison of model results and data was limited to a few cases, data on input, output and annual changes in the soil zinc content from the UK, Switzerland and the Netherlands resulted in a good match between measured data and modelled values.

Initially it was assumed that the Netherlands were an example of a 'worst case' in terms of the magnitude of input of zinc to soils. Since accurate data are still lacking on an EU scale, it is not unlikely that manure inputs indeed are among the highest in the EU (as suggested by the figure in Annex 2). The fact that *total* inputs do not deviate as much from other European countries (AROMIS study, Swiss database) is most likely due to the fact that inputs from sludge are much higher in most countries (in the Netherlands it is not used due to legal regulations). Also inputs from atmospheric deposition are somewhat higher in most countries.

Uncertainties in the area exceeding critical zinc concentrations in time
The area exceeding critical zinc concentrations at present and at steady state is determined by uncertainties in the critical content. Using the approach according to the RAR for Zn we investigated the impact of uncertainties in the values of the used Zn background concentrations and of the Predicted No effect Concentration of added Zn ($PNEC_{add}$). Results showed that the effect is limited on the area at which the critical limit for Zinc is exceeded at steady state, but the impact can be large on the time period before this critical limit will be exceeded. One has to be aware that the results are related to the approach according to the RAR for Zn. There are also other approaches possible to derive critical Zn limits, such as the one recently described by Lofts et al. (2004) in which the critical Zn content is estimated as a function of organic matter content and pH.

In this study, a limited analysis was also performed to assess the uncertainty (or perhaps better the impact) in future zinc accumulation rates resulting from different assumptions regarding Zn inputs, Zn uptake (specifically the plant Zn content), the soil properties affecting metal uptake and leaching, and the depth of the mixing layer. The results are also influenced by the reliability of soil-soil solution relationships and soil-plant relationships. Insight in the reliability can be obtained from a true statistical uncertainty analysis, studying the impact of the statistical uncertainty in those relationships on the absolute amount of the calculated leaching flux and plant uptake and hence on the accumulation rate of metals, but this aspect was not investigated here.

As with the results related to critical Zn concentrations, the outcome of the various analyses on the model results seem to indicate that the area at which the critical limit for Zinc is exceeded at steady state can be located with a high degree of confidence. The differences between various scenarios (whether based on different soil properties, zinc background levels or input levels) are usually less than 10%. This would imply that in about 50 to 55% of all plots the zinc critical limit will be exceeded at steady state.

In contrast to the certainty about *where* critical limits can be expected to be exceeded, much more uncertainty remained about *when* this critical limit will be exceeded. Clearly differences in soil type (soil acidity, organic matter content etc.) either speed up or retard the process of accumulation as is the case with the level of input (levels of zinc in manure, atmospheric deposition). This is of importance since the urgency to take measure partly depends on the time frame involved. It is more easy to convince people when critical limits will be exceeded (or predicted to be exceeded) within 50 years then for instance 2000 years, although the ultimate result is the same (if no measures were to be taken). Both the degree of accumulation and the timeframe involved until this degree of accumulation occurs are thus relevant as criteria to take measures.

A large part of this uncertainty arises from the lack of plot specific data which leaves model estimates of, for example, plant zinc levels or soil solution concentrations as the only option to obtain an estimate of the accumulation rate. Basically soil properties like pH, organic matter and clay are essential to obtain both plant uptake and leaching rates but even these properties are often not known on the desired scale although knowledge of the regional variation in soil properties has increased considerable due to large databases containing soil analyses. For the Netherlands a digital soil map on a scale of 1:50000 exists which allows for the schematization of the plots used in this study. For many other countries however this approach cannot be applied since this kind of spatial information is not available. Summarizing, despite the fact that the current approach allows for a more or less accurate allocation of sites where the critical limit will be exceeded, its capacity to predict when this will happen seems to be hampered by a lack of accuracy of input data. This clearly stresses the need for reliable input data (soil data, data on input levels in manure and fertiliser) as well as validated model concepts.

Conclusions

In view of the questions related to metal balances, posed at the beginning of this chapter, the following general conclusions can be drawn:

