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

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ABSTRACT

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This report describes a model study to assess whether current copper inputs on agricultural land lead to accumulation of copper and in time to an exceedance of a Predicted No Effect Concentration. A copper mass balance model was applied to the whole Netherlands. Future copper concentrations after 100 years and at steady were calculated based on geo referenced data on copper inputs and calculated uptake and leaching. The PNEC used in this study is based on ecotoxicological criteria (HC_5) and accounts for differences in bio-availability between soils. Model predictions show that copper accumulation takes place in 97% of agricultural; land. At present and after 100 years predicted concentrations are below the PNEC. At steady state the PNEC is exceeded for 18% of the area. The rate of copper accumulation is slow, the time to reach the PNEC is on average 801 years for grass land and 1656 years for arable land.

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

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Contents

Preface

At present, a Risk Assessment report (RAR) for copper has been prepared in which the safe threshold –the Predicted No Effect Concentration (PNEC)- is a function of soil properties. Aside from the evaluation of the present status of soils, it is of importance to assess the development of soil quality in the future based on current land use practices. It is relevant to know whether there will be an exceedance of the PNEC of Cu in rural (agricultural areas) in the future at ongoing Cu inputs. In case of an exceedance it is relevant to know how large the exceedance will become and at what time in future the PNEC is exceeded.

In this context, the European Copper Institute requested Alterra to assess copper balances for Dutch agricultural soils and make a prediction of future Cu concentrations at ongoing present Cu inputs at steady state (Predicted Effect Concentrations at steady state or $PEC_{steady\ state}$) and concentrations after 100 years in comparison to a critical or Predicted No Effect Concentration (PNEC) of Cu. The main aim of this report is to evaluate whether or not the current load of copper 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 Cu input was based on the estimated input in the Netherlands 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 using a scenario with a maximum N application rate of 250 kg $N.ha^{-1}.yr^{-1}$ for grass land and 170 kg $N.ha^{-1}.yr^{-1}$ for arable land and a strict scenario in which we used a maximum N application rate of 170 kg $N.ha^{-1}.yr^{-1}$ for both land use types. The PNEC of Cu which takes into account bioavailability was derived for each plot based on soil properties including organic matter, clay content and soil pH. The changes in the soil Cu concentration were based on a modelled net Cu accumulation or release over several hundreds of years in agricultural top soils until a steady-state situation was reached. In addition to this the soil copper concentration at t=100 is presented. In this study the soil quality has been evaluated in the light of the Cu concentrations in the upper topsoil only. The impact of an increase on the soil copper content on concentrations in ground- and or surface waters has not been considered.

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 copper 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 authors like to acknowledge ECI for their constructive criticism and for useful comments on the manuscript and Dr. Patrick van Sprang (EURAS) who calculated the PNEC's for this study. Furthermore, we like to thank Prof. Dr. Steve Mc Grath (Rothamsted) who supplied some valuable field data that were used to compare them 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 copper to soils often exceeds the removal of copper from soil by crops and by leaching. Accumulation in soil due to the net input of copper in arable systems can lead to unacceptable levels of copper in the soil.

To assess whether or not current forms of agricultural land use lead to accumulation of Cu and, with time, to an exceedance of Predicted No Effect Concentrations (PNEC) for Cu 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 copper content in soils is made on a national scale.

In this study the PNEC for copper in soils is based on ecotoxicological criteria (HC_5 level) and takes into account differences in bioavailability depending on soil properties (organic matter content and clay content) as well as soil acidity (pH). In addition to this a correction for the difference between laboratory and field conditions was incorporated (ECI, 2005).

A copper mass balance model was applied to the whole of the Netherlands using 4647 so-called STONE plots, limiting ourselves to agricultural land use. STONE 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 copper 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. Addition of manure is by far the major source of Cu input but varies between different types of land use and soil type. The contribution of all other sources (fertilizers, deposition, compost and pesticides) is usually less than 20%. Fertilisers are a comparatively small source of Cu (ranging from < 10% for arable soils to approx. 20% for grassland soils) whereas atmospheric deposition is almost negligible (< 2.5% of the total input). Other sources, mainly compost and pesticides are an additional albeit minor source of copper in arable land. For each plot, a PNEC was calculated (pers. commun. P. van Sprang)

The model simulations for the Dutch agro-ecosystems showed that

- Present Cu inputs exceed the uptake and present leaching at 97% 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 Cu concentrations. Copper accumulation rates are highest in calcareous clay soils due to low leaching rates of Cu.

- Present Cu inputs lead to changes in Cu accumulation and leaching rates over a period of several hundreds to thousands of years, depending on land use type and soil type considered. The increase in Cu soil concentrations is slow with average accumulation rates during the first 100 years of 0.05-0.07 $mg.kg^{-1}yr^{-1}$. In general steady state is reached within 1000 to 3000 years for Cu, but it can last up to more than 5000 years. Those time scales are an indication for the transition times in fertilised agro-ecosystems.
- The steady-state soil Cu concentrations that ultimately will be reached differ strongly from the present Cu concentrations in soil. On average, steady state levels are 4 times higher than current day levels of copper in soils. Consequently, at steady state the Predicted No Effect Concentration (PNEC) of Cu is predicted to be exceeded at 18% of the plots whereas at present and after 100 years there is no exceedance at all. Time periods to reach those values are however very long with an average for grassland of 801 years and an average of 1656 for arable land.

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

- In the Netherlands, there is not any exceedance today of the PNEC of copper. This excludes hot spots which were not included in this study.
- The percentage of plots where the predicted steady state copper content will exceed the PNEC is estimated at 18% when using current (year 2000) inputs and at 17% when the legislation for nitrogen will be respected.
- The predicted time period to reach the PNEC for copper is on average approximately 800 years for grassland and 1600 years for arable land when using current inputs. When respecting the N legislation, this time period increases a little.

In contrast to metals like Zn and Cd, uncertainty has risen on the contribution of other sources which have not been considered so far (and are also not included in this study). Inputs by disinfection solutions for the hoofs of animals (cows) that contain $CuSO_4$ may prove to be an important additional source of copper. Estimates of the total copper load that can be attributed to this source are still under debate but it has been suggested that these can be as high as half of the total copper load at present for dairy farms.

The reliability or plausibility of the results was assessed by comparing model outputs from this study with available Cu accumulation data. Both data from long-term monitoring sites (Rothamsted experimental station) as well as data from regular monitoring networks (Dutch 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). 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 copper content from the UK, and the Netherlands resulted in a good match between data and modelled values.

1 Introduction

Background
The main aim of this report is to evaluate whether or not the current load of copper to soils in different forms of land use (arable land, pasture) and soil types leads to an exceedance of the Predicted No Effect Concentration (PNEC), and if so at what time scale. Issues to address and/or clarify included the assessment of:

- Copper PNECs in the Netherlands for use in the risk characterisation.
- Present copper mass balance in different land use and soil types of agricultural soils, subject to different patterns of agricultural practice.
- Copper mass balances towards the future for the different land use and soil types, using a dynamic model, and integrating the effects of current N legislation.
- Present and predicted steady state copper 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 Cu 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 Cu concentration will exceed a given no-effect value (PNEC), and if so, when this will happen. In addition to this, an evaluation of the changes in the soil copper content after 100 years is presented. The Netherlands represents a realistic 'worst-case' region for intensity of agricultural practice in the EU; inputs to soils from agriculture are among the highest in Europe although inputs in other intensive animal husbandry areas (e.g. Denmark, NW France and Switzerland) are comparable. Available information on copper 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 metals
In the Netherlands, there is a concern about the excessive inputs of metals in agriculture, specifically Cd, Zn and Cu (e.g. Moolenaar & Lexmond, 1998). An excess of Cd in agro-ecosystems may result in agricultural products with unacceptable levels, violating food quality criteria, and even reduced crop production (Alloway, 1990; Fergusson, 1990). Elevated copper, zinc or cadmium 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 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).

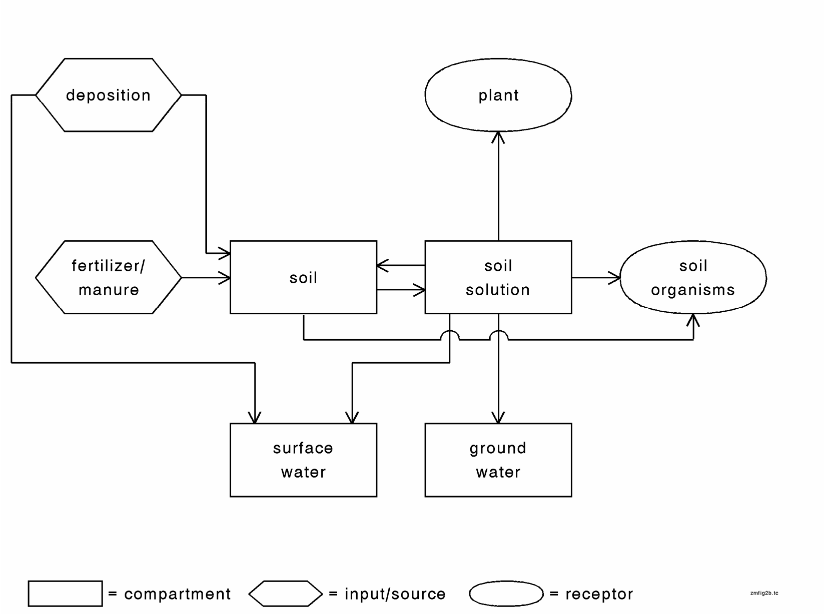

Figure 1 Overview of major pathways of metals in agro-ecosystems.

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 metals occurs or (ii) accumulation of metals does not lead to an exceedance of a previously accepted critical limit in defined compartments (e.g. soil/soil solution, plants or animal organs). Critical limits or PNECs for 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 Cu input in Dutch agricultural soils by making use of estimated inputs and outputs of Cu and present Cu 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:

- To what extend do the present Cu 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 copper concentrations that will ultimately be reached?
- What is the percentage of plots where the critical limit or PNEC for Cu in soil is exceeded at present, after 100 years and at steady state?
- What are the time periods in which steady-state soil copper concentrations are reached and critical soil copper 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 copper 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 the plausibility and representativity of 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 copper behaviour in Dutch agricultural soils

This chapter describes the methods that were used to calculate balances for Cu 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 assess the Predicted No Effect Concentration which is used in the risk characterisation (Section 2.1). Then the approach is described to calculate Cu accumulation or release on the basis of a continuing Cu 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 copper concentrations and of time periods to reach critical and steady-state concentrations is described in Section 2.3.

2.1 Calculation of critical copper concentrations

The PNEC used in this study is based on the recent European Union Risk Assessment on copper (ECI, 2005). This PNEC is based on a high number of chronic ecotoxicological data from a wide range of plant and invertebrate species and micro-organisms endpoints. Because of the data-richness, the PNEC was derived using the species sensitivity distribution approach and set equal to the HC_5.

Considering the bioavailability of copper in soils, two phenomena on the ecotoxicity of copper to soil organisms are apparent, i.e. the toxicity response is highly dependent on soil type, and the toxicity response is highly dependent on the time. Indeed, copper toxicity under field conditions is generally observed at much higher doses than under laboratory conditions. A relationship was found between copper speciation and toxicity for different soils species and/or processes. Further, a factor was derived to account for the difference in toxicity between lab and field. Both corrections were applied to derive ecologically relevant soil threshold values.

