Copper leaching from soils: an inventory of available data and model concepts

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ABSTRACT

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In this literature review, major processes controlling copper solubility and speciation in soils are discussed. Different mechanistic model concepts that are currently under development or have been applied at different scale levels are presented as well as empirical approaches that can be applied at the regional or national scale. Special emphasis is given to the role of Dissolved Organic Matter (DOM) since DOM controls both the solubility and transport of copper through soils. Field data on the measured concentrations of copper in Dutch groundwater bodies are presented to assess whether or not current forms of land use already have resulted in a change in groundwater quality. An example of an integrated model approach is presented that enables the user to assess the contribution of leaching of copper from soil to ground- and surface waters. Finally a list of important topics (processes as well as data) that need to be addressed in the future to better understand copper migration through soil are listed.

Keywords: Copper, Cu, groundwater, leaching, model, soil, speciation, review

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Preface

Heavy metals in soils are present in various phases; in the solid phase, either adsorbed onto the mineral phase (e.g. clay or Fe and Al hydroxides) or the organic matter fraction, and in soil solution. The distribution between metals in the solid phase and the soil solution is crucial for the fate and behaviour of metals in soil. Once in the soil solution, metals can leach to lower soil horizons and ultimately reach ground- and surface waters. In addition, uptake by crops and soil dwelling organisms is largely related to the presence of metals in the soil solution.

To predict the fate of metals, in this case copper, it is imperative to know which factors control the solubility and speciation in soil. Many laboratory studies have been performed to elucidate one or more processes that control copper solubility and speciation. Obvious examples include studies on the effect of pH, degree of contamination and soil type on the solubility in soils. Also the impact of Dissolved Organic Matter (DOM) in soils on the speciation of copper (here: the distribution of copper among various dissolved fractions including the free metal concentration and the complexed species) has been studied in detail.

Most studies have focussed on one or more single properties (e.g. pH, type of DOM). Studies aiming at predicting the behaviour (solubility, leaching) of copper under field conditions are limited. This is partly due to the complex and dynamic nature of metal sorption under field conditions. Differences in hydrological conditions, temperature, and the spatial variability of soil properties etc. contribute to a large degree of uncertainty about many soil processes at the field scale. Transport in soils can be extremely heterogeneous on a spatial scale of meters due to differences in soil physical properties.

Also model concepts that can be used on the field scale to predict the distribution between the solid phase and the soil solution are still scarce. Although considerable progress has been made - especially for copper - on model concepts to predict speciation and solubility in aqueous systems (lakes, rivers etc.), concepts for soils are far less developed.

However, despite the obvious difficulties involved when trying to predict metal behaviour at the field scale, it is essential to at least estimate how the interaction of soil - climate - hydrological conditions etc and metals in soil controls metal solubility. In this report the most important factors that control copper solubility speciation and leaching are listed and an overview is given of existing model concepts that are being developed to predict copper leaching to ground- and surface waters.

Summary

Copper leaching from soils to ground- and surface waters is one of the major pathways by which copper is displaced from soil to the water system. However, a clear analysis of the quantitative importance of leaching is still lacking, partly due to the complexity of processes that control copper solubility, speciation and transport within the soil-water system and partly because of a lack of reliable field data that can be used to validate model concepts.

In this literature review, major processes controlling copper solubility, speciation and transport are discussed. Emphasis was given to list those processes which are believed to contribute most to copper movement in soils. Also model concepts are discussed that can be used to simulate the behaviour and transport of copper from soil to water bodies.

Finally a list of major issues (both process knowledge and lack of data) that need to be studied in the future to obtain better estimates of leaching losses are listed. In this summary, some of the major issues are listed.

Leaching of copper from soils is controlled by both soil chemical properties and water fluxes in soil. A large number of laboratory studies clearly indicated that the solubility of copper under 'normal' (i.e. non-polluted aerated soils) conditions is controlled largely by the solubility and mobility of organic complexes. The concentration of the free copper ion in soils in the pH range between 4 and 8 is low, but due to the presence of dissolved organic matter, the total concentration of copper in soil solutions is raised to levels between 1 to 10 $\mu g\ L^{-1}$ in arable soils to several hundred $\mu g\ L^{-1}$ in soils at high dissolved organic carbon concentrations (not considering dissolved copper concentrations in heavily polluted soils).

The interaction of copper with several individual important soil components (clay minerals, organic matter, hydroxides) as well as organic ligands has been studied in detail. Results have revealed that copper binding to organic matter is more important than sorption on clay minerals and hydroxides although at low pH levels ($pH < 4$) sorption onto manganese oxides may become more important. Addition of organic matter, which contains copper as well, to soils (manure, compost, sludge) therefore not only alters the copper content of the soil but also the soils capacity to retain copper.

Also complexation with organic ligands in the pore-water (DOM) has been studied in detail. Due to specific sorption of copper onto carboxyl and phenolic groups, free ionic copper activity levels are low even at low DOM levels in the pH range between 4.5 and 8. Below pH 4.5, the free metal activity increases due increase protonation of sites on the organic ligand. Both sorption onto organic ligands and solid soil components can be described accurately by mechanistic models like Model VI (WHAM, for dissolved organic ligands), NICA Donnan, or CD-MUSIC .

Copper solubility in most non-polluted soils is controlled by sorption processes and the importance of precipitates is limited. An exception to this is the formation of copper sulphides under reducing conditions (e.g. peat soils). In general, the understanding of copper solubility in highly dynamic systems (like in case of changing redox conditions near the groundwater table) is less developed than that in well-drained aerobic soils.

The combination of a lack of process identification and the changing nature (chemical reactivity) of certain soil components with time (organic matter) also hampers a clear evaluation of the assumed process of 'ageing'. As of now it is still unclear whether or not ageing is a relevant process that affects copper solubility with time at all, and whether or not the changing retention with time is due to non-equilibrium in the sorption process or (in addition) due to very slow incorporation processes like diffusion into organic matrices or soil minerals.

An important factor that hampers a clear evaluation of whether or not ageing is relevant, is the lack of a clear characterisation of the adsorbed (available) amount of copper in soils (and the changes therein). Although different methods have been developed to assess the amount of available copper (ranging from dilute salt solutions to extractions with strong ligands like EDTA or dilute acid like HNO_3), still no consensus has been reached on how to characterise the total available 'pool' of copper in soils.

Although the applicability of mechanistic models has increased due to an increased understanding of processes controlling copper sorption and complexation, few studies are available where mechanistic models are tested at the field level. Alternative approaches like empirical models (based on Freundlich isotherms) have shown some potential for application at the regional scale level. Although predictions for specific sites show the same degree of noise as mechanistic models, application on a regional level resulted in a fair agreement between modelled values and measured concentrations in surface waters.

In general, predictions of copper leaching and run-off at the regional or national scale are difficult to validate. Data from monitoring networks (Provincial, National, Regional) are often obtained using different sampling strategies. Apart from methodological differences also temporal variation of dissolved copper concentrations (especially in soil solutions and upper groundwater) hamper a clear evaluation of model results.

Despite the obvious shortcomings of both mechanistic and empirical models to predict copper concentrations at a regional scale, copper leaching from soil has been identified as an important process that contributes significantly to the copper load in surface waters in areas with shallow groundwater tables like large parts of the Netherlands. Estimates of copper leaching rates however also suffer from a lack of data from the sub-soil (below the plough layer). In general regional or even national maps of the copper content in the topsoil exist but data on the subsoil (both the amount of copper as well as important soil properties) are scarce. This is also true for the composition and reactivity of DOM in the subsoil and upper groundwater which remains virtually unknown.

Apart from subsurface flow, also surface run-off (erosion) causes a substantial displacement of copper from soil to waters, but little data are available to assess the importance on a regional scale.

To obtain better, more reliable estimates of copper leaching from soils to ground- and surface waters it is therefore not only essential to improve models that are to be applied at the field scale but also to obtain more data on the composition of the soil below the surface layer, both on soil properties but also on the copper content and characteristics of DOM.

1 Introduction

Among the heavy metals, copper -like zinc- is an essential element. This means that soil organisms as well as crops need copper for an optimal growth. However, like all nutrients, optimum ranges exist and excess copper means that the functioning of both soil organisms and crops will be affected.

The derivation of minimum and excess levels of metals in soils (critical limits) is still an ongoing research issue and as such is not a part of this study. Once criteria for soils and waters exist, the balance between input and output of copper determines whether or not a certain land use or input from atmosphere will results in unacceptable effects. To evaluate if inputs exceed outputs, insight is needed in the major in- and outputs of copper.