- Differences in major sources of Zn inputs between different land uses and soil types are limited . In grassland animal manure contributes most (more than 90%) to the input of Zn. Fertilisers are a comparatively small source of Zn, whereas atmospheric deposition is also limited but still twice as high as the input from fertilisers. Other sources, such as compost and pesticides are a significant source in arable land (approximately 15%). It should be noted that compost additions were uniformly distributed among the total area of arable land. In reality, this is not the case and inputs due to compost are usually large at those plots where compost is used (special crops like bulbs, horticulture and on sandy soils low in organic matter) and zero when no compost is used.
- For the Dutch agro-ecosystems, the present Zn inputs of metals exceed the uptake and present leaching at 81% of the plots. This is an indication that present loads to agro-ecosystems in industrialised countries, such as the Netherlands, generally cause an increase in soil Zn concentrations. The highest accumulation of Zn occur on calcareous clay soils with lowest leaching and uptake of Zn.
- Present Zn inputs will cause changes in Zn accumulation and leaching over a period of several hundreds or even thousands of years, depending on land use type and soil type considered. In general steady state is reached within 100-1000 years for Zn, but it can last up to more than 4000 years Those time scales are an indication for the transition times in fertilised agro-ecosystems.
- The steady-state soil metal concentrations that will ultimately be reached can differ strongly from the present metal concentrations and is on average 5 times as large. Consequently, at steady state the PNEC is predicted to be exceeded at 53% of the plots whereas the present exceedance is less than 1%. Time periods to reach those values are however long.
- Despite the various uncertainties, the impact on the percentage of plots exceeding PNECs at steady state is small. Impact on time periods is however high.

More specifically towards the questions relevant to the RAR of zinc the following conclusions can be drawn:

- In the Netherlands, there is hardly any exceedance today of the PNEC of zinc. Plots where at present PNECs are exceeded only include historically polluted sites, such as the "Toemaakdekken" or floodplain soils.
- The percentage of plots where the predicted steady state zinc content will exceed the PNEC is estimated at 53% when using current (year 2000) inputs and at 47% when the legislation for nitrogen will be respected.

- The predicted time period to reach the PNEC for zinc is on average approximately 250 years for grassland and 650 years for arable land when using current inputs. When respecting the N legislation, this time period increases to approximately 600 years for grassland and 700 years for arable land.

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Annex 1 Overview of data underlying the Soil - Plant relationships used in this study

A prerequisite for the derivation and use of soil to plant relationships is that the data used originate from field studies. Major reasons for this are:

- The range of metals in soils reflects 'real' situations, i.e. the combination of soil properties (pH, organic matter, clay etc.) and heavy metal content is not changed due to addition of metals
- The availability of metals under field conditions reflects 'real' conditions. Addition of metals to soils in the form of salts invariably leads to different results due to equilibration processes.

During the 1980's several studies were performed to check the quality of soil and crops on a national or regional levels in the Netherlands. The largest study performed in the Netherlands is the one described by Wiersma et al. (1986). In this study all major food crops were monitored throughout the Netherlands. Unfortunately, this study included priority elements only (Cd, Pb, Hg and As). A second large scale (but regional) study is the so-called "Maasoever" study (Van Driel et al., 1987a, b; Van Driel et al., 1988). In this study contaminated floodplain soils along the rivers Meuse, Roer and Geul were monitored. As such the composition (soil properties) and Zn contents of the soils in this study are not representative for all soils in the Netherlands.

In Table A1.1 an overview is given of the soil and crop properties of the relevant crops included in this study. In general the zinc contents found in these soil samples are higher than those encountered in soils outside floodplains. For comparison, average data on the zinc content (and soil properties) for the STONE plots are listed in Table A1.2.

Despite the fact that the average zinc levels in the Maasoever soil exceed the levels in the STONE plots, the Maasoever data were used to derive soil to plant transfer functions for Zn, being the only Dutch source for deriving such relationships. One reason for using these data was that a comparison of the Maasoever data and the national monitoring study by Wiersma et al. (1986) for Cd showed that although the soil Cd content was significantly higher in Maasoever study, the plant Cd content was not. This was mainly due to rather high clay content and pH in the most contaminated soil samples. Since the behaviour of Cd and Zn is comparable (the availability of both metals is strongly influenced by pH), this indicates that predictions for Zn based on contaminated samples from the Maasoever should render 'normal' values for uncontaminated soils.

Since the soil to plant relationship is a statistically derived function, it should be evaluated what the range in the predicted zinc levels in crops is in case of combinations of soil properties outside the range present in the Maasoever database. For the zinc levels this is hardly a problem since the maximum levels of zinc in the soils does not exceed the levels in the Maasoever database. However certain combinations of soil properties (like peat soils or sandy soils) are not present in the

Maasoever database. In case of a strong contribution of organic matter in the statistical relationship, the application of the soil to plant transfer function could result in erroneous estimates. Therefore the combination of texture, pH, organic matter and zinc content in all STONE plots was used to calculate the zinc content in all crops using the soil to plant relationship. In Figure A1.1 an example of the frequency distribution of the calculated zinc levels in maize are shown.