First the NOEC based on the added amount of copper ($NOEC_{add}$) is corrected for the difference in toxicity between copper toxicity in field soils compared to freshly spiked laboratory soils using a generic lab to field factor of 2. Then the background copper concentration of the corresponding control soil (Cb) is added to the $NOEC_{add}$ to get the total $NOEC_{tot}$. To account for the differences in toxicity response for different soils, $NOEC_{tot}$ values were normalised based on soil properties of the specific soils (CEC, SOM, pH) using regression functions derived for microbial functions, plants and invertebrates. From the aggregated set of normalised

NOECs the generic PNEC is derived as the 5-percentile of the species sensitivity distribution (SSD). Where no CEC values are available CEC's were calculated from the soil organic matter content, clay content and pH-KCl according to:

CEC=(30+4.4 pH)*clay/100+(-34.66+29.72 pH)*OM/100;

the clay is the % clay in the soil (Helling et al., 1964).

2.2 Calculation of copper accumulation or release

Mass balance model for copper accumulation and release

Copper balances were calculated using a one layer mass balance model for the topsoil. We calculated mass balances on a yearly basis using annual average concentrations and fluxes. For grassland we used the top soil layer from 0-10 cm and for arable land the a soil layer from 0-30 cm.

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

$$Cu_{ac} = Cu_{in} - Cu_{up} - Cu_{le} \qquad (1)$$

where:

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

The following assumptions apply to the model:

- 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.
- The soil is in an oxidised state and metal partitioning can be described with equilibrium adsorption.
- Transport of water and metals only takes places in vertical direction (no seepage flow, surface runoff and bypass flow).
- Impacts of soil erosion and Cu weathering are neglected
- Cu input equals constant input by animal manure, fertiliser and deposition. Inputs due to Cu recycling (crop residues) are not included.
- 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:

- 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.
- 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.
- 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, Cu application by manure and fertiliser generally takes place in a period before cracking.
- 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.
- Recycling of Cu may have some effect when the Cu is leached below the considered zone for metal accumulation (0-10 cm for grass land and 0-30 cm for arable land). However, considering that most Cu is taken up in the topsoil, the effect of recycling is small.
- In drained peat soils, there may be a large net release of Cu by peat oxidation but this release generally occurs near the mean lowest ground water level and is not considered to influence the metal accumulation in the topsoil.
- Periodic events, such as manure application, may lead to high dissolved Cu 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 copper uptake

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

$$\mathrm{Cu_{up}} = \mathrm{Y} \cdot \mathrm{Cu_p} / 1000 \tag{2}$$

where:

Cu_{up} = Cu uptake rate (g ha^{-1} yr^{-1})
Y = crop yield (kg.ha^{-1}.yr^{-1})
Cu_p = Cu content in the plant or crop (mg.kg^{-1})

Yield 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 Cu uptake by plants, use was made of a fixed Cu concentration for each crop. The data on copper in the crops included in this study originate from several large field studies (Van Driel et al., 1988), Straetmans et al., 2005). In these studies an inventory of the metal content in arable crops and grass grown on both contaminated and uncontaminated soils was made. For copper no significant relationships between the soil copper content and the copper content of the crops could be derived. To assess copper uptake in the model calculations presented here, we used therefore constant levels of copper in the crops.

Calculation of copper leaching

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

$$\mathrm{Cu_{le}} = \mathrm{PE} \cdot [\mathrm{Cu}]_{ss} / 1000 \qquad (3)$$

where:
Cu_{le} = Cu leaching rate from the topsoil (g.ha^{-1}.yr^{-1})
PE = Precipitation excess (m^3.ha^{-1}.yr^{-1})
$[Cu]_{ss}$ = Cu 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 Cu concentration to the reactive soil Cu concentration and vice versa according to (Römkens et al., 2004):

$$\log \mathrm{Cu_{ss}} = \beta_0 + \beta_1 \cdot \log(\mathrm{OM}) + \beta_2 \cdot \log(\mathrm{clay}) + \beta_3 \cdot (\mathrm{pH\text{-}CaCl_2}) + \beta_4 \cdot \log(\mathrm{Cu_{soil,re}}) \qquad (4)$$

where:
$[Cu]_{ss}$ = concentration of Cu in the soil solution (mmol.l^{-1})
$Cu_{soil,re}$ = reactive concentration of Cu in the soil, in this case the 0.43 M HNO_3 extractable concentration (mol.kg^{-1})
β_0 ... β_4 = model coefficients
OM: = percentage organic matter
clay: = percentage clay (< 2μm or lutum)
pH-$CaCl_2$ = pH in dilute salt solution (or soil solution)

Values for the various regression coefficients to calculate the dissolved copper concentration were derived from laboratory experiments with approximately 1400 soil samples from Dutch locations (Römkens et al., 2004), as shown in Table 1.

Table 1 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 Cu, according to Eq. (4) after Römkens et al. (2004).

Metal	β_0	β_1	β_2	β_3	B_4	R^2	se(Y)
Cu	1.10	-0.28	-0.27	-0.18	0.87	0.42	0.49

An important factor that contributes to the rather low R^2 value of the copper isotherm is that DOC is not included in the equation. The database that was used to construct equation 4, contains data on DOC as well and including DOC improves the R^2 to 0.55, at the same time reducing the se(Y) to 0.40. It is of course possible to estimate DOC levels based on organic matter and pH, but this would not improve the overall prediction of copper since these parameters are already included in the regression equation to assess the solubility. We chose therefore to use this equation despite its low R^2 value. For the prediction of regionally average values of copper however we think this equation is still suitable.

Data on pH in the original STONE database are pH-KCL measurements. To calculate the dissolved copper concentration however, pH $CaCl_2$ is needed. Therefore, data for pH-$CaCl_2$ for each STONE plot were derived from pH-KCl data by a linear regression based on several of hundreds of both pH values (de Vries et al., 2005):

$$\mathrm{pH\text{-}CaCl_2} = 0.62 + 0.969 \cdot \mathrm{pH\text{-}KCl}\,;\ R^2 = 0.80,\ \mathrm{se(Y)} = 0.49 \tag{5}$$

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

$$\log \mathrm{Cu}_{\mathrm{soil,tot}} = \gamma_0 + \gamma_1 \log \mathrm{Cu}_{\mathrm{soil,re}} + \gamma_2 \cdot \log(\mathrm{OM}) + \gamma_3 \cdot \log(\mathrm{clay}) \tag{6a}$$

And reverse:

$$\log \mathrm{Cu}_{\mathrm{soil,re}} = \gamma_0 + \gamma_1 \log \mathrm{Cu}_{\mathrm{soil,tot}} + \gamma_2 \cdot \log(\mathrm{OM}) + \gamma_3 \cdot \log(\mathrm{clay}) \tag{6b}$$

Values for the various coefficients relating reactive and total soil concentrations of Cu 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. (2004) and presented in Table 2.

Table 2 Values for the coefficients γ_0- γ_3 in the relation between reactive and total concentration (mg.kg^{-1}) of Cu in the soil according to Eq. (6a and 6b) after Römkens et al. (2004).

	γ_0	γ_1	γ_2	γ_3	R^2	se-y_{est}[1)]
Cu_{tot}	0.318	0.76	0.04	0.19	0.94	0.10
Cu_{re}	-0.331	1.15	0.02	-0.17		

[1)] On a logarithmic basis

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

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

$$Cu_{soil}(t) = Cu_{soil}(t-1) + \frac{Cu_{ac}(t-1,t)}{\rho \cdot T \cdot 10} \tag{7}$$

where:

$Cu_{soil}(t)$ = total soil copper concentration at time t (in mg.kg^{-1})
$Cu_{soil}(t-1)$ = total soil copper concentration at time t-1 (in mg.kg^{-1})
$Cu_{ac}(t-1,t)$ = copper 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)

Changes in Cu leaching, due to a change in the soil Cu concentration were derived from Eq. (6) and (7).

Because of changes in leaching and outflow, the estimates of Cu accumulation (Eq. 7) changed over time. Time periods to reach steady state were calculated by requiring that the change in Cu concentration was less than 0.01% in one year. Practically, Cu accumulation was negligible when using this criterion. The procedure to calculate those time periods is further illustrated in Figure 2.

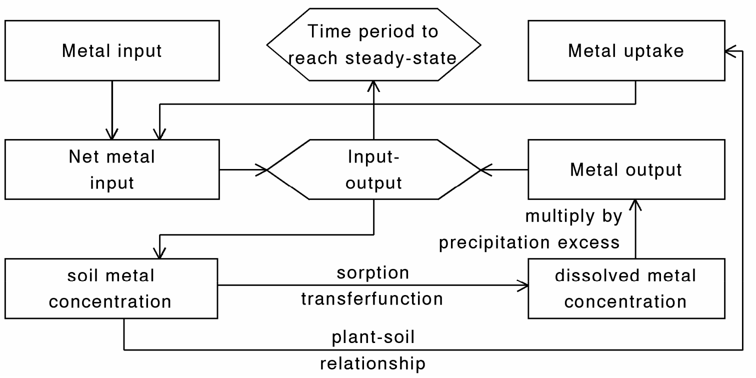

Figure 2 Diagram illustrating the calculation of time periods to reach steady-state.

To calculate the concentration at steady state, the factor time does not play a role. In this context, a simple steady-state model was also applied to calculate and map the exact steady-state Cu concentration. At steady-state, the Cu accumulation or release is negligible, leading to a steady-state dissolved Cu concentration according to (see Eq. (1) and Eq. (3) with Cu_{ac} =0) :

$$[Cu_{ss}] = (Cu_{in} - Cu_{up})/(PE/1000) \tag{8}$$

The steady-state soil Cu concentration was derived by combining Eq. (4), (6a) with Eq. (8). This steady state concentration was also compared with:

- the critical Cu 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 Cu concentration exceeds the present Cu concentration.

Regarding the dynamic behaviour of copper, there are six possible options depending on the present concentration (P), the critical concentration (C) and the steady-state concentration at present inputs (SS) see Figure 3:

1. P<C<SS: in this case, during the run the Cu concentration will exceed the critical Cu concentration and *the (damage delay) time can be calculated.*
2. P>C>SS: in this case, during the run the Cu concentration will drop below the critical Cu 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 Cu concentration but it will never exceed the critical Cu 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 Cu concentration but it will not drop below the critical Cu 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 Cu concentration but it is already at the start below the critical Cu concentration.
6. C<P<SS: in this case, during the run the model will calculate an increase in Cu concentration but it is already at the start above the critical Cu concentration.