Important sources of copper in the environment (i.e. in rural areas) are:

1. application of manure and other soil organic amendments (compost, sludge);
2. application of specific crop protection materials (e.g. Cu in vineyards and tomatoes) and other agro-chemicals (e.g. hoof disinfecting solutions);
3. fertilisers;
4. atmospheric deposition;
5. industrial waste.

Recent estimates for the Netherlands indicate that on a national basis more than 90% of the annual load of copper comes from animal manure and fertilisers (Delahaye et al., 2003). In some countries also the routinely application of copper as a micronutrient, pesticide and fungicide contribute to the copper load. For example, overall in the USA the use of copper hydroxide in agricultural production increased approximately sevenfold from 1987 to 1997 (Epstein & Bassein, 2001). It should be pointed out, however, that in many other European countries laws on the use and application of sludge and compost are less strict compared to the Netherlands. For example data on inputs in the UK (Alloway et al., 1998 see table 1) indicate that industrial wastes and sludge contribute significantly as well. It should be kept in mind though that the distribution on a national scale (expressed in tons yr^{-1}) does not reflect the importance of inputs on a local scale. The data in table 1.1 clearly show that the total input by atmosphere - on a national basis - is important. On a plot level where manure or sludge are applied, the contribution of atmospheric deposition is far less important (in g ha^{-1} yr^{-1}).

Table 1.1 Overview of copper inputs to arable land (in tons per year) in the UK (Alloway et al., 1998).

Source	Cu load (tons yr^{-1})
Atmospheric deposition	602
Animal manure	710
Sewage sludge	271
Industrial 'wastes'	154
Fertilisers and lime	116
Agro-chemicals	8
Irrigation water	2
Total	1863

However, to assess whether or not inputs on a plot level will result in unacceptable accumulation rates, *outputs* need to be quantified as well.

In agricultural systems major outputs can be identified:
1. crop uptake and removal of harvested products;
2. copper in animal products (milk, meat);
3. surface runoff and erosion of solid material;
4. leaching from soil to ground- and surface waters.

In general data on Cu levels in crops are fairly well documented and, in combination with crop production rates (in kg ha^{-1} yr^{-1}), Cu removal rates can be estimated. For example, in the Netherlands, the total Cu uptake by crops is estimated at 104 tons yr^{-1}, whereas the total supply amounts to 504 tons yr^{-1}. Removal of copper by animal products is far less important and is usually less than the removal by crops (25 tons yr^{-1} in 2003 in the Netherlands) (Delahaye et al., 2003).

In contrast to data on crops and animals, data on leaching and erosion are scarce. Regular measurements of heavy metals in groundwater are still lacking in most countries and estimates of leaching losses are based on average concentrations in solutions obtained from lysimeters or experimental stations. Also temporal changes in groundwater concentrations are largely ignored (or unknown).

Due to this inaccuracy in the calculation of outputs, copper balances in most soils are unreliable. In most cases, the input exceeds the output, indicating that accumulation occurs. However, data to support this accumulation are largely non-existent except for a few cases including examples of intensive animal husbandry or application copper bearing agro-chemicals in vineyards.

A field survey conducted in Brittany (France) by Legros et al. (2002) shows that the intensive breeding of pigs significantly increases the amount of total and EDTA-extractable Cu and Zn (see table 2.1). The sampling area was part of a 110 ha farm with 11500 pigs. The declared amount of slurry spread on arable land during the survey period was between 30 and 80 m^3 ha^{-1} $year^{-1}$ (mean 49 m^3 ha^{-1} $year^{-1}$). Results show that the total amount increases relatively slowly every year (less than 1,5%) but on the contrary the availability of Cu and Zn may increase more rapidly (about 5% a year). This point demonstrates that the speciation of both trace elements is different between the 'natural' form and the input from slurry, the latter being more bioavailable. Other field studies ended with the same conclusions (L'Herroux et al., 1997; Nicholson et al., 2003).

Table 2.1 Results of a field survey in Brittany (France) from Legros et al.(2002).

	Cu total (HF digestion)	Cu EDTA	Zn total (HF digestion)	Zn EDTA
Mean concentration measured in soil in 1989 (mg kg^{-1}) (standard deviation)	31.8	6.8 (0.7)	96.9	6.6 (3.2)
Mean concentration measured in soil in 1997 (mg.kg^{-1}) (standard deviation)	35.3	9.2 (1.8)	107.1	10.6 (2.5)
Total increase (1989-1997) (mg.kg^{-1})	3.5	2.7	10.2	4.1
Total increase (1989-1997) (kg ha^{-1})*	17.2	-	50.9	-
Mean increase/year (1989-1997) (mg.kg^{-1})	0.4	0.3	1.3	0.5
Mean increase/year (1989-1997) (kg ha^{-1})	2.1	-	6.	-
Mean increase/year (in %)	1.3	4.2	1.3	5.8

* Considering that 1 ha = 4 978 t dry mass (soil density : 1,31 in 1989)

Of course the documented accumulation in hot spots near smelters, mines and copper processing plants are exceptions and not included in this evaluation. Here emission from local sources has resulted in (well documented) increases of the copper levels in the surrounding areas.

Currently the importance of leaching and its contribution to surface waters has become evident (Xue et al., 2000; Xue et al., 2003); Aldrich et al, 2002; (Römkens et al., 2003; Zhang et al., 2003; Bonten & Römkens, 2004), at least for areas where a close contact between ground- and surface waters exists. However, modelling approaches like these are still scarce and model derivation is often hampered by a lack of data.

In general modelling approaches where leaching of copper has been quantified are scarce as well as data to validate such modelling results. The aim of this study is therefore:

1. to summarise the existing process level knowledge on the behaviour of copper in soils with an emphasis on processes that control solubility and speciation (Chapters 2 and 3);
2. to list existing examples of documented cases of copper leaching and see to what extend process knowledge has been incorporated in applied models (Chapter 4);
3. to evaluate whether essential process knowledge is lacking, knowledge that is needed to link the 'gap' between process oriented research and quantification of leaching at the field level (Chapter 5).

2 Soil and soil solution chemistry of copper

Transport of compounds as copper in soil systems is determined by both the water flow (soil hydrology) and the behaviour of the compound in the soil system. Soil hydrology and its effects on copper mobility are dealt with in Chapter 3. In this chapter the behaviour of copper in soil systems is discussed.

Mobility of copper depends on the concentration of copper in the soil solution, which is determined by sorption at the soil solid surface and the behaviour in the soil solution. The processes controlling copper behaviour in the soil solution are schematically depicted in figure 2.1. In the figure is indicated for each process in what section this process is discussed.

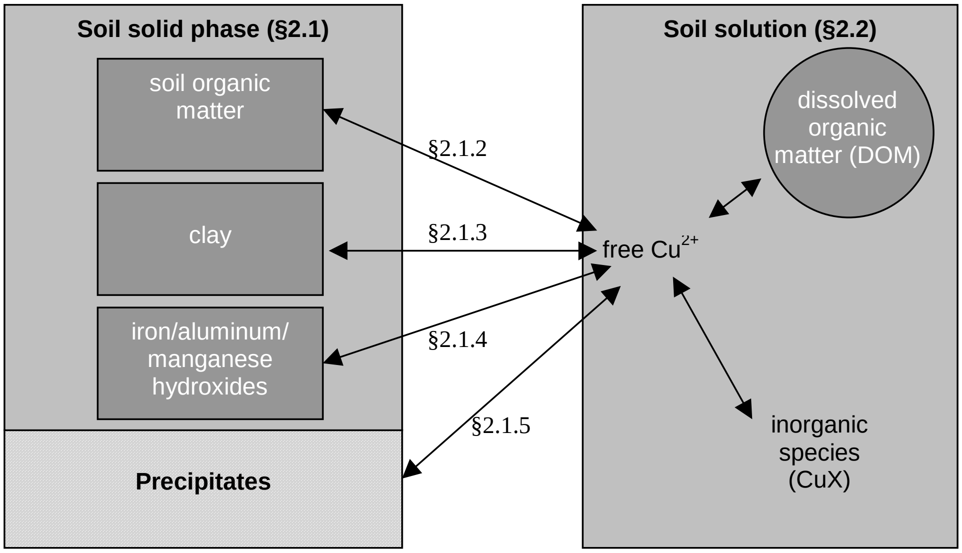

Figure 2.1 Schematic representation of soil and soil solution chemical processes controlling copper mobility

2.1 Soil chemistry (sorption and precipitation)

2.1.1 Sorption surfaces

Sorption of copper at the soil solid phase can take place at different soil surfaces: soil organic matter, clay minerals and metal hydroxides (iron, aluminium, and manganese). Besides, at very high concentrations of copper or under anaerobic conditions in the soil solution also copper precipitates can be formed. Because precipitates are part of the soil solid phase these are discussed in section 2.1 too.