Table A1.1 Overview of soil properties and plant zinc content in the "Maasoever" study

	Soil Properties					Crop	
	Org. Mat. %	$CaCO_3$ %	Clay % < 2 μm	pH KCl	Zn mg kg^{-1}	dm %	Zn mg kg^{-1}
Potato (n=25)							
Average	2.7	n.a.	13.2	6.2	185.8	22.7	17.0
Stdev	1.6	n.a.	5.8	0.8	138.7	1.9	3.5
Min	1.2	n.a.	4.2	4.7	41.0	19.1	12.0
5%	1.2	n.a.	4.6	5.0	57.6	19.6	12.2
50%	2.3	n.a.	13.6	6.5	159.0	22.9	16.0
95%	6.0	n.a.	23.3	7.2	478.6	25.6	21.8
Max	7.5	n.a.	25.2	7.3	538.0	25.7	25.0
Sugar Beet (n=64)							
Average	4.2	0.7	15.4	6.4	313.3	n.a.	104.8
Stdev	2.4	1.6	6.7	0.6	250.8	n.a.	68.1
Min	1.3	0.0	2.9	4.5	49.0	n.a.	30.0
5%	1.5	0.0	6.2	5.2	69.9	n.a.	38.9
50%	3.5	0.1	14.8	6.3	245.5	n.a.	87.0
95%	8.5	4.1	28.8	7.3	820.0	n.a.	256.5
Max	13.5	9.8	30.5	7.4	1140.0	n.a.	343.0
Grass (n=32)							
Average	7.5	3.9	18.3	6.4	732.0	n.a.	77.2
Stdev	2.9	4.6	8.5	1.1	431.0	n.a.	28.1
Min	2.8	0.0	6.7	3.8	71.0	n.a.	38.0
5%	3.5	0.0	8.6	4.6	165.4	n.a.	48.6
50%	6.7	2.2	15.8	7.1	736.0	n.a.	71.0
95%	12.7	13.2	34.7	7.4	1495.4	n.a.	125.8
Max	14.1	16.0	41.2	7.4	1686.0	n.a.	176.0
Maize (n=39)							
Average	4.6	n.a.	15.4	6.4	344.3	n.a.	69.6
Stdev	2.9	n.a.	7.4	0.8	334.1	n.a.	39.2
Min	1.9	n.a.	2.5	4.2	18.0	n.a.	28.0
5%	1.9	n.a.	5.3	4.5	42.1	n.a.	29.0
50%	3.8	n.a.	14.3	6.7	214.0	n.a.	59.0
95%	8.6	n.a.	29.4	7.3	857.9	n.a.	167.6
Max	14.0	n.a.	37.4	7.5	1520.0	n.a.	174.0
Wheat (n=18)							
Average	4.3	1.2	16.4	6.7	371.2		53.6
Stdev	2.1	2.7	4.7	0.4	244.5		15.3
Min	1.4	0.0	11.1	5.9	85.0		33.0
5%	1.5	0.0	11.4	6.0	95.2		36.4
50%	4.6	0.2	15.6	6.7	384.5		50.0
95%	7.0	7.7	23.7	7.3	647.5		77.9
Max	9.9	9.7	29.5	7.3	1138.0		94.0

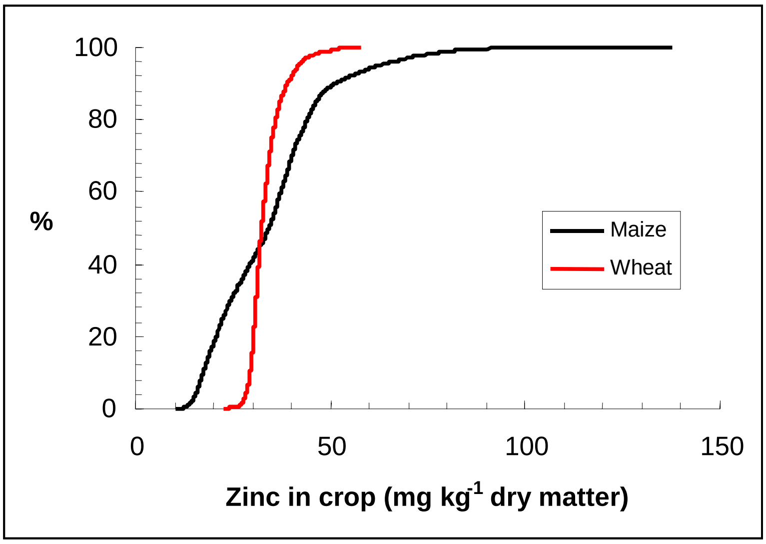

Figure A1.1 Frequency distribution of calculated zinc contents in maize and wheat for all STONE plots

The results in Figure A.1.1 clearly show that the predicted values of zinc in both wheat and maize fall within the normal ranges, even for peat soils and acid sandy soils. In Table A1.3 an overview of the range in the predicted values of zinc in all crops is given for 6 major soil types. To obtain these classes, all plots were clustered into 6 classes based on texture, pH and organic matter.