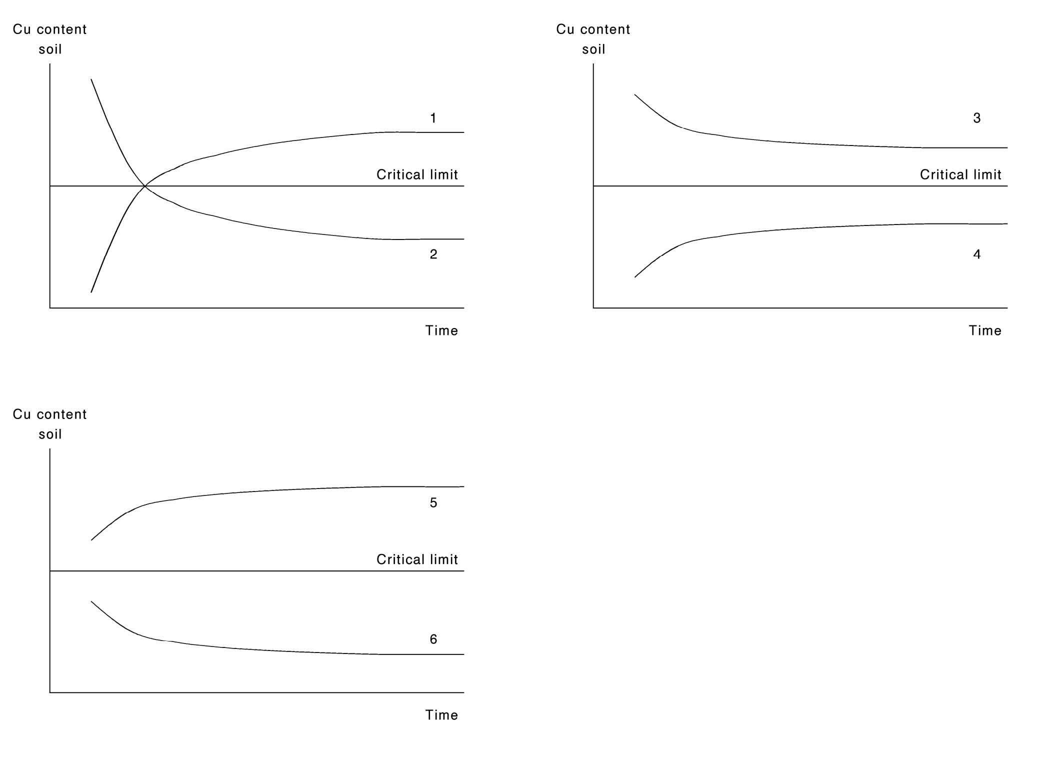

Figure 3 Possible options for development of the copper concentration in soil relative to the critical limit.

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

3 Assessment of input data

3.1 Study area

The Cu 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 copper 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 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.yr^{-1}. For this application, only data from the topsoil were used. metals are not included in the STONE schematisation. Based on the 500x500 grid map for Cu, an overlay of the STONE plots and the Cu map resulted in an estimate of the average Cu 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 4 major soil types: clay, sand, peat or loess. In total 6 soil types were distinguished: sand and clay (calcareous and non-calcareous for both sand and clay) and peat. For both clay and sandy soils a subdivision between calcareous and non-calcareous soils was made. This was done since Cu leaching fluxes depend on pH and leaching losses from non-calcareous (acidic) soils are substantially higher than those from calcareous soils. In combination with two types of land use (arable land or pasture) this results in 12 combinations of soil type and land use.

Information on areas of those land use–soil type combinations is given in Table 3. 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. The total area covered by agricultural land on calcareous sands is rather small, approx 1% of the total surface area. The area of grassland on calcareous sandy soils is negligible (0.03%) and therefore not further used in this study.

Table 3 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 Cu uptake and leaching and thus Cu accumulation is presented in Figure 4. 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 4).

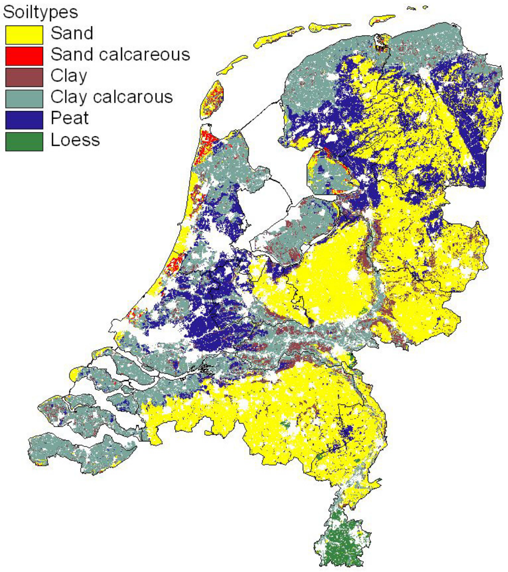

Figure 4 Geographic distribution of the major distinguished soil types

To apply the model, most recent available data were used (year 2000) on the copper inputs through deposition, manure and fertiliser application. By using the year 2000 the effects of quite recent legislation and policy measures were included.

3.2 Soil properties and present copper concentrations

Dissolved copper concentrations are calculated using a transfer function that describes the relationship between dissolved and solid phase concentrations of Cu 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 median values for each STONE plot. Ranges of soil properties for the STONE plots are given in Table 4.

Table 4 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	5.3	(3.9-7.6)	4.9	(3.2-8.6)	5.0	(4.8-5.3)	4.7	(4.4-5.0)
	clay	5.9	(3.6-9.0)	26	(11-41)	6.7	(5.9-7.7)	5.9	(5.0-7.2)
	peat	21	(7.3-39)	34	(4.1-55)	5.4	(4.9-5.8)	5	(4.4-5.5)
Arable land	sand	5	(2.7-7.4)	4.7	(2.9-8.2)	5.1	(4.7-6.4)	4.8	(4.3-6.4)
	clay	3.9	(2.6-5.5)	23	(13-35)	7.3	(6.0-7.8)	6.7	(5.1-7.2)
	peat	13	(3.3-23)	13	(2.4-41)	5.5	(5.0-6.7)	5.1	(4.5-6.7)

Present copper concentrations were estimated using the same geostatistical approach as used for the soil properties (Brus et al., 2002). To estimate the copper concentrations additional use was made of the relation between the copper concentration in the soil and the organic matter and clay content. For each STONE plot median values of the 500x500 grid cells were calculated. The average Cu 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 5). The average Cu concentrations in soil generally increase going from sand < clay < peat due to the increase in organic matter and clay content.

Table 5 Average values and ranges of the soil Cu 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	13	(10-15)	20	(13-32)	30	(15-58)	20	(11-45)
Arable land	13	(10-17)	18	(12-26)	21	(14-28)	17	(11-25)
Total	13	(10-16)	19	(12-28)	27	(15-58)	18	(11-35)

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) accoding to:

$$\rho = 1000/(0.625 + 0.05 \cdot \%OM + 0.0015 \cdot \%clay) \qquad (9)$$

For mineral soils, where:

ρ = bulk density ($kg.m^{-3}$)

%OM = organic matter content of the soil (%)

%clay = clay content of the soil

And for peat soils:

$$\rho = 1000 \cdot (0.725 - 0.337 \cdot \log(\%OM)) \tag{10}$$

3.3 Copper input

Geo-referenced data on annual copper 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 copper 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 Cu/N ratio in the various types of manure (cows, pig, poultry etc) according to:

$$\mathrm{Cu}_{\mathrm{in,am}} = \mathrm{N}_{\mathrm{in,am}} \cdot \mathrm{ctCu}_{\mathrm{am}} / \mathrm{ctN}_{\mathrm{am}} \tag{11}$$

where:

$\mathrm{Cu}_{\mathrm{in,am}}$ = Copper input by animal manure application (in $g.ha^{-1}.yr^{-1}$)

$\mathrm{N}_{\mathrm{in,am}}$ = Nitrogen input by animal manure application (in $kg.ha^{-1}.yr^{-1}$)

$\mathrm{ctCu}_{\mathrm{am}}$ = Copper concentration in animal manure (in $mg.kg^{-1}$)

$\mathrm{ctN}_{\mathrm{am}}$ = Nitrogen concentration in animal manure (in $g.kg^{-1}$)

Most recent available data on Cu and N concentrations in animal manure are given in Table 6.

Table 6 Median values (in mg kg^{-1} dry matter) of Cu and N in animal manure (Driessen & Roos, 1996) and the resulting ratios in both 1996 and those scaled to 2000.

Animal manure	Cu ($mg.kg^{-1}$)	N ($g.kg^{-1}$)	Cu/N (mg $Cu.g^{-1}$ N)	
			1996	2000
Cattle	42	53	0.79	0.41
Pig	422	76	5.55	2.91
Poultry	81	55	1.47	0.77

The values of copper and nitrogen content in different types of animal manure are based on data from Driessen & Roos (1996) who determined concentrations of metals, and nutrients in 198 random samples of animal manure in the Netherlands.

For each STONE plot we calculated the input of Cu with manure for the year 2000 with Equation 11 using the N inputs per STONE plot calculated with the CLEAN model for 2000 and the Cu/N ratio for 1996 (Table 6). The total Cu input, calculated from the sum of all plots for the Netherlands, is exactly in line with input data by Cu for the year 1996 given by CBS (CBS, 2003) who calculated the total input for the Netherlands from manure inputs and average Cu contents in manure. Presumably Cu contents in manure decreased since 1996 due to the reduction of Cu suppletion in animal forage. Because more recent data on Cu contents in animal manure are not available, Delahaye et al. (2003) estimated the annual Cu input by animal manure indirect from the sum of the supply of animal fodder minus the removal with animal products. Using this method they calculated a Cu input for 2000 of 439 ton. To account for this decrease the Cu/N ratio for 1996 was multiplied by a factor 0.52 (being equal to 439/838) to obtain the corrected Cu/N ratio for 2000 (Table 6). By doing so, the estimated total Cu input in 2000 equals the input by Delahaye et al. (2003). The calculated N input at each plot determines the spatial variation in the copper input.

Data for the copper input via fertilisers were also based on the known annual national input of Cu in fertilisers (country statistics; CBS data) while allocating the input STONE plots with the N fertiliser application rate, according to:

$$\mathrm{Cu}_{\mathrm{in,f,STONEplot}} = \mathrm{N}_{\mathrm{in,f,STONEplot}} \cdot \mathrm{Cu}_{\mathrm{in,f,country}} / \mathrm{N}_{\mathrm{in,f,country}} \tag{12}$$

where:

$\mathrm{Cu}_{\mathrm{in,f,\ STONEplot}}$ = Cu input by fertilizer ($\mathrm{g.ha^{-1}.yr^{-1}}$)

$\mathrm{N}_{\mathrm{in,f,\ STONEplot}}$ = N input by fertilizer ($\mathrm{kg.ha^{-1}.yr^{-1}}$)

The national values used were 423 $\mathrm{kton.yr^{-1}}$ for N and 48,6 $\mathrm{ton.yr^{-1}}$ for Cu, based on a compilation of national data from Delahaye et al. (2003). A more sophisticated approach would be to gain insight in the use of N,P, K and Ca fertilizer and the known Cu concentrations in it, but this approach was not feasible within this study.

Cu deposition data were based on modelled Cu deposition data by TNO at a 10 km x 10 km grid scale for the year 2000 (Bleeker, 2004). 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). The emission was estimated from the emission inventory in 1995 (RIVM, milieunatuurcompendium) and scaled with the emission scenario of RIVM (RIVM, 1997) to the emission for the year 2000. The total Cu emission for the Netherlands thus estimated equals 21 ton For the agricultural plots an overlay of those data with the plot area was made. Inputs by deposition were kept constant at the level of 2000.

Data on the copper input by compost and pesticides were based on a national value of 16.5 $\mathrm{ton.yr^{-1}}$, 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 7). It is clear, however, that animal manure (due to feed concentrates) is by far the largest source of Cu to both grassland and arable land, whereas atmospheric deposition is the smallest source of Cu. (Table 7). The results show that the overall average Cu input is close to 270 $g.ha^{-1}.yr^{-1}$. Differences between grassland and arable land are small, although the total input to arable land is slightly higher than the input on grassland. This is mainly due to the larger input of pig and poultry manure with a (much) larger Cu/N ratio than cattle manure (see Table 6).

Changes in the manure legislation and regulations dealing with animal food quality), therefore, will affect the input of copper to arable land more than any other regulation (input by compost, fertilizers and atmospheric deposition). It should be noted however that especially for copper there is an ongoing debate on the potential contribution of copper from disinfection solutions. Results from a survey under cattle farmers by CLM (Boer et al., 2006) in the Netherlands show that a large part of the copper present in disinfection solutions for hoofs is disposed of with manure and spread on to the land. If this is indeed common practice, the total input of copper to grassland increases drastically. In the present study this has not been considered.