The relative amount of copper sorbed to the each sorption surface depends on the amount of sorption surface, the affinity of copper for each surface and the concentrations of other compounds in the soil solution. In many soils the contribution of organic matter to copper binding is the most important -especially the upper horizons - because the total amount of organic matter is higher than the amount of metal (hydr)oxides. In lower horizons, sorption to metal (hydr)oxides can be very important (Sims, 1986). In subsequent sections mechanisms and models for sorption of copper to the individual surfaces will dealt with.

2.1.2 Sorption of copper onto soil organic matter

Generally soil organic matter (SOM) is the most important sorbent for copper in top soil systems. Soil organic matter contains several reactive groups, like carboxylic and phenolic groups, which after deprotonation can complex cations, like copper. Compared to other heavy metal contaminants, copper is very strongly complexed by soil organic matter. Studies on agricultural soils showed that on average more than 90 % of all copper added to a soil systems is bound to SOM (Lofts & Tipping, 1998; Weng et al., 2001).

Because SOM can complex not only copper but also other cations, these other cations compete with copper for the available sorption sites with copper. This means that copper binding to SOM is reduced in ground waters with high ionic strength (salt waters, carbonate rich waters) and in waters with low pH (this means high H^+ concentration).

Modelling metal sorption to natural organic matter has been found difficult due to the heterogeneous nature of the material. Recently, advanced models such as Model VI (Tipping, 1998), the NICA-Donnan model (Kinniburgh et al., 1999) and the Stockholm Humic Model (Gustafsson & van Schaik, 2003) have been developed and have shown to be able to predict the competitive sorption of metals to natural organic surfaces. The basis for these three models is more or less the same. They distinguish two different reactive groups, a group which deprotonates at low pH and a group that deprotonates at high pH. Each group has a distribution of binding strengths, either a discrete distribution (model VI and SHM) or a continuous distribution (NICA-Donnan). Due to the negative charge of the SOM after deprotonation, electrostatic effects are also very important in cation binding and are included in these models too. Parameters for these three models have been derived for most common cations and heavy metals, including copper (Milne et al., 2003). Several authors have used these models to describe copper sorption to whole soil samples and obtained good results (Benedetti et al., 1995).

2.1.3 Sorption of copper to clay minerals

Clay minerals are alumino-silicates build upon layers of aluminium octahedrals and silicon tetrahedrals, which have a permanent negative charge due to substitutions of a number of Si for Al in the layer of tetrahedrals. To compensate for this negative charge cations are sorbed. At the clay platelet edges hydroxyl groups are situated which can be deprotonated at high pH values (> 7) and can form chemical bonds with copper similar to surface groups on metal(hydr)oxides (so-called surface complexation).

Metal sorption to clay can be calculated using either a specific or a non-specific cation exchange model. For a non-specific model accumulation of metal ions at the clay surface depends only on their charges and their concentration in the bulk solution. Weng et al. (2001) used a Donnan model for this in which clay minerals are treated as negatively charged volume in which cations can accumulate.

In specific cation exchange models, differences between the binding of the cations (due to the size of the hydrated cations) are accounted for in the different equilibrium constants. This type of ion-exchange models (Vanselow, Gapon and Gaines-Thomas conventions) are specifically meant to describe the adsorption on the plates and not at the edges. Therefore, these models can only be used for low pH systems or for ions where adsorption on the edges is relatively unimportant such as Na and Ca. Exchange coefficients (Gaines-Thomas convention) for various cations, including copper, have been presented by Bruggenwert and Kamphorst (1982).

In the case of copper also the surface reactions with the hydroxyl groups at the edges might become relevant. Kraepiel et al. (1999) proposed a model to account for the effect of the specific sorption at the edges of clay minerals.

2.1.4 Sorption of copper to metal hydroxides

In soils containing little organic matter sorption of copper to metal hydroxides can be an important process. Parat et al. (2002) showed for vineyard soils, which contained little organic matter, high iron contents and high copper contents, that iron hydroxides was the most important sorbent. Similar results were obtained by Abollino et al. (2002), who showed in a study on heavy metal speciation in Italian agricultural soils, that sorption to metal hydroxides can be important in some soils.

Sorption of copper to metal oxides and metal hydroxides (abbreviated as metal (hydr)oxides) is very different from sorption to clay minerals: the sorption is very dependent on pH and the sorption of heavy metals such as copper, lead and zinc is much stronger than base cations such as calcium or magnesium. An overview of sorption processes at metal (hydr)oxides is given by Brown et al. (1999; Brown, 2001).

The most abundant metal(hydr)oxides are (hydr)oxides of iron, aluminium, manganese and silica. Iron(hydr)oxides are ubiquitous is most soils systems, although most iron(hydr)oxides in moderate climates are poorly crystalline. Especially in strongly weathered tropical soils, high contents of aluminium (hydr)oxides and crystalline iron(hydroxides are found. The contents of manganese oxides in most soils are generally much smaller, but their reactivity is far higher. Therefore manganese(hydr)oxides might be relevant in some soils, especially at low copper contents and soils with relative low pH (< 4) (McBride, 1981; Lofts & Tipping, 1998). It can be generally assumed that oxides of silica are relatively unimportant for copper due to the very low specific surface area (large particles).

Most knowledge is based on a combination of laboratory studies on common minerals and selective extraction techniques. Recent progress in spectroscopic techniques has given direct evidence for the contribution of the different metal (hydr)oxides to the sorption of heavy metals, including copper (Cancès et al., 2003).

Different models have been proposed to describe the sorption behaviour on metal(hydr)oxides. Most models are able to describe a certain limited range of data. A model for which parameters have been derived for many cations and anions is the commonly used model proposed by Dzombak and Morel (1990). In this model sorption to a poorly crystalline iron hydroxide is described assuming two types of sorption sites, sites with strong affinity for sorption and sites with a weaker affinity for sorption. The site density of the weaker sites on the iron hydroxide surface is larger than the site density of the stronger sites. Dzombak and Morel derived complexation constants for this model for various anions and cations, including copper. In this model electrostatic interactions are calculated by a diffuse double layer model. Sorption to aluminium hydroxides is often calculated using the same constants as for iron hydroxides. Recently, complexation constants for manganese hydroxide have been derived (Tonkin et al., 2004).

Although these models are able to describe a range of sorption data, advancements in spectroscopy have shown most models are not able to use realistic surface complexes. Further, strong interactions between different adsorbed ions at the surface might lead to deviations. Recent models, like the CD-MUSIC model (Hiemstra & van Riemsdijk, 1996, 1999), that take into account these spectroscopically determined surface complexes, are able to predict the interactions well. However, parameters for these models have only been derived for a small number of cations and anions and only for a few types of metal (hydr)oxides, mainly crystalline iron hydroxides.

Besides sorption at metal (hydr)oxides surfaces, copper can also be bound within the metal (hydr)oxide volume due to co-precipitation, especially for iron hydroxides. Karthikeyan & Elliot. {, 1999 #21} showed that total sorbed copper contents can be 3 times larger in case of co-precipitation with iron hydroxide than for sorption at the surface. This co-precipitation can be important under changing redox-conditions, which causes iron hydroxides to dissolve and precipitate in cycles.

Several authors have shown that mass transport processes can play an important role in sorption metal (hydr)oxides. Diffusion of solutes into micro-pores in the metal (hydr)oxides leads to slow sorption and desorption phenomena. For example, Scheinost et al. (2001) showed that copper sorption to ferrihydrite (a iron hydroxide) has not reached equilibrium after 1 month. Trivedi and Axe (2000) proposed a model to describe diffusion and sorption of cations into metal (hydr)oxides.

2.1.5 Precipitates

In most soils, all copper in the solid phase will be sorbed to soil organic matter, metal hydroxides and clay minerals. Only for very high contents in the soil or very poor sandy soils containing little reactive surfaces, copper precipitates can be formed. The most common precipitates are malachite ($Cu_2(OH)_2CO_3$), and cuprite (Cu_2O).

In the environment copper is found in two redox states, Cu^{1+} and Cu^{2+}. In soil and the soil solution Cu^{2+} is the most common redox state. However under anaerobic conditions Cu^{2+} can be reduced to Cu^{1+}. The solubility of Cu^{1+} precipitates is much smaller than of Cu^{2+} precipitates. This means that precipitates are more easily formed. Additionally under anaerobic conditions (i.e. sulphate reducing) sulphide precipitates can from, which are very poorly soluble. Copper might either precipitate as copper sulphides (Cu_nS) or as iron-copper sulphides (Nriagu, 1979; Vink, 2002). The iron-copper sulphide compound chalcopyrite ($CuFeS_2$) is the most common copper compound in copper ores.