Table A1.2. Soil properties from STONE plots used in the calculations

	Soil Properties			
	Org. Mat. %	Clay %	pH- KCl	Zn mg kg^{-1}
Average	11.1	18.7	5.6	64.7
Stdev	9.3	14.3	0.8	27.7
Min	3.1	3.4	4.2	22.4
5%	4.4	4.9	4.7	33.4
50%	7.8	13.7	5.2	59.4
95%	31.4	44.3	7.2	114.6
Max	79.4	76.8	7.3	222.7

Table A1.3. Predicted plant zinc levels in the STONE plots for 6 major soil types

Crop	Soil Type	Predicted plant zinc content (mg.kg^{-1})				
		Min	5%	50%	95%	Max
Grass	Non-calcareous Sand	37	61	71	80	102
	Calcareous Sand	35	36	38	42	42
	Non-calcareous Clay	25	28	34	45	54
	Calcareous Clay	22	25	28	31	35
	Other, mainly Loess soils	28	30	50	60	69
	Peat	24	36	52	81	87
	All Soil Types	22	28	53	78	102
Maize	Non-calcareous Sand	19	32	40	53	74
	Calcareous Sand	19	20	25	29	30
	Non-calcareous Clay	12	16	22	31	54
	Calcareous Clay	10	13	17	22	34
	Other, mainly Loess soils	14	16	30	41	64
	Peat	21	33	56	85	138
	All Soil Types	10	16	34	62	138
Potato	Non-calcareous Sand	11	15	18	20	24
	Calcareous Sand	10	11	12	13	13
	Non-calcareous Clay	7.4	8.8	11	13	17
	Calcareous Clay	6.6	7.7	8.7	10	12
	Other, mainly Loess soils	8.2	8.9	14	16	20
	Peat	9.3	13	18	25	32
	All Soil Types	6.6	8.6	15	21	32
Wheat	Non-calcareous Sand	23	29	31	34	41
	Calcareous Sand	23	23	25	27	27
	Non-calcareous Clay	27	30	35	42	45
	Calcareous Clay	27	27	30	34	38
	Other, mainly Loess soils	25	27	34	38	42
	Peat	31	33	38	51	58
	All Soil Types	23	29	32	42	58
Sugar Beet	Non-calcareous Sand	8.9	37	53	75	148
	Calcareous Sand	10	10	11	14	14
	Non-calcareous Clay	5.6	8.7	15	31	48
	Calcareous Clay	3.8	6.0	8.5	11	17
	Other, mainly Loess soils	5.9	8.8	32	51	69
	Peat	4.9	16	30	52	69
	All Soil Types	3.8	8.2	34	68	148

Annex 2 Comparison of input data on manure and slurries with data from other EU countries

The data used in this study on the input of Zn by manure are based on estimated N inputs for the year 2000 based on country statistics for animals and N excretion values multiplied by a Zn/N ratio, based on the composition of manure in a Dutch inventory (Driessen & Roos, 1996). This leads to an average Zn input close too 1000 $g.ha^{-1}.yr^{-1}$. To evaluate whether these inputs of zinc in manure are comparable with those in other EU countries, a comparison was made using an (unpublished) overview of manure production, use and composition made by ADEME (A. Bispo, C. Schubetzer and I. Feix). In Table A2.1 an overview of the composition, production and zinc levels in manure in 16 EU countries is shown. In Figure A2.1 the mid range values as well as minimum and maximum ranges of zinc loads (in gram per hectare per year) due to input of manure and slurries are shown (data from Table A2.1).