Also the real distribution of compost on arable land is different than assumed in this study. But specific data on where and how much compost is used are lacking so that it was necessary to distribute the input of compost evenly among all of the arable land.

Table 7 Average inputs of Cu in fertiliser, manure and deposition to all STONE plots on agriculture.

Land use	Soil type	Cu flux ($g.ha^{-1}.yr^{-1}$)				
		Manure	Fertiliser	Deposition	Other sources	Total
Gras	Sand	196	34	11	0	240
	Sand calcareous	148	33	12	0	193
	Clay	206	35	10	0	251
	Clay calcareous	225	37	9.6	0	272
	Loess	257	38	11	0	306
	Peat	169	33	11	0	213
Arable	Sand	303	14	11	17	345
	Sand calcareous	220	11	9.0	17	256
	Clay	197	14	11	17	239
	Clay calcareous	252	17	9.9	17	295
	Loess	297	10	11	17	335
	Peat	207	18	9.0	17	251
Total	All	225	25	10	8.5	269

The overall ranges (5%-95%; not shown in Table 7) are 53-488 $g.ha^{-1}.yr^{-1}$ for the input by animal manure, 6.7-40 $g.ha^{-1}.yr^{-1}$ for the fertiliser input and 6.8-14 $g.ha^{-1}.yr^{-1}$ for the input by deposition. The overall range for all inputs is 95-535 $g.ha^{-1}.yr^{-1}$.

3.4 Copper uptake and copper leaching

Uptake

Geo-referenced data on annual copper outputs by net uptake were estimated by assessing yields and Cu 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 Cu 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 8. 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 9. 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 8 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 9 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

Copper levels in the crops considered in this study are based on literature data. No relation between soil and crop was included and it has been assumed that within the range of soils used here the copper content in the crops is similar.

Table 10 Median concentrations of copper in crops used to calculate the total copper uptake.

	Median Cu concentration (mg.kg^{-1} dry matter)				
	Grass	Maize	Potato	Wheat*	Sugar beet
Data	12	4.1	4.2	5.2	8.9

* including other crops, other cereals

The data shown in Table 10 originate from several field studies (Van Driel et al., 1988); Straetmans et al., 2005). The level of copper in grassland is somewhat higher than data from recent monitoring programmes reported by the BLGG for the years 2000-2003 (BLGG, www.blgg.nl). In the study by BLGG, average copper levels range from 8 to 10 mg kg^{-1}. For maize no differences between the data from the field studies used here and data from the BLGG were observed.

Leaching

Geo-referenced data on annual copper outputs by leaching were estimated by a multiplication of water leaching fluxes and dissolved metal concentrations. For the assessment of water leaching fluxes, we refer to De Vries et al. (2004).

4 Copper concentrations and copper fluxes at agricultural sites in the Netherlands

In this chapter we present the results of the model study. The first paragraph gives an overview of copper concentrations for the present situation, concentrations after 100 years and at steady state together with the critical concentration. Thereafter we present copper balances for the different soil vegetation combinations. The last paragraph deals with the changes in copper fluxes and concentrations in time and the times to reach critical levels in soils

4.1 Present, 100-year, critical and steady state copper concentrations

Present, 100-year, critical and steady state concentrations and their exceedances

Table 11 and Figure 5 give an overview of the present concentrations, concentrations after 100 years, steady state and critical concentrations of copper in all plots.

In order to interpret the data in Table 11 when comparing present copper concentrations, copper concentrations after 100 years and at steady state the following facts should be kept in mind:

- Differences in soil properties between grass land and arable land. Within the same ‘soil type’ category soil properties (i.e. organic matter content, clay content and pH) differ significant. For example the average organic matter content in 'peat soils' for grass land equals 27% whereas in arable land this is only 20%.
- Different layer thickness for grass land and arable land. The soil layer considered for accumulation under grassland was set to 0.1 m. For arable the accumulation was calculated for a layer of 0.3 m, equal to the depth of the plough layer. The smaller layer thickness for grass land results, in case of comparable inputs and soil properties, to higher accumulation rates (when expressed as an increase in concentration)
- Differences in input rates between grassland and arable land. On average inputs to arable land are higher than inputs to grass land.

Present concentrations

Differences between grassland and arable land are negligible except for peat soils. This is due to the largest differences in soil properties for these soils. The variation in present copper concentrations in soils is small. In general the highest copper levels are found in peat soils followed by clay soils, loess soils and with the lowest concentrations in sandy soils. This order mainly reflects the order in capacity to retain metals that have been added in the past, with the highest retention capacity in peat soils and the lowest capacity in sandy soils. The higher copper levels in peat soils also reflect the addition of household waste in some peat areas (not all peat soils have been used as waste areas). However, the real 'hot-spots' in terms of copper levels in soil have not been included in this study. Apart from 'polluted' peat soils this also includes floodplain soils along the major rivers. In the database used to construct the copper maps of the Netherlands, specific data from these two areas were excluded since the presence of the contaminated area often is confined to a certain (local) area. A more detailed discussion on the procedure by which the maps were made is presented by Brus et al. (2002).

Concentrations after 100 years

All soil vegetation combinations show an increase in copper concentrations after 100 years compared with present concentrations. The average increase is about 40% with the highest increase for peat soils which as with present concentrations reflects the high retention capacity of these soils. Despite higher inputs to arable soils, the increase in copper concentrations is in most cases the higher for grassland (about 0.07 $mg.kg^{-1}yr^{-1}$) compared to arable land (about 0.05 $mg.kg^{-1}yr^{-1}$). This is due to the thinner soil layer considered for grassland.

Steady state concentrations

Grassland and arable land show about the same range in steady state concentrations for the different soil types. The highest steady state concentrations are calculated for clay soils, followed by peat soils an the lowest concentrations for sandy soils. In contrast to the accumulation after 100 years the highest increase is now calculated for arable soils. Differences in steady state concentrations are due to differences in inputs and soil properties. Layer thickness however only influences dynamics and thus the time to reach steady state or critical concentrations.

Critical concentrations and exceedance

Critical concentrations depend solely on soil properties (pH, organic matter content and clay content). Due to high carbon and clay contents of peat soils these are the soils with the highest critical concentrations followed by clay and loess soils and the lowest critical concentrations for sandy soils. Critical concentrations for grassland soils are generally higher than for arable soils due to higher organic matter and clay content for the same type of soils with grassland.

Table 11 and Figure 5 show that on average and for all cases present concentrations are far below critical concentrations (present-critical <0). Although nearly all plots accumulate copper (96%, see Table 12), there is not a single plot with exceedance of the critical concentration after 100 year.

Table 11 Average present, critical, after 100 year and steady state soil Cu concentrations.

Land use	Soil type	Cu concentration (mg.kg^{-1})							
		Present	Critical	100 year	Steady state	Present-Critical	100 year-Critical	Steady state-Critical	Steady state-Present
Grass	Sand	13	85	18	25	-72	-67	-60	12
	Sand calc.	15	143	17	28	-128	-126	-114	13
	Clay	20	154	28	96	-134	-126	-59	76
	Clay calc.	19	150	27	115	-131	-122	-35	96
	Loess	16	110	25	63	-94	-84	-47	47
	Peat	30	238	39	68	-207	-199	-170	37
Arable	Sand	13	82	19	41	-69	-63	-41	27
	Sand calc.	11	79	15	47	-68	-64	-31	37
	Clay	20	141	24	89	-121	-117	-51	70
	Clay calc.	18	128	23	138	-110	-104	10	120
	Loess	15	107	21	65	-92	-86	-41	50
	Peat	21	162	27	56	-141	-134	-106	35
All	All	18	134	25	75	-115	-109	-59	56

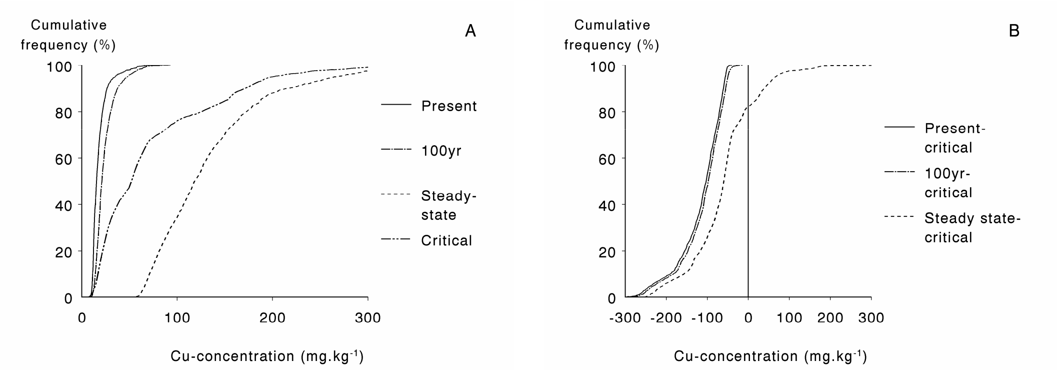

Figure 5 Cumulative frequency distributions of present, 100yr, steady-state and critical Cu contents (A) and the present-critical, 100yr-critical and steady state-critical content (B)

The average concentrations at steady state is for all soil vegetation combinations below the critical concentration (Table 11). However Figure 5b shows an exceedance of the critical concentration for 18% of the surface at steady-state (steady-state – critical)

Table 12 Percentage of area with accumulation and percentage of area with exceedance of the critical limit at present, after 100 years and at steady state.

Land use	Soil type	% area with Cu accumulation	% area exceeding critical Cu limit		
			Present	100y	Steady-state
Grass	Sand	97	0	0	2.3
	Sand calcareous	100	0	0	0
	Clay	100	0	0	13
	Clay calcareous	100	0	0	24
	Loess	100	0	0	9.8
	Peat	100	0	0	1.2
Arable	Sand	90	0	0	2.4
	Sand calcareous	100	0	0	15
	Clay	100	0	0	24
	Clay calcareous	100	0	0	61
	Loess	99	0	0	0.6
	Peat	76	0	0	6.2
All	All	96	0	0	18

The impact of soil type and land use reflects the degree to which the critical limit will be exceeded. Clay soils, especially the calcareous clay soils, show the highest increase in copper concentration at steady state. The highest increase is calculated for arable land clay soils due to the higher inputs compared to grassland. This high accumulation results in the highest area of exceedance of the critical limit for these soils. 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 Cu 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 concentrations, concentrations after 100 years, steady state and critical concentrations and their exceedances

The geographic variation of present Cu concentrations, concentrations after 100 years, steady state and critical Cu concentrations and their exceedances are mapped as shown in Figure 6.

In Figure 6A present copper levels in soil are presented. The figure shows that the largest part of the area has copper concentrations in the range of 10 to 20 mg.kg^{-1}. This area includes all sandy soils and the largest part of the clay soils. Cu concentrations in the range of 20 to 30 mg.kg^{-1} mainly refer to peat soils in the northern part of the Netherlands and to flood plain soils (clay soils) along major rivers (Rhine, Meuse) that are affected by deposition of polluted sediments. Strong local variation exists in the degree of contamination.