The solubility of a precipitate can be calculated using the solubility constant of a precipitate. For example, the solubility constant of copper sulphate ($CuSO_4$) is defined as: $K = [Cu^{2+}] \cdot [SO_4^{3-}] = 9.77 \cdot 10^{-4}$, which means that if the product of copper and sulphate activities exceeds the value of $9.77 \cdot 10^{-4}$ copper sulphate will precipitate. Several data-sets with solubility constants for copper precipitates are available, like the database of geochemical model, e.g. Minteq (US-EPA, 2000), or other public available databases, e.g. Martell and Smith (1989). A simple program (Puigdomenech, 2004) to calculate Pourbaix diagrams (pH-pe) for copper is available from Internet.

Summarising, in many soils having moderate or high organic matter contents, copper sorption takes many place to the soil organic matter. Recent developed models have shown to be able to predict this sorption to organic matter well. For soils containing very little organic matter, sorption to manganese (hydr)oxides or iron (hydr)oxides might dominate. Models for sorption on these surfaces are probably not as reliable as models for sorption on organic matter.

Slow diffusion into aggregates is one of the explanations for ageing. Ageing is a term that is used for the often noted slow change of the availability of a metal such as copper. In a series of papers McBride and co-workers have shown that the copper concentration can decrease even after 2 years in a system where copper has been co-precipitated with alumina. During this period the re-crystallisation of the alumina changes and copper becomes less part of the crystal and more sorbed. The amounts of co-precipitated copper in soil minerals are however probably very low (Martinez & McBride, 2000).

2.1.6 Soil

Ageing

The notion that soil is a mixture of different materials and that the behaviour of chemicals such as copper can be explained on the basis of an integration of the different processes on these materials is called the component additivity approach. The processes mentioned in the previous chapters represent this approach. A large part of the literature about copper leaching in soils is however concerned with soils and the behaviour of copper is not explained in view of the component additivity approach.

With respect to the effects of wetting-drying cycles, time and temperature it has been shown that soils can show non-equilibrium behaviour that is often called ageing. For example, in a recent comparison of uncontaminated, freshly contaminated and historical zinc contamination it could be shown that the pore water copper and extractable zinc concentrations (0.01 M $CaCl_2$) where significantly higher in the freshly contaminated soils (Lock & Janssen, 2003a). However in a similar study using copper the effect of ageing could not be shown (Lock & Janssen, 2003b).

Important in soils can also be redistribution between the soil phases, especially in dynamic systems. For example, under a wetting-drying cycle a redistribution can occur of copper causing it to be (Han et al., 2001). Compared to soils at field capacitance, soils with wetting-drying cycle have a tendency to bind copper more strong, in other words distribution copper to more stable fractions.

Studies suggest that in case of copper addition via metal-contaminated organic substances such as applications of manure or sludge on soil that copper becomes more available as a function of time (Hooda & Alloway, 1993; Sadovnikova et al., 1996). Laboratory studies suggest that this is due to changes of the organic matter (Martinez & McBride, 2001; Martinez et al., 2003).

Redox

The influence of redox processes on the behaviour of copper is only qualitatively known. Under reducing conditions, such as anoxic aquifers or soils with a high groundwater table, copper is bound to organic matter and metalhydroxides (except Fe and Mn) and clay minerals. If enough sulphur is in a anoxic material infiltrating copper can also be (co)precipitated with sulphide (Schlieker et al., 2001). In practice it seems that for sulphide-rich water the speciation models for copper do not predict data well. This is probably due to copper which is erroneously assumed to be dissolved, due to incomplete understanding of its speciation and to incomplete data-sets for the copper-sulphide system (Gammons, 2001).

One study has tested the incorporation of reduction in a surface complexation model (Davranche & Bollinger, 2001). The dissolution of the solids by reduction was taken into account by changing the total number of reactive sites based on experimental CEC values. This explained the change of the heavy metal adsorption from a non-reductive conditions to reductive conditions very well.

Partitioning

As mentioned there is an assemblage of models for the different materials in soils to calculate copper sorption for soils systems. These models have been developed to explained the very large differences in partitioning of metals such as copper. In a comparison of field-based partitioning data large range of K_d values is given for copper (0.1-4318 L kg^{-1}) (Janssen et al., 1997). Partitioning coefficients (L kg^{-1}) here relate the particle concentration to the dissolved concentration ($< 0.45\ \mu m$). For copper these partition coefficients are often relatively are low due to complexation of copper to DOM ($\log K_d < 4$).

2.2 Behaviour of copper in soil solution

The concentration of free copper in the soil solution is in principle in equilibrium with the amount sorbed to the soil solid phase. However, the total concentration of copper in the soil solution can be much larger than the concentration of free copper, due to complexation and adsorption to dissolved, colloidal or suspended compounds. Similar to adsorption at the solid phase the most important sorbent in the soil solution is organic matter. In most soils systems, even containing little dissolved organic matter, more than 90% of copper in solution is bound to dissolved organic matter (Nolan et al., 2003; Tipping et al., 2003). Similar to sorption of copper by solid organic matter, sorption by DOM is dependent on pH and ionic strength of the soil solution (Cao et al., 2004).

Sorption to dissolved organic matter can be calculated using similar models as for sorption to solid organic matter. Most dissolved copper that is not bound to DOM is present in the soil solution as free copper $(Cu^{2+})_{aq}$. Depending on pH and concentrations of other ligands also other species might be present. The most important inorganic ligands for copper speciation are OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}. Complexation constants for copper and its ligands can be found in several databases, e.g. Martell and Smith (1989) or the databases of geochemical programs as Minteq (US-EPA, 2000) or PhreeQC (Parkhurst & Appelo, 1999).

The potential role of multinuclear sulphide clusters in surface water has recently been shown to be relevant for the speciation of copper in well-aerated surfaces water (Rozan et al., 2000). Complexation constants for copper on the sulphide colloids are not available yet and the role of the sulphides in soil solution is not known.

2.3 Modelling copper behaviour in soil and groundwater

One method to calculate copper behaviour in soil systems is to combine several of the models discussed in the previous section into a so-called assemblage model. Assemblage models are comprised of several advanced models for calculating sorption to different soil surfaces. For example, Lofts and Tipping (1998) could describe metal sorption to river and estuarine sediments with their SCAMP model, an assemblage model comprising adsorption to solid and dissolved organic matter

(Model VI), clay and metal hydroxides (2-site DDL). Weng et al. (2002b) calculated the speciation of several heavy metals in a sandy soil with an assemblage model, comprising adsorption to solid and dissolved organic matter (NICA-Donnan), poorly crystalline- (2-site DDL) and crystalline iron hydroxides (CD-MUSIC) and clay (non-specific exchange). Cancès et al. (2003) used a similar assemblage model to calculate free metal ion concentrations and the distribution of sorbed metal ions among the different surfaces; the calculated distribution was confirmed by EXAFS measurements.

For performing model calculations using assemblage models, several modelling tools are available. Often used are geochemical models PhreeQC (Parkhurst & Appelo, 1999) and Minteq (US-EPA, 2000) Recent version of these modelling tools are Windows based and relative user friendly. However, for modelling copper sorption these models are less suitable as they do not comprise the advanced model for calculating sorption to solid organic matter. Tools that contain these models are the DOS-based Ecosat (Keizer & van Riemsdijk, 1994) and the Java-based ORCHESTRA (Meeussen, 2003), which has been developed to facilitate the implementation of advanced models in aquatic and soil chemistry. Although the latter is most advanced it requires a thorough knowledge on geochemistry and does not contain a database with complexation constants.

A different approach is to use empirical equations that describe relations between copper concentrations and soil properties (Sauve et al., 2000; Impellitteri et al., 2003; Tipping et al., 2003; Römkens et al., 2004). Momentarily, these empirical relationships are mostly used for practical applications like soil remediation, risk assessment, transport calculations etc. (Reinds et al., 1995; Horn et al., 2003). The reason for using these empirical relations is that in general only a limited number of parameters are required compared to process oriented assemblage models. Because of their simplicity these models can easily be coupled to other models, such as hydrological models or plant-uptake models. As long as the empirical relations are applied to the conditions for which they have been calibrated for, a reasonable estimate of the solid-solution partitioning of the metals can be obtained. The disadvantage of empirical models is that they hardly provide any insight in the mechanisms controlling the distribution and speciation processes. Insight in these processes is especially important for dynamic calculations. For example, in studies trying to predict the effects of land use changes on copper distribution, one need to be able to predict the integrated effects of the changes in soil properties such as pH and organic matter content (Römkens & Salomons, 1998). Also competition effects with other cations are often not included. This can be overcome by using soil composition dependent exchange coefficients, which however leads to large increase in required parameters (Voegelin & Kretzschmar, 2003). Another limitation for the application of the empirical models is that extrapolation of calculations is in general not possible outside the range of data for which the empirical relations have been calibrated for.