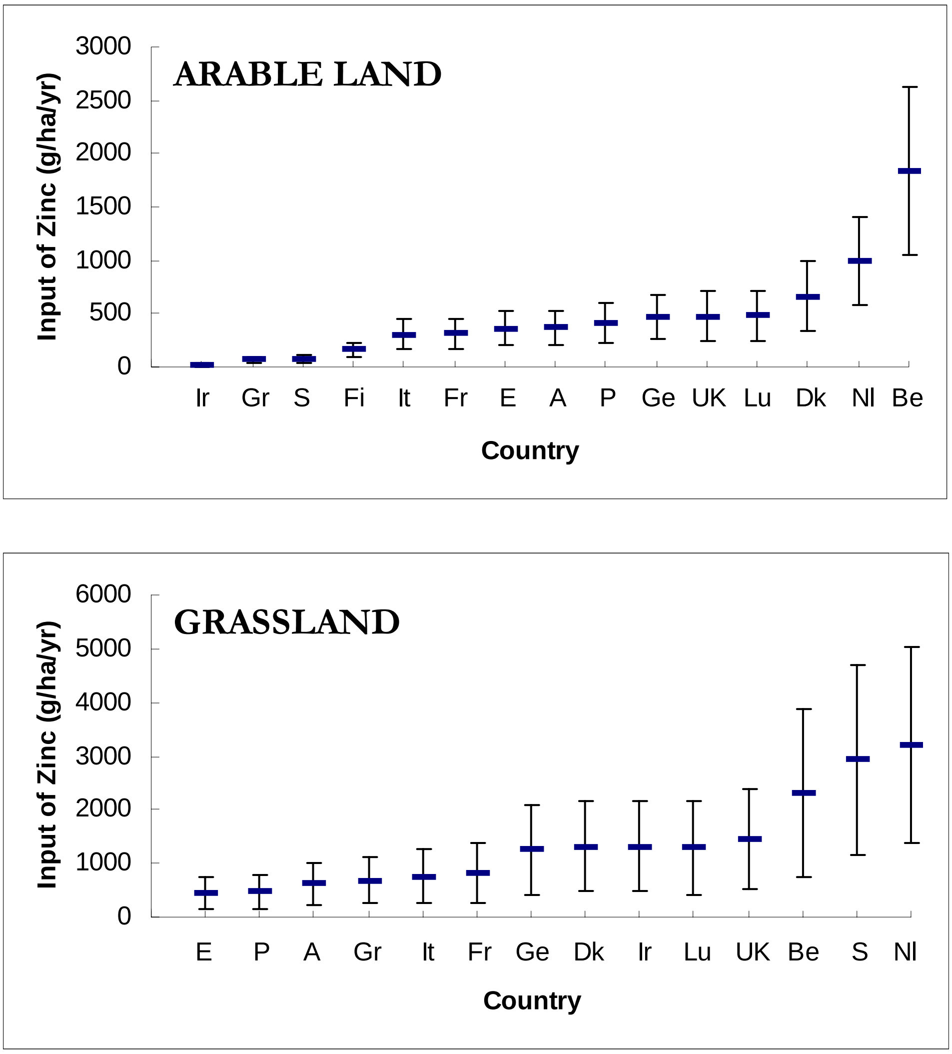

Figure A2.1 Overview of mid range (min/max) levels of zinc inputs to arable land and grassland due to the use of solid and liquid manure

One of the hypotheses was that the Netherlands reflects a worst case scenario in terms of inputs. The assumption that inputs in the Netherlands are high (compared to other countries) indeed seems to be correct. On the other hand, the input levels are not extreme, ranges reported in this overview are in the same order of magnitude. It should be stated here that the numbers in Table A2.1 have not been checked by individual member states (with the exception of Denmark) and the validity of the data in absolute terms is therefore questionable. An example (not shown in the graph) was the extremely high reported input of zinc in grassland in Finland. According to the data in Table A2.1, the maximum input in grassland in this country equals almost 30000 grams ha^{-1} yr^{-1}. This number seems to be incorrect. The high inputs for Sweden are also questionable. In relative terms (comparison between countries) the data are however worthwhile.

In fact, the data reported for the Netherlands in this ADEME study are high compared to data from the Dutch Bureau of Statistics (CBS) as used in our study. In Table A2.1 the total load due to manure and slurries ranges from 2100 to more than 6000 tons. An estimate for the Netherlands based on CBS data for 1994 (Westhoek et al., 1997) amounts to 1900 tons, whereas estimates of the gross load of soils due to manure addition for 2002 equals 1300 tons only (CBS, 2004[1]). The annual inputs calculated from the data in Table A2.1 for arable land (between 589 and 1406 $g.ha^{-1}.yr^{-1}$) are nevertheless in good agreement with the data used in our study (see Table 12 in the main text). For grassland the annual inputs based on the data of ADEME (between 1381 and 5032 $g.ha^{-1}.yr^{-1}$) are, however, much larger than the ones used in our study (on average 1250 $g.ha^{-1}.yr^{-1}$, see Table 12). One of the reasons could be the very high production rate of dry manure. According the national bureau of statistics, the annual production of solid manure equals 1.1 million tons versus 53 million tons of liquid manure. The sum of DRS and liquid manure in Table A2.1 is close to this (54 million tons) but the dry manure production equals 26 million tons. Further clarification is needed, but this difference could almost explain the large discrepancy for grassland.

In summary, the average Zn input near 1250 $g.ha^{-1}.yr^{-1}$, used in our study for the Netherlands is quite comparable to those reported in the ADEME study for Germany, Denmark, Ireland, Luxembourg, UK and Belgium (see Figure A2.1) although these data may also be overestimated for those countries. At least for Denmark, the value has been verified and is thus comparable to the Netherlands. The input data used thus represent a worst case but seemingly not an extreme one.