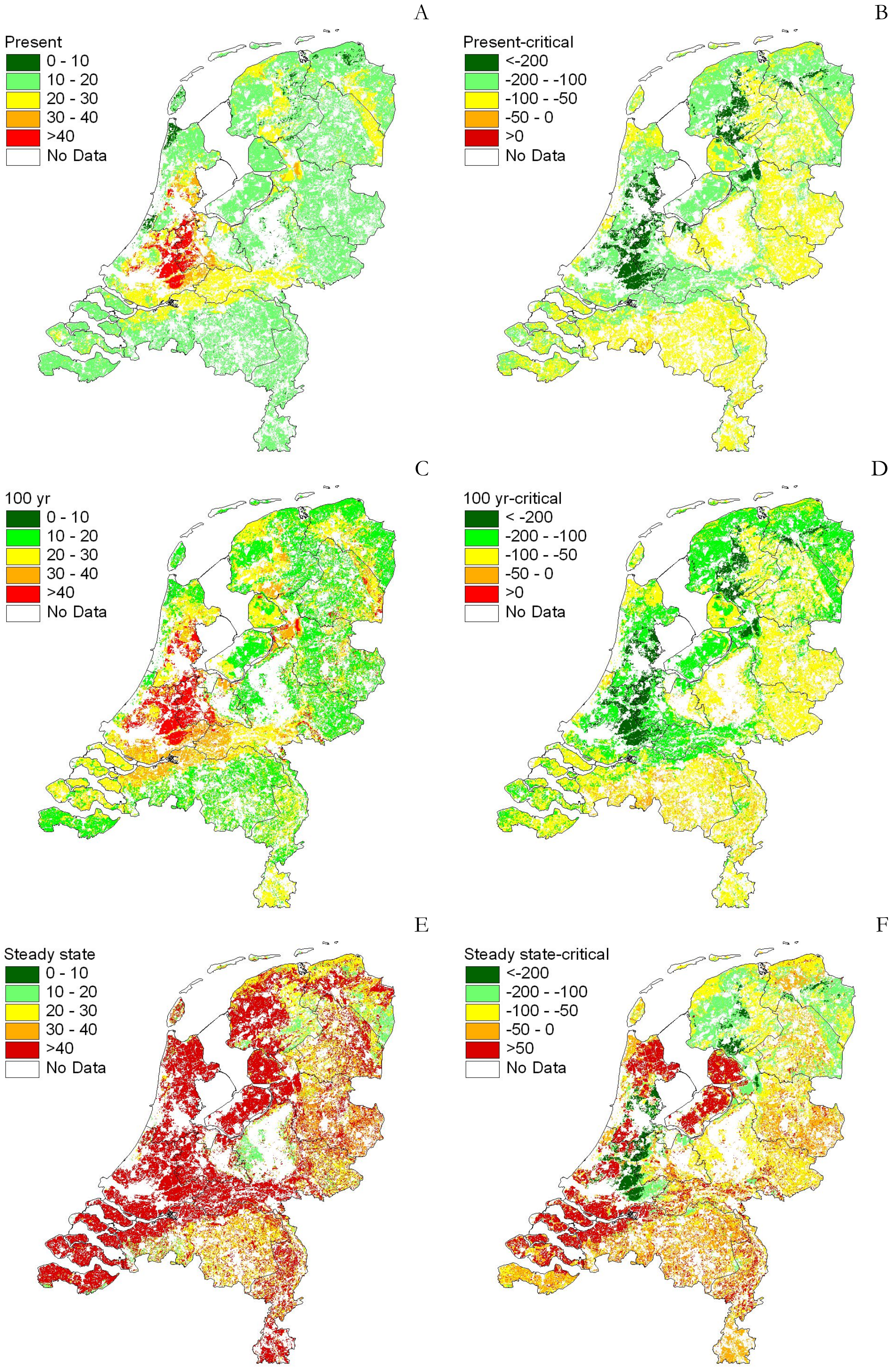

Figure 6 Maps of present (A), 100 year (C), and steady state Cu contents (E) and the differences of the present- critical content (B), 100 year - critical content (D) and steady state – critical content (F).

Concentrations above 30 mg.kg^{-1} are confined to peat 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 Cu, Zn and Pb.

Concentrations after 100 years are only slightly higher than present Cu concentrations as can be seen in Figure 6C. Figure 6C gives the difference between concentrations after 100 years and the critical concentration. The figure shows again that after 100 years there is not any exceedance of the critical concentration.

Steady state concentrations (Figure 6E) for all soils are clearly higher than present concentrations which shows that accumulation of Cu takes place for (nearly) all soils. Steady state concentrations show the highest increase in copper concentrations for the (calcareous) clay soils. Figure 6F shows where accumulation of copper ultimately leads to an exceedance of the critical concentration (PNEC). The figure shows that exceedance of the critical concentration are mainly found in calcareous clay soils of the south western part of the Netherlands, in the polders (Flevoland and Noordoost polder and polders in the north of North Holland). Clay soils in the north of the Netherlands (Friesland and Groningen) do not show exceedances of the critical concentration. This is due to lower inputs of pig manure in this area. Generally steady state concentrations in peat soils, although they have the highest present concentrations, stay below the critical limit. This is both due to the fact that the calculated accumulation for peat soils is less than for clay soils and the higher critical limit for peat soils.

4.2 Present copper balances

In Table 13 and Figure 7 an overview is given of the fluxes considered in this study. In general accumulation in arable soils exceeds that in grassland soils (Figure 7D) due to higher inputs of manure (Figure 7A) in combination with lower uptake rates (Figure 7B). Even at reduced uptake rates by grass (taking into account the lower measured values from 2005 by BLGG), this difference still remains. Differences in leaching losses between grassland and arable land (Figure 7C) are small relative to those of manure or uptake. The net water flux under arable soils is larger than that under grassland which results in higher leaching losses under arable land. On the total metal balance (at least at present day levels in soil) leaching losses are of minor importance.

Differences between uptake rates for different plots of the same land use category are due to differences in crop yield. The concentration in crops within each land use category are equal and do not depend on the Cu concentration in soil.

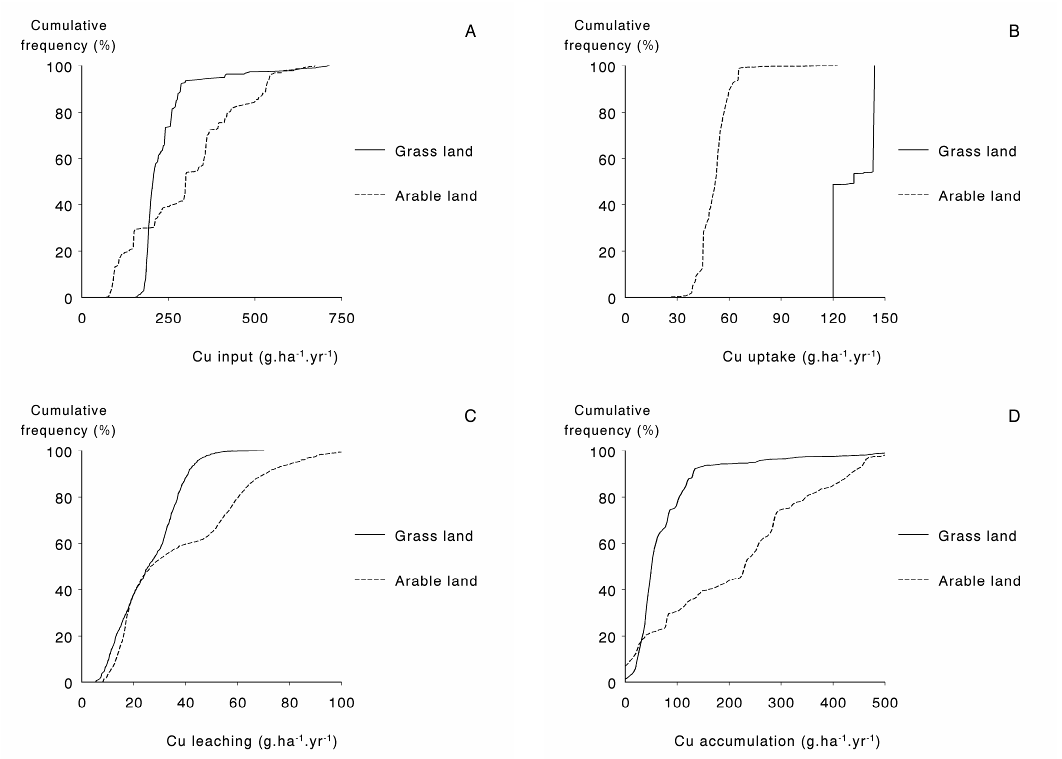

Figure 7 Ranges in the input (A), uptake(B), leaching (C) and accumulation flux (D) of Cu on grassland and arable land in the year 2000.

Table 13 gives an overview of the different contributions to the mass balance per land use and soil type. The differences in leaching losses between soil types reflect the differences in the apparent binding capacity with leaching losses increasing in the order calcareous clay < clay < calcareous sand < loess < peat < non calcareous sand.

Table 13 Average fluxes of Cu 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	Cu flux (g.ha^{-1}.yr^{-1})			
		Input	Uptake	Leaching	Accumulation
Grass	Sand	240	133	36	71
	Sand calcareous	193	144	17	31
	Clay	251	138	13	99
	Clay calcareous	272	143	12	117
	Loess	306	140	24	142
	Peat	213	122	26	65
Arable	Sand	345	48	59	237
	Sand calcareous	256	42	29	185
	Clay	239	57	24	158
	Clay calcareous	295	54	17	224
	Loess	335	62	36	237
	Peat	251	49	61	141
All		269	92	32	145

4.3 Changes in copper fluxes and concentrations in time

Changes in copper fluxes in time

Soil copper concentrations change over time, thus influencing Cu leaching. Ultimately, a steady state will be reached where soil Cu accumulation is negligible and the excess soil Cu input (Cu input minus Cu crop uptake) is equal to the amount lost by leaching. Those changes are illustrated in Table 14.

Table 14 Average input, uptake, leaching and accumulation fluxes of Cu in the topsoil at different time periods and at steady state.

Land use	Situation	Cu flux (g.ha^{-1}.yr^{-1})			
		Input	Uptake	Leaching	Accumulation
Grass land	2000	237	132	36	69
	2100	237	132	62	43
	Steady-state	237	132	105	0
Arable land	2000	301	52	51	199
	2100	301	52	93	157
	Steady-state	301	52	250	0

Results show that on average the accumulation decreases from near 70 and 200 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 and leaching are of equal magnitude in grass land (132 versus 105 g.ha^{-1}.yr^{-1}) whereas for arable land leaching is about 5 times the uptake by crops.

Changes in copper concentrations in time

Trends in soil Cu concentrations in time in accumulation and release are illustrated in Figure 8. The results for all plots were split into two categories, i.e. plots wit an increase in copper concentration and plots with a decrease in copper concentration. The change in copper concentration in time and the variation due to differences in soil type, inputs and hydrology is shown in the graphs with 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, mainly soils used as arable land, and soils with a median increase, mainly soils used as grass land is relatively constant during the first 500 years.. Plots wit a decrease in Cu concentration are scarce (only a few % of the plots)and are in general peat soils with a high initial concentration (about 60 mg.kg^{-1}) due to historical pollution.