The quality of the predictions using an assemblage model depends on the ability to predict the sorption on the individual materials. The relation between the copper sorption onto soils and the copper activity in soil solutions can be predicted very well (Weng et al., 2001). However the binding of copper to dissolved organic matter in these soil solutions is not predicted well. Because copper adsorption to purified humic materials can be described very well (Milne et al., 2003) the results suggest that copper binding to natural dissolved humic substances involves more processes than currently are described by the NICA model and Model VI. It should be mentioned that Model VI is able to predict copper binding to dissolved NOM from fifteen British freshwaters. The prediction is expected to be correct within a factor 3.6 in 95% of all cases (Bryan et al., 2002). The ability to describe the copper binding to natural DOM in freshwater might be related to the more simple composition of DOM in freshwater than in soil solutions.

3 Transport

Transport of solutes in soil systems depends on the movement of water through soil systems (geohydrology) and the behaviour of sorbing solutes in the moving water (reactive transport). A overview of literature on geohydrology is outside the scope of this study although when discussing copper transport to surface water the pathways of water are discussed in short. In the next section an overview is given of the important processes governing copper transport in soil systems. Section 3.2 gives an overview of the models available for modelling copper transport in soil systems. Because most copper in the soil solution is complexed by the dissolved organic matter (DOM), understanding DOM behaviour in soil systems is of greatest importance to model copper transport. In chapter 4 additional information on the composition of DOM in relation to transport is given. Transport of copper to surface water is often by runoff and therefore erosion is also discussed here.

3.1 Transport and copper speciation

Soils as a source of surface water contamination with copper has only received little attention. The publications are discussed as they demonstrate the various relevant aspects of copper transport: copper speciation, preferential flow, surface run-off.

In field experiments in Florida eleven drainage outlets have been monitored of citrus and vegetable farms (Zhang et al., 2003). These farms routinely use foliar application of copper and copper in pesticides. The mean dissolved copper concentrations for each outlet were extremely high and they varied from 5 $\mu g\ l^{-1}$ to 550 $\mu g\ l^{-1}$. The authors claim that the mean concentrations are correlated well with $CaCl_2$ extractable copper from the upper 15 cm of the different soils. Their results suggest that the total runoff copper can be explained based on soil-extractable copper and total runoff discharge.

In Switzerland Sigg and co-workers (Aldrich et al, 2002; Xue et al., 2000; Xue et al., 2003) have studied leaching of copper and zinc form soils to surface waters. Long-term copper inputs of 0.02-0.3 $g\ Cu\ m^{-2}\ yr^{-1}$ to grassland soils resulted in concentrations of approximately 2 $\mu g\ Cu\ l^{-1}$ in the different rivers, thus exceeding the Swiss surface water criteria[1]. In this area, 75% is grassland and 40% is artificially drainage. During rain events the total copper concentrations in the water were linearly related to the discharge and during these events copper is mainly associated to particles, and only 3% constituted of dissolved copper (<0.45 μm). At low flow rates, the copper load constituted of about 50% of dissolved copper (<0.45 μm). The dynamics of dissolved copper followed that of DOM. In the Swiss circumstances, it seems that artificially drained soils contribute significantly to the elevated copper

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[1] Values to guide the reader: Dutch target values 19 $mg\ Cu.kg^{-1}$ soil, and 15 $ug\ Cu.l^{-1}$ in groundwater. Sanitation is necessary at 365 $mg\ Cu\ .kg^{-1}$ soil, or 75 $ug\ Cu.l^{-1}$.

concentrations. Especially during relatively dry weather conditions water seeping from organic-rich soils contributes to the total water discharge. Also important is that it is estimated that one storm event, and therefore copper bound to particulate matter, contributed to one third of the yearly copper load to the river.

Speciation

The above mentioned studies reveal transport of copper through soil and to surface waters. They demonstrate that rain events have strong effects. The reasons for this can be manifold. In one of the earlier mentioned studies on the drainage water in agricultural soils Aldrich et al. (2002) showed that more than 99% of copper in solution was complexed by DOM (at pH 7). The DOM was small (<10 kD) and mainly hydrophilic. For a very different material, DOM from municipal solid waste incinerator ash, Meima et al. (1999) showed that copper also mainly bound by DOM. Weng et al. (2002c) showed that the presence of DOM increased copper leaching from a copper treated agricultural soil. They also showed that an increase in calcium concentrations led to increased sorption and coagulation of DOM, and consequently to a decrease in copper concentrations in the leachate. Therefore rain events can change the flux of DOM through soil by changing the macrochemistry.

DOM

Momentarily, behaviour of DOM in soil systems is still hardly understood, and consequently models to describe DOM behaviour are still in development. Studies and models on the distribution, accumulation and fluxes of organic matter in soils often assume that the effect of leaching on the carbon budget is insignificant (Feng et al., 1999). However the average annual DOM export from some Swiss catchments was 185 kg DOM ha^{-1} yr^{-1}, for the forest, 108 kg DOM ha^{-1} yr^{-1}, for the grassland and 84 kg DOM ha^{-1} yr^{-1} for a catchment without ditches (Hagedorn et al., 2000). As noted previously the type of DOM, which is exported from catchments and that binds copper in leachates, is small and hydrophilic (Aldrich et al., 2002).

Aldrich et al. and Hagedorn et al. (2000) have shown that DOM concentrations in the soil drainage solution can greatly increase after events of high precipitation. This increase in concentrations can be partly attributed to changes of the hydrological pathways during rain events. The change of the origin of water can cause differences of DOM in the drainage water but also the decrease in ionic strength of the soil solution can lead to a release of sorbed or coagulated DOM. The increase in DOM concentrations after a storm event can also lead to an increase in copper concentrations in the soil drainage water (Aldrich et al., 2002).

In unsaturated systems transport of DOM can be retarded due to sorption of DOM at the air-water interface (Lenhart & Saiers, 2004).

It is clear that the behaviour of DOM in soil systems is dependent on the properties of DOM itself, on the composition of the soil solution and the composition of the soil solid phase. Han and Thompson (2003) showed that the properties of DOM are of great influence on its mobility in soil. Low molecular weight DOM is more mobile than high molecular weight DOM. Further hydrophobic DOM is more retarded in soil systems than hydrophilic DOM.

Preferential flow
Another aspect is transport of copper by vertical macropores or preferential flow. This has been not demonstrated for copper but it has been demonstrated for phosphate (Gächter et al., 1998) in the same soil (clayey loam) and catchment as Xue et al. (2000; 2003) and has been demonstrated for radionuclides (Bundt et al., 2000). This can result in higher concentrations of radionuclides in the preferential flow paths (originating form the upper horizons) thus resulting in higher transport as could be expected on the basis of soil water extraction.

3.2 Copper transport modelling

A model to account for differences in sorption and desorption behaviour of different DOM fractions was described by Van de Weerd et al.(1999). They showed that different DOM fractions not only have different adsorption affinities but also different adsorption rates. The highest adsorption rates were found for hydrophobic and low molecular weight compounds.

Sorption and coagulation are two different processes that affect DOM behaviour in soil systems. Sorption of DOM mainly takes place at metal (hydr)oxide surfaces and is a similar process as sorption of ions to metal (hydr)oxides (see section 2.1.4). A model to describe DOM sorption and its dependence on soil solution composition and pH has been described by Filius et al. (2003).

At low pH or high salt concentrations DOM colloids can become unstable and start to coagulate and aggregate. This point of coagulation depends largely on the electrostatic potential of the DOM (Weng et al., 2002a).

In an attempt to model copper transport in a soil column in combination with humic acid or fulvic acid Weng et al.(2002c) argument that coagulation due to Ca and Al binding to humic acid can explain the transport behaviour of humic acid and therefore of the humic acid-facilitated transport of copper. The transport behaviour of fulvic acid could however not be explained on the basis of coagulation at a certain degree of metal binding and is therefore probably regulated by sorption to the mineral surfaces in soil.

A different approach to model DOM behaviour in soil systems is to use semi-empirical relationships between DOM concentrations and the properties of soil and soil solution (Lofts et al., 2001; Weng et al., 2002b). Currently the disadvantage of one of these approaches is that to model the DOM partitioning it is necessary to characterise the DOM for the different soil layers (Weng et al., 2002b).
An empirical approach is determining the partitioning of organic matter as a function of pH and other known well-known parameters such as CEC (You et al., 1999).