[1] Data from STATLINE http://www.cbs.nl/nl/cijfers/statline/index.htm

Table A2.1 Overview of annual production and application rates of Zn in manure and slurries in EU countries

Country	Type of manure	Solid and liquid manure production		Annual Zn load in solid and liquid manures (ton/year)		Land Use	Surface area (1000 ha)	Solid and liquid manure application rate (t ha^{-1} yr^{-1})		Zn application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low[1]	High			Fresh Matter	Dry Matter	Low	High
Austria	Solid Manure[2]	11	2.6	348	860	Arable crops	1374	7	1	212	534
	Liquid manure [2]	7.4	0.6	160	479	Grassland	1935	13	2	234	1006
	DRS[3]	16	1.8	236	1342	Total	3309			225	810
	Total	35	4.9	744	2681						
Belgium	Solid Manure	18	4	641	1522	Arable crops	833	34	6	1050	2625
	Liquid manure	14	1.1	311	857	Grassland	536	48	5	732	3890
	DRS	23	2.6	339	1926	Total	1369			943	3145
	Total	55	7.7	1291	4305						
Denmark	Solid Manure	6.4	1.5	265	558	Arable crops	2490	14	2	330	989
	Liquid manure	32	2.7	635	2163	Grassland	373	28	3	473	2153
	DRS	6.7	0.7	99	545	Total	2863			349	1140
	Total	45	4.9	998	3265						
Finland	Solid Manure	5.3	1.2	150	372	Arable crops	2185	3	1	87	232
	Liquid manure	3.2	0.3	68	213	Grassland	25	367	42	5709	29588
	DRS	8	0.9	117	664	Total	2210			151	565
	Total	17	2.4	335	1248						
France	Solid Manure	97	23	2580	6321	Arable crops	18309	7	1	168	457
	Liquid manure	50	4.5	1103	3391	Grassland	9924	17	2	252	1368
	DRS	154	17	2235	12701	Total	28233			210	794
	Total	301	44	5918	22413						

[1] low and high based on measurements in manures and slurries
[2] manure and slurry collected in stables and used elsewhere (either on or off the farm)
[3] Direct Return to the Soil: manure produced while animals are on the field (cattle, sheep)

Table A2.1 (2) Overview of annual production and application rates of Zn in manure and slurries in EU countries, continued

Country	Type of manure	Solid and liquid manure production		Annual Zn load in solid and liquid manures (ton/year)		Land Use	Surface area (1000 ha)	Solid and liquid manure application rate (t ha^{-1} yr^{-1})		Zn application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low	High			Fresh Matter	Dry Matter	Low	High
Germany	Solid Manure	76	17	2390	5867	Arable crops	11788	9	2	256	666
	Liquid manure	51	4.1	1109	3293	Grassland	4970	26	3	416	2082
	DRS	110	12	1591	9040	Total	16758			304	1086
	Total	237	34	5090	18200						
Great Britain	Solid Manure	68	17	1773	5307	Arable crops	4495	9	2	240	706
	Liquid manure	27	2.4	582	1831	Grassland	5422	30	4	519	2379
	DRS	109	12	1585	9004	Total	9917			397	1628
	Total	204	31	3940	16143						
Greece	Solid Manure	8.7	2.5	288	1021	Arable crops	2796	1	0.2	35	98
	Liquid manure	2.6	0.2	69	162	Grassland	1789	12	2	251	1112
	DRS	13	1.4	190	1080	Total	4585			119	494
	Total	24	4.2	547	2263						
Ireland	Solid Manure	32	7.2	566	1625	Arable crops	1118	0.5	< 0.5	8	36
	Liquid manure	11	1.1	186	828	Grassland	3193	30	4	478	2166
	DRS	55	6	796	4525	Total	4311			359	1619
	Total	97	14.3	1548	6977						
Italy	Solid Manure	39	9.4	1153	3002	Arable crops	8234	6	1	166	446
	Liquid manure	21	1.8	478	1398	Grassland	4284	16	2	244	1280
	DRS	60	6.5	864	4906	Total	12518			199	743
	Total	120	18	2494	9307						
Luxembourg	Solid Manure	0.8	0.2	15	41	Arable crops	62	14	3	250	711
	Liquid manure	0.3	0.03	5.8	25	Grassland	65	27	3	410	2172
	DRS	1.5	0.2	21.1	120	Total	127			331	1459
	Total	2.6	0.4	42.1	185						

Table A2.1 (3) Overview of annual production and application rates of Zn in manure and slurries in EU countries, continued