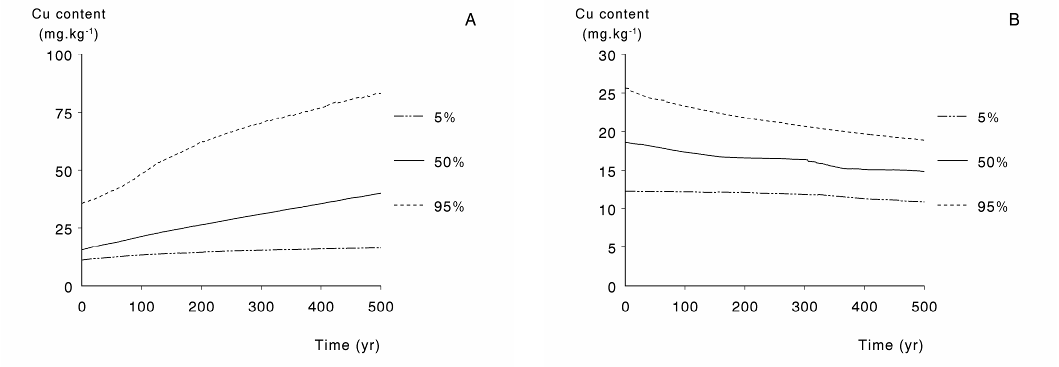

Figure 8 Graphs of the 5%, 50% and 95% of trends in soil Cu concentrations in accumulation (A) and release plots (B) in the period 2000-2500.

An indication of the differences in trends in accumulation plots for the various distinguished soil types is presented in Figure 9.

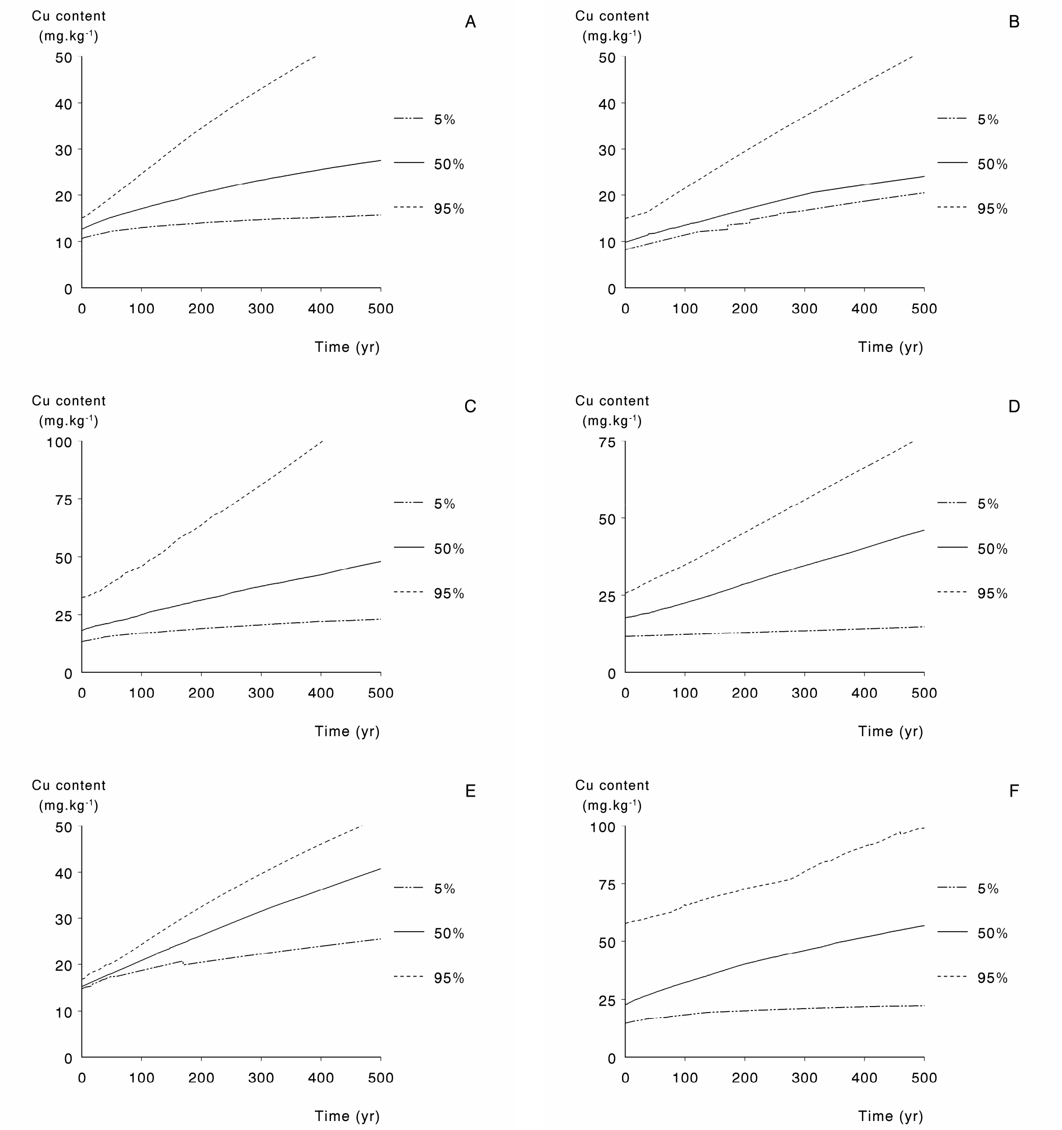

Figure 9 Graphs of the 5%, 50% and 95% of trends in Cu concentrations in accumulation plots of non-calcareous sandy soils (A), calcareous sandy soils (B), non-calcareous clay soils (C) calcareous clay soils (D), loess soils (E) and peat soils (F).

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

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

As stated before, regarding the dynamic behaviour of copper, there are four major possible options (see Chapter 2.3) depending on the present concentration (P), the critical concentration (C) and the steady-state concentration at present inputs (SS).

Because present concentrations are always below critical limits the options of interest are soils with concentrations always below the critical limit and soils where the concentration increases above the critical limit. The percentage of the area from the options listed above are given in Table 15. This table shows that the area with an increase above the critical concentrations occurs mainly in arable land.

Table 15 Percentage of plots with copper concentrations above or below critical limit.

Land use	Percentage of plots with copper concentrations above or below critical limit			
	Always above	Always below	Decrease below critical limit	Increase above critical limit
Grass land	-	48	-	2.8
Arable land	-	34	-	15
Total	-	82	-	18

The geographic variation of the plots over the four options is illustrated in Figure 10. Results are in accordance with the spatial pattern of soil types and land use in the Netherlands (Figure 4). The areas with Cu concentrations in soil increasing to critical limits are located in the south western part of the Netherlands and the polders with calcareous clay soils. The northern area with calcareous clay soils stays below the critical concentration due to lower inputs with pig manure in that region

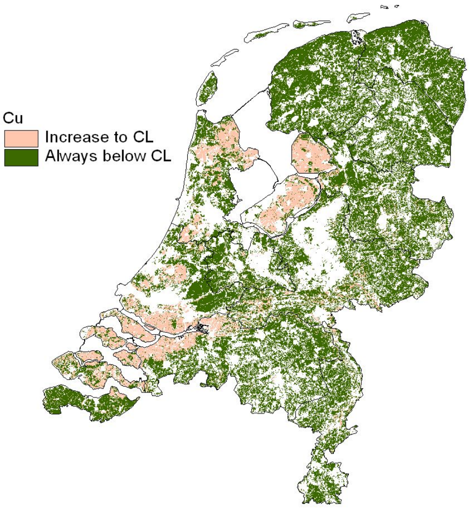

Figure 10 Geographic distribution of plots with copper concentrations always below critical limit and increasing to critical limit.

Time periods to reach critical soil copper concentrations

During the period to steady-state, the increase in soil Cu concentrations at 18% of the plots was such that critical values were exceeded. Time periods to reach critical soil Cu concentrations at sites where they are ultimately reached are given in Table 16. The time periods to reach critical soil Cu concentrations are very long ranging from minimal 150 years in some sandy soils to about maximally 3000 years in some calcareous clay soils, with an average time of 801 years for grass land soils and an average time of 1656 years for arable soils. The shorter time period to reach critical concentrations in grass land soils is due to the thinner soil layer to which the accumulation is attributed.

Table 16 Averages of time periods to reach the critical limits for Cu 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). ranges).

Soil type	Time period to reach critical Cu limits (yr)					
	Grass		Arable		Total	
Sand	216	(162-252)	892	(493-1136)	519	(166-1123)
Sand calcareous	-	-	1222	(892-1496)	1222	(892-1496)
Clay	952	(367-1758)	1776	(1058-2782)	1175	(401-2356)
Clay calcareous	1050	(638-1421)	1853	(962-2963)	1839	(961-2962)
Loess	416	(265-737)	960	(960-960)	461	(265-868)
Peat	518	(152-1090)	1601	(1088-2142)	1283	(271-2141)
All	801	(199-1705)	1813	(960-2955)	1656	(425-2913)

The geographic variation of the time periods to reach critical limits, limiting ourselves to the plots at which the Cu concentrations increases until the critical limit is exceeded, is given in Figure 11. Results show that the soils with the largest area of exceedance have the longest time period before they reach the critical concentration. Time periods to reach the critical concentration are smaller for a large area in the south, most sandy soils and some calcareous clay soils, which is due to high inputs of pig manure in this area. However time periods to reach critical limits are still very long (250-500 years). There are no significant large areas with shorter time periods to reach critical concentrations.

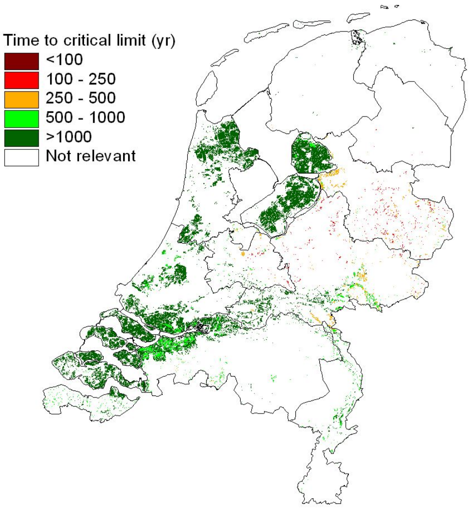

Figure 11 Geographic distribution of the time periods to reach critical limits

Time periods to reach steady state soil copper concentrations

Information on the time periods to reach steady state is given in Table 17. Results show that the overall average time period is approximately 2500 year. The time periods increase in the order non-calcareous sandy soils < loess and peat soils < calcareous sandy soils < non-calcareous clay soils < calcareous clay soils, with the largest time periods for arable soils. The results clearly illustrate that the time period to reach steady state is very large in soils where Cu accumulation ultimately leads to problems, i.e. clay soils and calcareous sandy soils.

Table 17 Averages of time periods to reach steady-state for Cu 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	1198	(706-1608)	2032	(1351-2607)	1564	(843-2404)
Sand calcareous	2211	(2211-2211)	2910	(2450-4032)	2886	(2184-4020)
Clay	3115	(2167-3976)	3524	(1706-4952)	3183	(2114-4275)
Clay calcareous	3345	(2520-3795)	4477	(2688-4954)	4428	(2674-4954)
Loess	2037	(1491-2433)	3145	(2707-3392)	2711	(1936-3302)
Peat	1743	(769-2691)	1785	(519-4315)	1756	(725-3082)
All	1966	(854-3678)	3221	(1069-4953)	2584	(922-4953)

4.5 Impacts of N legislation

In this study we investigated the impact of using present (year 2000) Cu inputs. The present Cu inputs are dominated by the application of animal manure. The uncertainties in the Cu inputs for each plot are thus dominated by the uncertainty in the N application rate and the Cu/N ratio in the manure. To gain insight in the impact of Cu input, also in view of the representativity of the results (see Section 5.3), we used as an alternative the Cu 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 present N inputs (year 2000) are considerably higher for grassland with an average N input of 342 $kg.ha^{-1}.yr^{-1}$ with nearly 100% of the grassland area exceeding 250 $kg.ha^{-1}.yr^{-1}$. On average arable land is below 170 $kg.ha^{-1}.yr^{-1}$ already (average 133 $kg.ha^{-1}.yr^{-1}$), however 30% of the area with arable land has an input higher than 170 $kg.ha^{-1}.yr^{-1}$. The Cu/N ratio was assumed to remain constant in this approach.