To calculate transport of sorbing species as copper, a model is required that incorporates both soil chemistry and hydrology. Because of the complexity of both parts, often either soil chemistry or hydrology is greatly simplified. Most geochemical models also contain a reactive transport module with which one-dimensional transport can be calculated (Parkhurst & Appelo, 1999; US-EPA, 2000). Hydrological models often include simple sorption isotherms to calculate reactive transport (Clement et al., 1998; Kroes et al., 2003).

Models that include a process-oriented description of both soil chemistry and hydrology are very rare. The only commercial available model is PHT3D (Prommer et al., 2000), a combination of the geochemical model PHREEQC and the hydrological model MODFLOW. However, advanced models to describe sorption to solid and dissolved organic matter, which are very important in copper modelling, are not included in this model.

Additionally, models incorporating DOM sorption are momentarily non-available, which limits the possibilities for process-oriented modelling of copper transport in soil systems.

4 Field data and model concepts to predict copper leaching from soils

4.1 The role of DOM in metal mobilisation: DOM characteristics

The concepts presented in chapter 2 clearly stress the importance of dissolved organic carbon (DOM) or organic colloids on the mobility and speciation of copper in soils. In fact, transport of copper in almost all systems is believed to be related to the transport of DOM or colloids. Kalbitz and Wennrich (1998) showed that mobilisation and translocation of copper (and other elements) in polluted wetland soils was closely correlated to the levels of DOM in percolating soil solutions (from lysimeters under controlled irrigation regimes). Differences between soils were largely explained by differences in DOM (and levels of pollution of course). The importance of DOM diminished below pH 4.5, which can be largely attributed to the decrease in the surface charge of DOM at low pH. Also copper leaching into soil affected by run-off from roofs largely depended on the binding of copper to DOM (Mason et al., 1999).

In paragraph 3.1 a short description on the main impact of DOM on mobility of copper was given. Here, differences between DOM fractions are explained.

An important issue is to what extent the composition of DOM affects the mobilisation and transport of copper in soils and aquifers. DOM consists of a wide range of organic acids with different molecular size and type of reactive groups (e.g. Stevenson, 1994). Various ways of separation can be applied, ranging from a crude separation in humic and fulvic acids based on precipitation at low pH to a size fraction followed by a separation based on the degree of hydrophobicity. A classic (chemical) approach by now is the fractionation according to the IHSS-XAD-8 procedure which is based on the Mantoura and Riley method (1975). This results in 3 different types of DOM: non-humic substances, humic acids and fulvic acids. A recent basic characterisation of DOM from different sources (Frimmel and Abbt-Braun, 1999) revealed that differences between DOM from soils and solid materials like brown coal were limited. Between 20 and 50% of the total DOM consisted of humic and fulvic acids. In groundwater samples however, the contribution of fulvic and humic acids decreased to less than 5%. Also the binding capacity as expressed in μmol charge per mg DOM decreased from 19.2 (in fulvic acids from brown coal) to 11.4 in groundwater (Frimmel and Abbt-Braun, 1999).

These changes are mainly due to differences in molecular weight and chemical reactivity between HA's and FA's Major differences between both types of acids include molecular weight (MW_{HA}: 1,500 - >100,000; MW_{FA}: 600-1000) and total acidity (HA: 570-890 cmol kg^{-1}, FA: 890-1420 cmol kg^{-1}). HA solubility is limited below pH 4, at high ionic strength and at elevated Ca, Fe and Al concentrations, and a substantial part of the HA's can be removed from the soil solution by flocculation-precipitation processes (Sholkovitz & Copland, 1981; Duchafour, 1982; Tipping &

Ohnstad, 1984; Römkens & Dolfing, 1998). A large part of both the high molecular weight (HMW) HA and low molecular weight (LMW) FA components in soils are generated in the litter layer and A-horizon of the soil. As a result of both precipitation of Fe/Al-humates and preferential adsorption of HMW components, HMW HA-type components are preferentially removed from solution during DOM transport through the soil (Davis & Gloor, 1981; McCarthy et al., 1993; Gu et al., 1995; Wang & Benoit, 1996).

In short, the mobility of smaller DOM fractions with a high specific charge density are probably responsible for the main transport of copper in soils as was shown by Han & Thompson (2003, see paragraph 3.1).

In order to predict metal leaching associated with DOM it is therefore essential to know which factors control the composition (in terms of molecular weight, charge density etc.).

Obvious factors that control the composition of DOM include source material (manure, sludge, biowaste), soil type (clay, sand, peat) but also *land use changes* have become an issue. Due to abandoning arable land (common practice in Germany and the Netherlands), previously limed sandy soils will acidify within a few decades (Römkens, 1998) resulting in a change in the nature of the solid organic matter fraction in soils. This will affect the composition of DOM as well. Data from Schenkeveld (unpublished results) show that the total charge density as well as the distribution between HA and FA shifts after the conversion of arable land to forest. In the arable soil, the total charge density in the different soil horizon showed little diversity and ranged from 9.5 to 11.2 mmol charge per gram C. However the charge density in the topsoil decreased after the conversion to forest from 9.5 to 8.2 (after 26 years) and reached 6.6 in a mature forest. In general the charge density in the forest soil samples increased with depth which coincided with an increase in the FA fraction. Model calculations showed that the entire difference in the total charge density could be explained by the change in the HA/FA distribution in the profile. The average charge density of the HA fraction was 6.6 mmol/gC and 17.8 mmol charge/gC for FA respectively.

However, for peat soils, the difference between HA and FA was considerably less pronounced (8.1 mmol charge gC^{-1} for HA and 11.6 mmol charge gC^{-1} for FA).

On the other hand a study by Strobel et al. (2001) showed only small differences in characteristics from DOM from mature forests within different tree species and on different soil type. The total charge was quite comparable to the data from Schenkeveld and ranged from 5.3 to 20.6 mmol charge per gram C (median value 11.5 mmol charge per gram C). Only 3 out of 17 samples had charge densities larger than 13 or smaller than 7 mmol charge per gram C, indicating a rather high degree of uniformity among DOM types.

Since charge density is one of the essential aspects in model calculations to predict copper speciation, differences like the ones described here will have a considerable effect on model results. However a good reference database on the charge density of DOM from different sources is still lacking. Also differences between DOM from soils and DOM present in aquatic systems can be significant. In a study by Buerge-Weirich et al. (2002) the binding characteristics of DOM and affinity constants were derived from natural untreated DOM from lakes. The differences in conditional binding coefficients between 'low' and 'high' affinity sites appears to be much higher than in DOM from soils (Strobel et al., 2001).

Apart from this, also the treatment of soils to extract DOM will affect the composition and reactivity. Usually DOM is extracted using 0.1 M NaOH, which results in a pH of the medium around 13. The question can be raised whether or not DOM extracted under these conditions resembles DOM found in the pH range under field conditions. For this reason the study by Frimmel and Abbt-Braun (1999) started using water as an extractant. Also in the study by Schenkeveld (unpublished results), water was used, but pH was raised to 7 to obtain sufficient DOM.

Harmonisation of extraction methods is therefore highly desirable to compare results from studies. Ideally only leachates or soil solutions obtained by 'artificial roots' should be considered as representative DOM samples.

The differences in the nature of DOM between soils, aquatic systems, landfills, sludge treated soils etc. obviously will result in differences in leaching characteristics. Until now, little consensus exists on the processes in control of the production and transformation of DOM. Also during transport from soils to streams, further fractionation of DOM occurs, not only in terms of molecular size but also in terms of reactivity and type of functional groups. This clearly will affect the capacity of DOM to mobilise copper (or on the other hand cause retardation due to enhanced sorption on metal(hydr)oxides.

4.2 Field data on copper leaching from soils: an inventory of experimental results

4.2.1 Surface runoff and land use

Runoff and leaching of copper have been described as a source of water contamination. Also surface runoff can cause water contamination. Surface runoff has been described for copper due to the use of impermeable surfaces. In the case of tomatoes more than half of a planted field can be covered. This significantly increases the amount of rain that runs off into nearby lakes and streams carrying copper associated with soil particles (Rice et al., 2001). Concentrations of up to 5.8 mg/l Cu were determined in the runoff from the polyethylene.

Surface runoff from vineyards is also an important source of water contamination. This is due to the high copper contents in these soils, and related to the Mediterranean rainfall regime. Ribolzi et al. (2002) found concentrations of suspended matter of up to 6 grams per litre water in a catchment outlet during a rain event and with 245 mg Cu kg^{-1} in the suspended matter. The soils had an average copper concentration of 55-175 mg Cu.kg^{-1}. Such a rain event resulted in erosion amounts of 113-267 kg soil ha^{-1}, and an estimated loss of 125 g Cu ha^{-1} during one hour. In this case the copper is bound to the suspended material: organic matter and metalhydroxides. The effect of the flux of copper and material on systems downstream depend on the conditions in these systems (pH, copper content etc.). The net effect of erosion is that it accelerates the transport of copper from the soils with high copper contents to systems with possibly low copper contents.