Country	Type of manure	Solid and liquid manure production		Annual Zn load in manures and slurries (ton/year)		Land Use	Surface area (1000 ha)	Solid and liquid manure application rate (t ha^{-1} yr^{-1})		Zn application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low	High			Fresh Matter	Dry Matter	Low	High
Netherlands	Solid Manure	26	6.1	1128	2615	Arable crops	1005	17	3	589	1406
	Liquid manure	23	1.8	563	1423	Grassland	881	63	8	1381	5032
	DRS	31	3.5	456	2593	Total	1886			1138	3516
	Total	81	11	2147	6631						
Norway	Solid Manure	5.4	1.3	123	372	n.a.	-	-	-	-	-
	Liquid manure	2.1	0.2	40	147						
	DRS	8.7	1	127	721						
	Total	16	2.4	290	1240						
Portugal	Solid Manure	9.3	2.4	314	891	Arable crops	1634	7	2	223	607
	Liquid manure	5	0.4	120	319	Grassland	1390	10	1	140	795
	DRS	13	1.5	195	1105	Total	3024			208	765
	Total	28	4.2	628	2314						
Spain	Solid Manure	48	12	1959	5213	Arable crops	13027	6	1	201	527
	Liquid manure	36	2.7	855	2173	Grassland	7235	9	1	144	751
	DRS	60	6.6	869	4939	Total	20262			182	608
	Total	143	21	3684	12325						
Sweden	Solid Manure	8.7	2	237	597	Arable crops	2665	2	0.3	38	105
	Liquid manure	5	0.4	104	335	Grassland	372	62	8	1161	4703
	DRS	13	1.5	193	1098	Total	3037			176	668
	Total	27	3.9	534	2029						

Annex 3 Impact of schematisation of soil profiles on the distribution of soil properties, reactive Zn content and solution concentrations

One of the uncertainties tested here was the effect of the schematisation of the soil profile. This was either done based on a generic approach with a limited number of soil profiles (21 in total) or based on a geostatistical approach, where relevant soil properties were assigned to each STONE plot based on interpolation of all available data. One of the conclusions was that these two schematisation procedures resulted in a significantly different assessment of the leaching flux. Higher dissolved metal concentrations were observed using the generic approach although the ultimate impact on the number of plots exceeding critical limits was less significant (see Section 6.2).

To assess whether these differences are indeed due to systematic differences in the soil properties assigned to the STONE plots, a second analysis was performed using the geostatistical approach. In the original approach, presented in the main text (Section 6.2), the values for organic matter, clay and soil pH were obtained by averaging the values of individual 500 m x 500 m grid cells in one STONE plot. The value in each grid cell was calculated as the average value of the frequency distribution (chance distribution) for each soil property (see Brus et al., 2002). In the alternative approach, we used the *median* (i.e. the 50-percentile) value of the pH, organic matter and clay distribution instead of the average value. The dissolved zinc concentrations were calculated based on this alternative approach.

In Figure A3.1, the distribution of pH, organic matter and clay in all STONE plots of the original (based on average values) and alternative (based on median values) approach are shown. The results show that the soil profiles based on median values have significantly lower organic matter, clay, and pH levels. This of course affects the estimate of the dissolved zinc concentration since all properties are shifted in a direction that would cause an increase in the dissolved zinc concentration. This is illustrated in Figure A3.2, where both the estimates of the reactive zinc content (hardly an effect) and the dissolved zinc concentration are show for the two approaches. The data in Figure A3.2 show that dissolved zinc concentration based on median values exceed those based on average values. The relative increase ranges from 0.93 (7% lower dissolved zinc concentrations) to 5.87 (up to 6 times higher zinc concentration in the alternative approach) with a median value of 2.2.

A considerable contribution to this increase is due to the lower soil pH in the schematisation based on median values. In Figure A3.3, the relation between soil pH and the relative increase in the dissolved zinc concentration is shown. It appears that the ratio increases from values around 1.5 at pH 7 to more than 4 at pH levels below 4. In fact the increase in the dissolved zinc levels due to the combined effect of the lower organic matter and clay content was less important than that of pH alone.