The impacts of these targets on the Cu inputs is very large for grass land but very limited for arable land as shown in Figure 12. The much larger input of Cu 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 larger input of cattle manure (especially by grazing) on grassland than on arable land, with a much lower Cu/N ratio than pig and poultry manure (see Table 6) and (ii) the input of compost and pesticides occurring on arable land only.

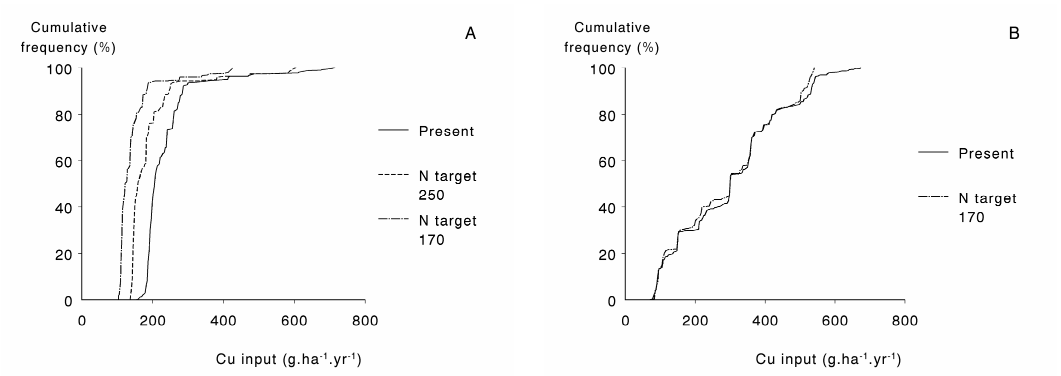

Figure 12 Cu inputs to grassland (A) and arable land (B) using the year 2000 N inputs and applying the N legislation.

The impacts of the two alternative inputs on the percentage of plots at which the steady-state Cu content exceeds the critical Cu content is presented in Table 18. Not surprisingly the effect is largest for grassland soils where the changes in input were large whereas for arable soils the changes in the area exceeding the critical concentration is marginal due to the small change in (average) inputs. The total area (grassland and arable land together) decreases only a little from 18% to 17% (or 15% for 170 kg N on grass land) as a result of the lowering of N inputs.

We also calculated changes in copper concentrations for a scenario with the high Cu inputs of 1996. With this high input a much higher area with exceedance was calculated (50% instead of 18% with the standard scenario). Times to reach critical concentrations were however also very long in this scenario.

Table 18 Percentage of plots at which the steady-state Cu content exceeds the critical Cu content for the alternative Cu input (Cu 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 Cu limit				
	Grass land			Arable land	
	N input 170	N input 250	Standard input	N input 170	Standard input
Sand	0	1.5	2.3	1.6	2.4
Sand calcareous	0	0.0	0.0	15	15
Clay	2.9	7.8	13	21	24
Clay calcareous	0	17	24	61	61
Loess	6.2	9.8	9.8	0.6	0.6
Peat	0	1.0	1.2	6.2	6.2
All	1.0	3.6	5.5	30	31

The impact of the alternative approaches on the average time period before a critical limit is reached is illustrated in Table 19. On average the time to reach the critical Cu concentration increases but for some cases this time may decrease as a result that soils which reached the critical concentration after a relative long time with the addition of the standard input do not reach the critical limit anymore with the reduced input scenario.

Table 19 Averages of time periods to reach critical Cu limits on the considered land use types and soil types, where exceedance did occur in the course of time for the standard and alternative Cu inputs

Soil type	Time period to reach critical Cu limits (yr)				
	Grass land			Arable land	
	N input 170	N input 250	Standard input	N input 170	Standard input
Sand	-	278	216	1053	892
Sand calcareous	-	-	-	1222	1222
Clay	884	682	952	1712	1776
Clay calcareous	-	1086	1050	1870	1853
Loess	620	442	416	998	960
Peat	747	667	518	1658	1601
All	859	645	801	1838	1813

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 model). In addition to the model performance boundary conditions like uncertainties in critical limits and data will affect model inputs and model outputs. 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 copper inputs to the soil) and model outputs (in this study specifically copper 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 Cu accumulation data in time (Rothamsted experimental station) and in space (data from Dutch 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 average copper inputs were used to get insight in the representativity of this study 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 copper 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 20, the present soil copper contents in two clay soils are shown for a control plot and a FYM treated soil. Because the concentrations of the control plots do not show any downward or upward trend in Cu concentrations we averaged the measurements of the whole time period to calculate the 'background' concentration of the control plots. The soils treated wit FYM show a trend of increasing Cu concentrations from the start of the experiment until the year 1965 after which Cu concentrations remain constant. The present concentration was therefore calculated as the average of the concentrations measured from 1965-2000. The constant concentration of the control soils throughout the whole time indicate that Cu sources other than FYM (e.g. deposition) do not lead to accumulation of Cu in soils. This is in line with our calculations that show that deposition is a negligible source of Cu inputs.

Table 20 Overview of Cu content in two experimental field at Rothamsted experimental station (data kindly supplied by S. McGrath).

Soil	Cu content (mg kg^{-1})	Time period
Broadbalk		135
Control	14.0	
FYM treated soil	19.5	
Hoosfield		118
Control	14.1	
FYM treated soil	25.6	

The annual change in the soil copper content is calculated as the difference between the FYM treated soil with the control soil divide by the time period of the experiment. Calculated annual changes in copper content range from 0.04 to 1.0 mg.kg^{-1}.yr^{-1}. These values are in the same range as the accumulation in clay soils in our model study which show an increase between 0.04 and 0.08 mg.kg^{-1}.yr^{-1} during the first 100 years (Table 11). This rather exact match must be fortuitous since a lot of (unknown) differences between these particular two field plots and the average conditions of plots in the model study were not taken into account. However the comparison shows that the rather low accumulation rates calculated in the model study are in a good order of magnitude and realistic.

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

Data on Cu supply and removal based on farm level Cu metal balances of 17 dairy farms were 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 copper accumulation rate (i.e. inputs minus outputs) on all farms averaged over the period 1997-2001 equalled 180 g.ha^{-1}.yr^{-1}. Data from individual farms (in 2001) ranged from 17 g.ha^{-1}.yr^{-1} to 574 g.ha^{-1}.yr^{-1}. These data are close, although a little lower, to those reported in Table 13. 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 copper content in grass and maize are given. For grass and maize measured copper levels ranged from 7.5 to 10.2 mg.kg^{-1} dm (average 8.4 mg.kg^{-1}) and from 2.7 to 5.5 mg.kg^{-1} (average 4.4 mg.kg^{-1}), respectively. Data for maize are in agreement with model values used of 4.1 mg.kg^{-1} (table 10). Model data for copper contents in grass (12 mg.kg^{-1}) show to be high again thus overestimating Cu uptake.

Because of the uncertainty in the uptake of Cu by grass, we also calculated the accumulation of Cu using the lower estimate of 8.5 mg.kg^{-1} Cu in grass. Results show that the difference after 100 years is rather small. The average soil concentrations for grassland soils calculated with the lower Cu uptake are about 10% higher compared to the standard run. Furthermore we did not calculate any exceedance of the PNEC for all grassland soils as with the standard run. Larger deviations become apparent at steady state especially for the calcareous and non calcareous clay soils for which the area of exceedance of the PNEC about doubled. For other soils differences are much smaller . The large difference for clay soils is due to the low leaching from these soils making uptake the most important sink. One should take in mind that the uncertainty for steady state predictions is rather large due to the long time period to come to steady state (about 3000 years for clay soils) and due to the large difference between steady state concentrations and present concentrations. Therefore the uncertainty in the predicted leaching flux is likely of more importance than the uncertainty in uptake.

Assessment of validity of model predictions of dissolved copper concentrations

Leaching is an important term in the mass balance for copper in agricultural systems. To test the validity of the calculated leaching fluxes they should ideally be compared with measured fluxes. Measured numbers are however not available to make this comparison. The calculated leaching flux in the model is most sensitive to the model estimate of the copper concentration in the water leaching from the topsoil. This is the concentration at 10 cm depth in case of grass land and the concentration at 30 cm depth for arable land. Therefore a comparison of calculated copper concentrations gives insight in the validity of the calculated leaching of copper.

A direct comparison of copper concentrations is however not possible. Measurements of copper concentrations are usually done for concentrations in ground water at larger depths. Copper concentrations are measured for ground water at different depths at a national scale (Fraters et al., 2001). From these measurements it is clear that concentrations decrease with depth. Data on surface water concentrations show that these are generally lower than ground water concentrations.

Table 21 gives an overview of calculated Cu concentrations together with measured concentrations in the upper phreatic water and concentrations of measured concentrations in surface waters.

The trend of the decrease of Cu concentrations with depth, and towards surface waters is in agreement with the expectation. Data from Table 21 also show that differences between calculated copper concentrations for different soil types agree with the trend of the measured median concentrations in ground water with the decreasing in the order sand > peat > clay > clay calcareous.

The agreement of this trend and the fact that calculated concentrations leaching from the upper soil layer are higher than concentrations measured in ground- and surface water gives confidence in a qualitative way on the model estimates for the median concentration calculated with the model.

The 95 percentile shows that model concentrations are often lower or about equal to concentrations in the upper ground water. Therefore the model presumably underestimates concentrations in soil solution at the high end of the distribution. This underestimation is most likely due to the solid-solution partitioning model used to calculate the copper concentrations in solution in equilibrium with the copper concentration in the solid phase of the soil. This is further discussed in chapter 6.

Table 21 Comparison between modelled Cu 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 Cu concentrations (ug.l^{-1})		
			5%	50%	95%
Sand	Soil solution[1]	Model	12.0	16.1	20.8
	Upper ground water[2]	Measured	1	11	22
	Surf. Wat. Arable[3]	Measured	1.5	4	16.4
Clay	Soil solution	Model	3.4	6.2	9.3
	Upper ground water	Measured	2	5	14
	Surf. Wat. Arable	Measured	1.7	3.5	10.2
Clay calcareous	Soil solution	Model	2.5	4.3	6.7
	Upper ground water	Measured	<1	2	5
	Surf. Wat. Arable	Measured	-	-	-
Peat	Soil solution	Model	4.8	15.9	25.0
	Upper ground water	Measured	2	5	55
	Surf. Wat. Arable	Measured	1.5	3.2	8.9

[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

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 copper inputs as described below.

The data used in this study on the input of Cu 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 Cu/N ratio, based on the composition of manure in a Dutch inventory (Driessen & Roos, 1996). This leads to an average Cu input near 260 $g.ha^{-1}.yr^{-1}$. To evaluate whether these inputs of copper 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 A1.1 of annex 1 an overview of the composition, production and copper levels in manure in 16 EU countries is shown.

Figure 13 shows the mid range values of copper loads (in gram per hectare per year) due to input of manure and slurries (data from Table A1.1).