4.2.2 Leaching and land use

Copper leaching from soils to deeper layers and groundwater has been monitored in soil with large copper loading rates such as sludge treated soils.

Richards et al. (1998) observed a considerable displacement of metals including copper. Binding of copper to soluble organic ligands in combination with preferential flow resulted in a rapid vertical transport of copper to groundwater. Only limited accumulation was observed which suggested that copper bound to ligands in the soil solution does not reabsorb to the soil in deeper layers.

In a similar leaching study but now using soil columns, the measured leachate concentrations were similar to those observed in the field, suggesting that data obtained in column studies can be used as estimates for field leaching rates (Richards et al., 2000).

In contrast to the findings of Richards et al. (1998), Keller et al. (2002) observed a significant increase in the metal content after sludge application, especially in the topsoil. Also increased dissolved copper concentrations in the soil solution samples were observed although clear trends could not be detected. In this study the increased levels of copper in the leachates was attributed to mobilisation by DOM from sludge. Both the Richards et al. (1998) and the Keller et al. (2002) data indicate that copper is in a soluble form, that is, little or no copper was transported by colloids larger than 0.45 μm. This in contrast to other elements (like Zn, Ni and Cr) which were translocated by soil colloids. On the other hand studies by Karathanasis (1999) showed that copper can be displaced by soil colloids although the impact decreased with colloid size, and decrease in surface charge. Also in the presence of Fe- and Al hydroxides (which in most soils are present in rather large quantities), colloid mobility was limited.

In fact, the difference between colloidal and dissolved seems to be arbitrary. Work by Jensen et al. (1999) shows that even in the fraction between 0.001 μm and 0.45 μm (which is called dissolved by many) a large part of the metals is bound to solid colloids that can be retained by cross filtration. For copper only a small (less than 10%) fraction passed the 0.001 μm size filter. Their findings were in agreement with those from Karathanasis (1999) who also observed that little or no copper was associated with larger colloids (> 0.45 μm). Also at DOM concentrations below the detection limit (<0.5 mg/l C) the speciation of copper can be completely governed by DOM (Buerge-Weirich et al., 2002).

Despite the fact that copper mobility is controlled largely by DOM, also pH remains an important factor. The effect of DOM on mobility of copper diminished below pH 4.5 Kalbitz and Wennrich (1998). On the other hand the decrease in soil pH induced by sludge application as measured by Speir et al. (2003), resulted in a large initial release of most metals. Control of soil pH by liming reduced metal leaching rates to background values despite elevated total metal levels in the soil. Inmost cases however, pH in sludge treated soils increases rather than decreases.

A recent study by Ashworth and Alloway (2004) further illustrates the complicated equilibrium (if there is such a thing) between pH, DOM release on one hand and copper mobility in sludge treated soil on the other. Although the release of DOM resulted in a release of copper, the increase in the leachate concentration was insignificant compared to that of e.g. nickel. Also the leaching pattern of DOM did not match that of copper. The authors concluded that speciation of DOM (different size classes) is an important process affecting metal leaching. Differences in molecular weight and affinity (as was explained earlier) appears to be of great importance as well as the impact of soil pH and electrical conductivity on the release of different DOM fractions. The leaching pattern of copper showed a much more pronounced tailing than that of (total!) DOM. Apparently specific fractions of DOM which make up a small portion of the total DOM can be responsible for a noticeable increase in the total dissolved copper concentrations (see figure 4.1 from Ashworth & Alloway, 2004 below).

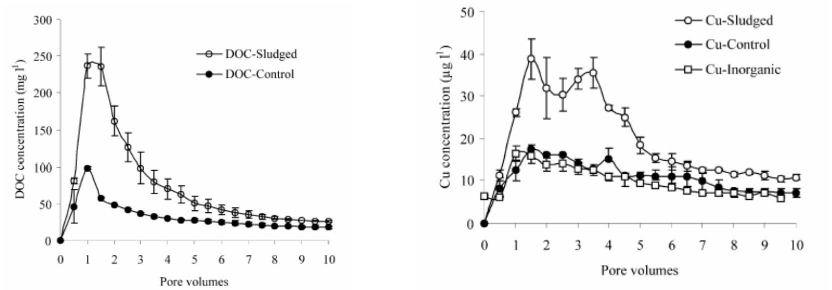

Fig. 3. Elution profiles of DOC concentration through both the control and sludge-amended soil columns. Error bars represent the range of values found.

Fig. 5. Elution profiles of Cu concentration through the control, sludge-amended, and metal nitrate-amended soil columns. Error bars represent the range of values found.

Figure 4.1 impact of source of DOM on copper leaching from soils (Ashworth & Alloway, 2004)

In contrast to the study by Ashworth and Alloway (2004), Madyiwa et al. (2002) found almost no displacement of nickel and a considerable increase in the adsorbed amount of copper in deeper soil layers. Due to rapid re-adsorption no or little leaching to groundwater occurred. In these soils (tropical soils) the high amount of Fe- and Al-hydroxide can be responsible for the limited impact of DOM on metal mobility. Since DOM is adsorbed preferentially by amorphous iron and Al (hydr)oxides, soils high in Fe and Al will show limited DOM-facilitated transport.

Also the pre-treatment of sludges appears to affect leaching rates. Grove et al. (2001) observed that copper leaching from soils treated with composted sludge exceeded that of fresh or dried sludge. Apparently changes in the nature of organic ligands during composting can occur that seem to favour the production of more mobile ligands. Work done by Calace et al. (2001) confirms that changes over time in the composition of DOM (in this case landfill leachates) affect the size distribution. In older leachates a wider range in molecular size was observed compared to younger leachates. Retention of copper by the underlying soil material was found to be higher in case of the low molecular weight (young) leachates. No explanation for the observed changes was given but the work by Conte & Piccolo (1999) could possibly explain this phenomenon. In their work they show that high molecular weight (or size) molecules are in fact an aggregation of individual small molecular weight compounds. Depending on the conditions, either aggregation or disruption of small organic molecules results in differences in molecular size.

4.2.3 Dissolved Copper concentrations in Dutch groundwater: an overview of data

Regional or national reports on the quality of shallow (< 10 m below the surface) groundwater are scarce. Usually the quality of deeper groundwater that is used for drinking water purposes is monitored at drinking wells. However, it can be expected that the relation between soil quality, and land use on one hand and the quality of groundwater in deep aquifers on the other is absent due to very long retention times. In shallow groundwater, and especially freatic groundwater, i.e. the groundwater that is in contact with the soil, it can be expected that the influence of land use on the composition of the groundwater can be detected. Especially in areas with intensive agriculture (i.e. manure application). Here we will not discuss the impact of local sources like smelters or other heavy industry.

For most heavy metals a decrease with depth in the concentration has been observed. Therefore we present data for freatic (less than 5 meter), shallow (5 to 10 meter) and deeper groundwater (10 - 30 meter)

In figure 4.2 an overview of measured concentrations of copper in the upper or freatic (less than 5 meter) in various combinations of soil type and land use is shown (Fraters et al., 2001).

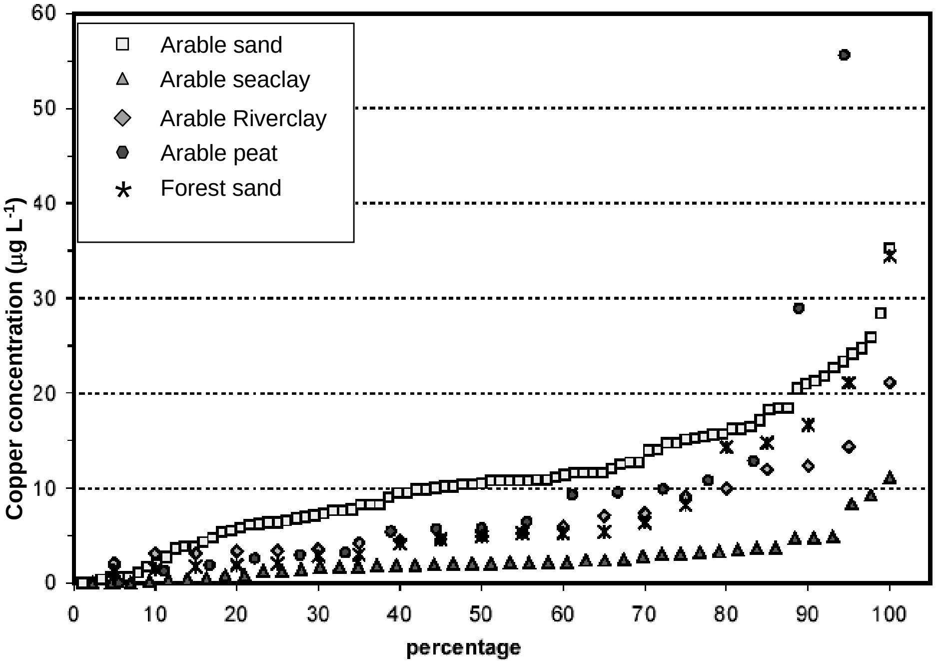

Figure 4.2 Distribution of dissolved copper concentrations in upper groundwater (0 - 5 m depth). Source: Fraters et al. (2001)