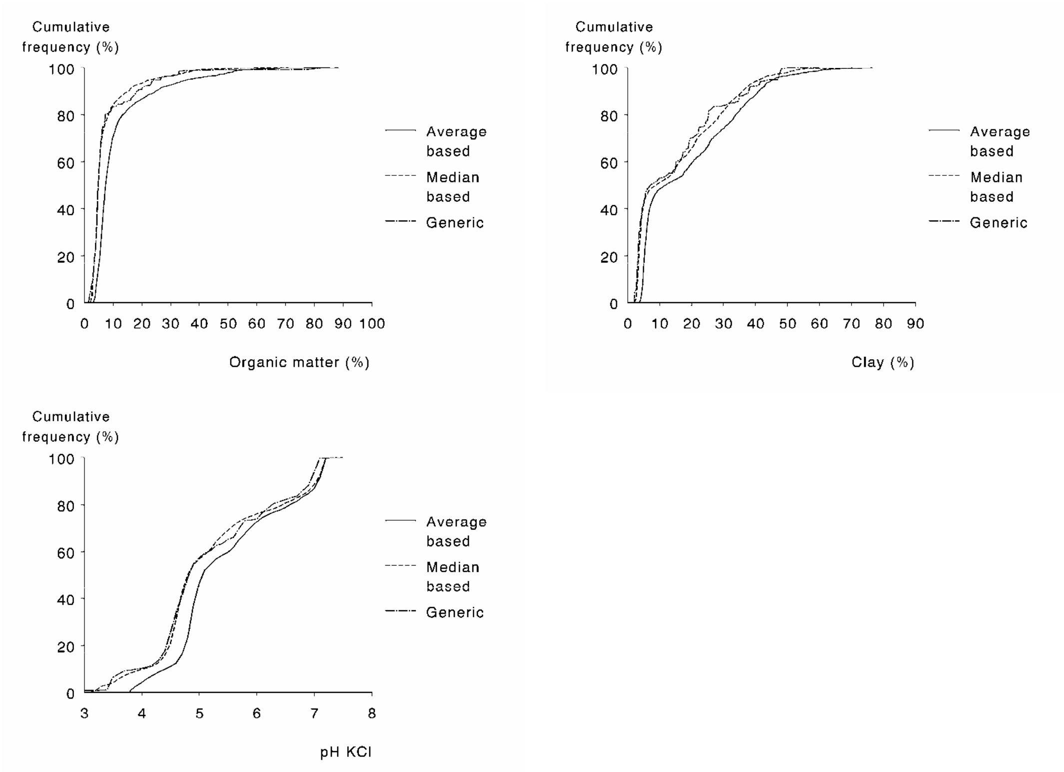

Figure A3.1. Impact of using average versus median values for each 500 m x 500 m grid cell on the frequency distribution of organic matter, clay and pH of all STONE plots

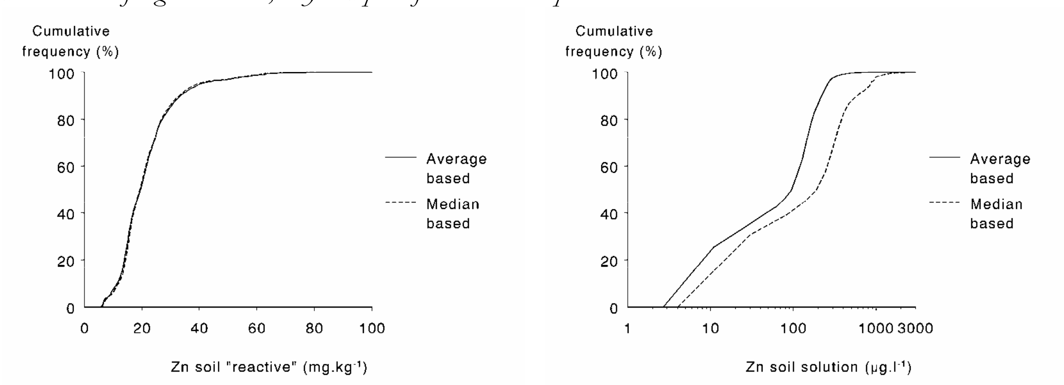

Figure A3.2. Impact of using median and average values for soil properties for each 500 x 500 m grid cell on the calculated reactive zinc content (left) and dissolved zinc concentration (right)

In conclusion, the use of median values to assign soil properties to each grid cell results in dissolved zinc levels that are close to those obtained by the generic approach. Also from a statistical point of view it might be more realistic to use median values as the representative value for each grid cell and not average values. As of now it remains unclear, however, what causes the systematic difference between values of soil properties based on average values versus median values of the distribution curve.

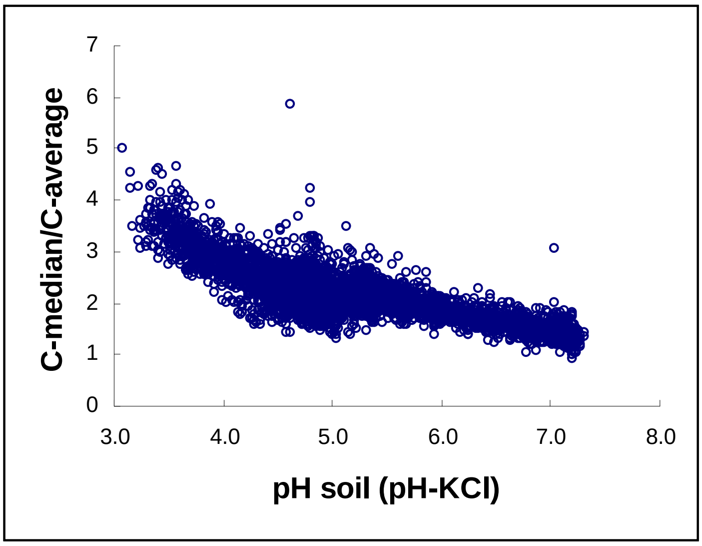

Figure A3.3. Relationship between soil pH and the relative increase in the dissolved zinc concentration