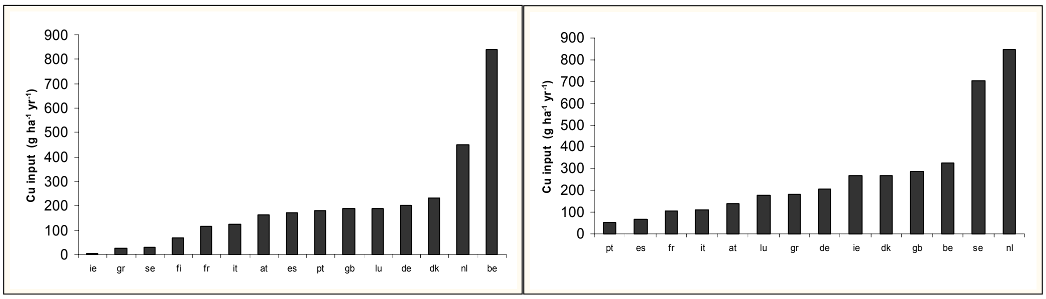

Figure 13 Overview of mid range levels of copper inputs to arable land (left) and grassland (right) due to the use of solid and liquid manure.

The quality of the data is somewhat questionable. Numbers presented were not controlled by the member states except for Denmark after which the estimates were lowered. Therefore absolute numbers have to be considered with care. The uncertainty in the numbers is mainly due to estimates in metal contents of manure and the loads of manure for the different forms of land use. Copper contents in manure may change in time, copper contents in manure in the Netherlands decreased substantially (about a factor 2) in the period 1996-2000 (see Chapter 3.3). Therefore the numbers should only be used in relative terms. The absolute numbers presented for the Netherlands which ranges from 200-1200 g.ha^{-1}.yr^{-1} are too high. Especially inputs to grass land are overestimated One reason for overestimation could be the very high production rate of dry manure used by ADEME. 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 A1.1 is close to this (54 million tons) but the dry manure production equals 26 million tons.

The overestimation of copper inputs for the Netherlands together with the overestimation for Denmark and (not shown in the graph) the extremely high reported input of copper in grassland in Finland, indicates that the numbers are probably too high for other countries as well and can be reduced by a factor 2-4.

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.

The average Cu input near 260 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 A1.1) 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 in our study thus represent a worst case but seemingly not an extreme one. Therefore accumulation of copper in most areas of Europe is likely to occur, but due to the lower inputs in other countries compared to the Netherlands soils in other countries will be closer to equilibrium (where the output equals the input).

6 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 Cu accumulation data varying in time at Rothamsted experimental station and at a fixed point in time at various Dutch 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. However in reality a larger variability in copper inputs is expected than used in the model study in which differences in inputs are 'averaged out' to a certain extend.

However 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 kept constant 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. The soil solution model are similar to published models albeit that model parameters are derived from data from the Netherlands. 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). The soil-soil solution partitioning model (transfer function) as used in this study has a low explained variance and a relative large error in the model estimate. A large part of the unexplained variance in this model is due to the variance in DOC which was not taken into account because no DOC data are available. The model therefore gives Cu solution concentrations for average DOC concentrations for soils with a certain organic matter content, clay content and pH. On a plot scale this may lead to large deviations (in case of deviations from average DOC concentrations), but for all plots together the average behaviour is expected to be described well. Again as with the averaging effect of data more extreme situations are filtered out.

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.

Also the approach to calculate the PNEC will influence results especially with respect to the area with exceedance of critical concentrations. One has to be aware that the results are related to the approach according to the RAR for Cu. There are also other approaches possible to derive critical Cu limits, such as the one recently described by Lofts et al. (2004) in which the critical Cu content is estimated as a function of organic matter content and pH.

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 solubility of 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 assuming similar inputs). Although the comparison of model results and data was limited to a few cases, data on input, output and annual changes in the soil copper content from the UK 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 copper 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.

A potential important source of copper input to agricultural land by hoof disinfectants containing copper sulphate was not taken into account in this study. It is recommended to investigate the contribution of this source to the copper input of agricultural soils within the EU.

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 Cu inputs between different land uses and soil types are limited. In grassland animal manure contributes most (more than 80%) to the input of Cu. Fertilisers are a significant but much smaller source of Cu, whereas atmospheric deposition is negligible. Other sources, such as compost and pesticides are a significant source in arable land (approximately 10%). 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 Cu inputs exceed the uptake and present leaching at 97% of the plots. This is an indication that present loads to intensive agro-ecosystems in industrialised countries, such as the Netherlands, generally cause an increase in soil Cu concentrations. The highest accumulation of Cu occur on calcareous clay soils with lowest leaching and uptake of Cu.
- Present Cu inputs will cause changes in Cu accumulation and leaching over a period of more than several hundreds to thousands of years, depending on land use type and soil type considered. Times to reach steady state are 1000-3000 years for Cu, 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 4 times as large. Consequently, at steady state the PNEC is predicted to be exceeded at 25% of the plots whereas at present and after 100 years there is no exceedance.

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

- In the Netherlands, there is at present and after 100 years no exceedance of the PNEC of copper.
- The percentage of plots where the predicted steady state copper content will exceed the PNEC is estimated at 18% when using current (year 2000) inputs and at 17% when the legislation for nitrogen will be respected.
- The predicted time period to reach the PNEC for copper is on average approximately 920 years for grassland and 1620 years for arable land when using current inputs. When respecting the N legislation, this time period changes only very little to approximately 960 years for grassland and 1670 years for arable land.

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Appendix 1 Input data for copper by manure and slurries with data from other EU countries

Table A1.1 Overview of annual production and application rates of Cu in manure and slurries in EU countries

Country	Type of manure	Solid and liquid manure production		Annual Cu 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})		Cu application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low[1]	High[1]			Fresh Matter	Dry Matter	Low	High
Austria	Solid Manure[2]	11.3	2.6	123.6	451.2	Arable crops	1374	7	1	73	251
	Liquid manure [2]	7.4	0.6	58.5	174.5	Grassland	1935	13	2	71	210
	DRS[3]	16.3	1.8	55.5	125.2	Total	3309	20	3	144	461
	Total	34.9	4.9	237.5	750.9						
Belgium	Solid Manure	17.5	4.0	232.7	806.5	Arable crops	833	34	6	386	1291
	Liquid manure	13.6	1.1	113.8	340.9	Grassland	536	48	5	189	458
	DRS	23.3	2.6	79.6	179.8	Total	1369	82	11	575	1749
	Total	54.5	7.7	426.1	1327.1						
Denmark	Solid Manure	6.4	1.5	75.7	250.2	Arable crops	2490	14	2	114	351
	Liquid manure	32.0	2.7	238.2	713.2	Grassland	373	28	3	143	391
	DRS	6.7	0.7	24.1	56.2	Total	2863	42	5	257	742
	Total	45.1	4.9	338.0	1019.6						
Finland	Solid Manure	5.3	1.2	51.8	191.1	Arable crops	2185	3	1	30	105
	Liquid manure	3.2	0.3	24.1	71.1	Grassland	25	367	42	1482	3785
	DRS	8.0	0.9	27.4	61.9	Total	2210	370	43	1512	3890
	Total	16.6	2.4	103.3	324.1						
France	Solid Manure	97.3	22.6	722.8	2924.6	Arable crops	18309	7	1	49	186
	Liquid manure	49.5	4.5	315.7	855.2	Grassland	9924	17	2	62	149
	DRS	154.0	16.9	525.0	1185.4	Total	28233	24	3	111	335
	Total	300.7	44.1	1563.4	4965.2						

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[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 A1.1 (2) Overview of annual production and application rates of Cu in manure and slurries in EU countries, continued

Country	Type of manure	Solid and liquid manure production		Annual Cu 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})		Cu application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low	High			Fresh Matter	Dry Matter	Low	High
Germany	Solid Manure	76.3	17.4	850.7	3075.8	Arable crops	11788	9	2	91	310
	Liquid manure	50.9	4.1	404.3	1206.4	Grassland	4970	26	3	112	297
	DRS	109.6	12.1	373.7	843.7	Total	16758	35	5	203	607
	Total	236.8	33.5	1628.6	5125.9						
Great Britain	Solid Manure	68.2	16.9	447.6	2577.4	Arable crops	4495	9	2	60	314
	Liquid manure	26.5	2.4	163.4	438.2	Grassland	5422	30	4	130	449
	DRS	109.1	12.0	372.2	840.4	Total	9917	39	6	190	763
	Total	203.8	31.4	983.2	3856.0						
Greece	Solid Manure	8.7	2.5	63.7	517.9	Arable crops	2796	1	0.2	7	43
	Liquid manure	2.6	0.2	18.5	49.3	Grassland	1789	12	2	60	306
	DRS	13.1	1.4	44.6	100.8	Total	4585	13	2.2	67	349
	Total	24.4	4.2	126.8	668.0						
Ireland	Solid Manure	31.7	7.2	149.6	760.9	Arable crops	1118	0.5	< 0.5	2	6
	Liquid manure	10.8	1.1	53.0	139.3	Grassland	3193	30	4	121	411
	DRS	54.8	6.0	187.0	422.3	Total	4311	30.5	4	123	417
	Total	97.4	14.3	389.6	1322.5						
Italy	Solid Manure	39.2	9.4	341.1	1471.8	Arable crops	8234	6	1	50	196
	Liquid manure	21.1	1.8	149.2	421.2	Grassland	4284	16	2	62	163
	DRS	59.5	6.5	202.8	457.9	Total	12518	22	3	112	359
	Total	119.7	17.7	693.1	2350.9						
Luxembourg	Solid Manure	0.8	0.2	4.6	19.3	Arable crops	62	14	3	75	304
	Liquid manure	0.3	0.03	1.8	5.0	Grassland	65	27	3	103	256
	DRS	1.5	0.2	5.0	11.2	Total	127	41	6	178	560
	Total	2.6	0.4	11.3	35.5						

Table A1.1 (3) Overview of annual production and application rates of Cu in manure and slurries in EU countries, continued

Country	Type of manure	Solid and liquid manure production		Annual Cu load in manures and slurries (ton/year)		Land Use	Surface area (1000 ha)	Solid and liquid manure application rate (t ha^{-1} yr^{-1})		Cu application rates (g ha^{-1} yr^{-1})	
		Fresh	Dry	Low	High			Fresh Matter	Dry Matter	Low	High
Netherlands	Solid Manure	26.0	6.1	403.1	1376.2	Arable crops	1005	17	3	210	687
	Liquid manure	23.3	1.8	200.5	597.6	Grassland	881	63	8	430	1262
	DRS	31.4	3.5	107.2	242.0	Total	1886	80	11	640	1949
	Total	80.7	11.4	710.7	2215.8						
Norway	Solid Manure	5.4	1.3	35.1	187.3	n.a.	-				
	Liquid manure	2.1	0.2	13.2	37.7						
	DRS	8.7	1.0	29.8	67.3						
	Total	16.2	2.4	78.1	292.2						
Portugal	Solid Manure	9.3	2.4	91.5	452.2	Arable crops	1634	7	2	63	294
	Liquid manure	5.0	0.4	38.6	111.1	Grassland	1390	10	1	33	74
	DRS	13.4	1.5	45.7	103.1	Total	3024	17	3	96	368
	Total	27.7	4.2	175.8	666.4						
Spain	Solid Manure	47.6	11.9	673.4	2795.5	Arable crops	13027	6	1	70	269
	Liquid manure	35.8	2.7	314.6	947.1	Grassland	7235	9	1	38	95
	DRS	59.9	6.6	204.1	461.0	Total	20262	15	2	108	364
	Total	143.3	21.1	1192.1	4203.6						
Sweden	Solid Manure	8.7	2.0	81.0	306.5	Arable crops	2665	2	0.3	13	47
	Liquid manure	5.0	0.4	37.2	109.7	Grassland	372	62	8	344	1059
	DRS	13.3	1.5	45.4	102.4	Total	3037	64	8.3	357	1106
	Total	27.0	3.9	163.6	518.7						