The data in figure 4.2 show that the dissolved concentration increases in soils with a low pH (sandy soils). Up to 30% of the measured concentrations of copper in shallow groundwater exceeds the target value of 15 μg L^{-1}. For other combination of soil type and land use this percentage is much lower. The highest levels of copper are found in forest soils and under peat soils. This is due to either a low pH (in forest soils) or the combination of elevated copper levels in soil and moderately acid pH levels (peat soils). The fact that dissolved copper levels in sandy arable soils exceed those in forest soils was attributed to differences in dissolved organic carbon (DOM, Fraters et al., 2001). This suggests that application of manure (leading to high DOM levels in soil solution) already affects the quality of the freatic groundwater.

Median levels of copper in these combinations of soil type and land use range from 2.1 μg L^{-1} in arable soils on sea clay to 11 μg L^{-1} in sandy arable soils. Up to 20% of all samples under sea clay soils was below the detection limit of 0.7 μg L^{-1}.

However, data from provincial monitoring networks show that regional data can deviate substantially from national monitoring networks. In table 4.1 data from the provincial network of Gelderland are shown (Japenga et al., 2000).

Table 4.1 Measured mean copper concentrations (in μg L^{-1}) in the freatic groundwater in areas with sandy soils in the province of Gelderland (Japenga et al., 2000).

	Land use		
Area	Grassland	Forest	Arable
Western part	10.1	12.3	32.3
Central part	5.5	9.2	23.9
Eastern part	12.9	15.1	28.9
Other	9.6	11.0	26.1

The data in table 4.1 not only show that mean concentrations can differ between areas (ranging from 5.5 μg L^{-1} in the central part to 12.9 μg L^{-1} in the eastern part under grassland) but they also seem to indicate that in this areas the impact of land use has a larger effect compared to the national average. The measured concentrations in groundwater under arable soils ranges from 23.9 μg L^{-1} to 32.3 μg L^{-1}, which is 2 to three times the median value from the national monitoring network. This is, however, not so surprising since especially in the province of Gelderland (and also in other eastern provinces) intensive animal husbandry is quite common. These data therefore confirm the suggestion by Fraters et al. (2001) that application of manure already results in a substantial increase of dissolved copper concentrations in freatic groundwater.

It should be kept in mind though that differences in sampling technique can have a significant impact on the levels obtained. A survey by Meinardi (see also furtheron) already indicated that comparison of data from different Provincial monitoring networks proved to be difficult due to differences in sampling technique and set-up of the wells (Meinardi et al., 2003).

In contrast to the freatic groundwater general the quality of shallow groundwater has not been affected on a large scale. In Table 4.2 an overview is given of the exceedance of the copper quality target value (0.015 mg L^{-1}) in shallow groundwater (5 - 10 m depth) from 1990 to 2001.

Table 4.2 Overview of exceedance of groundwater criteria in shallow groundwater

	% of the observation higher than the target value			
Year:	1990	1995	2000	2001
Soil type-land use				
Sand-Arable	5	4	4	3
Sand-Nature	5	5	7	7
River clay - arable	0	0	0	0
Sea clay - arable	0	0	0	0
Peat - arable	0	0	4	0

Source: http://www.rivm.nl/milieuennatuurcompendium/nl

Apart from unexplained higher values in peat soils in 2000, exceedance of the target value only occurs in sandy soils. Between 3 and 7% of all samples exceeds the 0.015 mg L^{-1} criterion. Up to 70% of all samples, however, had concentrations below the detection limit (see also table 4.3).

The fact that the highest exceedance is observed in sandy soils under nature suggests that the degree of exceedance is correlated to differences in soil acidity (pH) and not so much differences in the load of copper to soils. Also the fact that no trend is observed suggests that the influence of current land use is not yet reflected by the composition of the shallow groundwater. This is mainly due to the rather strong retention of copper in the soil. Ultimately, however ongoing deposition (atmospheric, but especially manure and sludge) will lead to an increase in the concentration in the groundwater as well.

Table 4.3 Overview of measured concentration in groundwater at -10 m (Van Direct et al., 1996)

	Land use and Soil type					
	Arable/ Sand		Nature/ Sand		Arable/ Clay & Peat	
	north	south	north	south	north	south
10-percentile	< 0.63	< 0.63	< 0.63	< 0.63	< 0.63	< 0.63
median	< 0.63	< 0.63	< 0.63	< 0.63	< 0.63	< 0.63
90-percentile	2.3	4.4	0.8	14	< 0.63	< 0.63

A separate analysis of data from both national monitoring networks and provincial networks was performed by Meinardi et al. (2003). In this study a comparison of groundwater bodies of different retention times was made. A distinction was made between groundwater with retention times below 25 years, between 25 and 50 yr. and more than 50 yr. In total 272 wells from the Provincial monitoring networks and 189 wells from the National monitoring network were considered.

In figure 4.3 an overview of the ratio of measured copper levels in sandy aquifers (distributed among the three age classes) to the 'background' copper level is shown. The background level, in this case 0.83 $\mu g\ L^{-1}$ was based on measurements of dissolved copper levels in the oldest groundwater bodies (> 50 yr.). In these groundwater bodies no difference between soil type and/or land use was observed and it was assumed that this level represents the natural background level of copper in groundwater bodies not affected by anthropogenic influence.

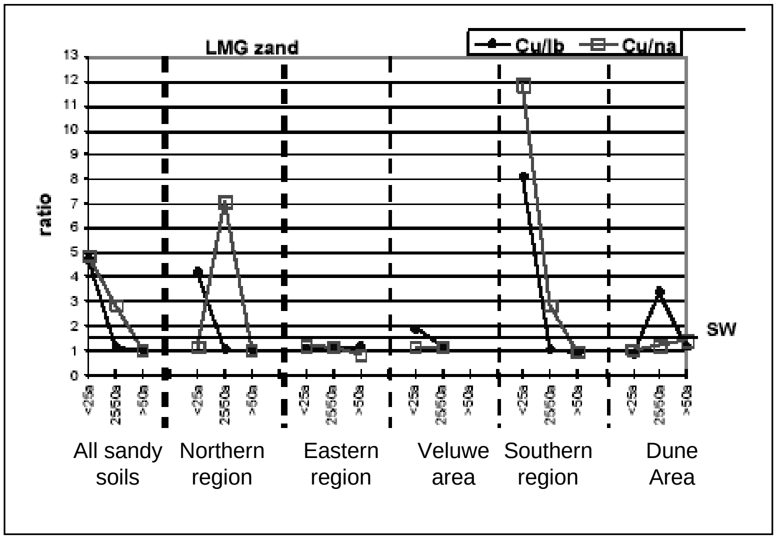

Figure 4.3. Copper in national monitoring network (LMG): ratio between measured levels in different regions and the background level (0.83 μg L^{-1}). Purple lines are groundwater bodies with nature, blue lines are groundwater bodies with agriculture. SW = Target Value for deep groundwater (1.3 μg L^{-1}). Source: Meinardi et al. (2003).

Differences between the southern area and other areas are clear (see also table 4.3) and are related to both higher levels of atmospheric deposition in the past, lower pH levels (especially in the southern area) and influence of the intensity of cattle breeding. Especially in the youngest groundwater bodies ($t < 25$ yr.) differences between intensive and extensive animal husbandry were significant. Dissolved copper (and DOM) levels were 1.5 to 2 times higher in areas with intensive animal husbandry compared to areas with extensive animal husbandry. In this factor differences between regions was accounted for.

4.3 Copper leaching from soils at a regional or national scale: model approaches

The simplest approach to quantify the leaching from soils to groundwater and surface water is to use measured copper concentrations in freatic groundwater and measured groundwater fluxes to calculate the copper flux. This approach has been used to obtain a first estimate of the total leaching flux of metals from soils to surface waters in the river Rhine basin and in the Netherlands as a whole (Römkens et al., 2002). A problem with this approach is that it is not representative for a country as a whole since only measurements from a limited number of sites are used. Differences in soil type and water fluxes are not considered. The impact of land use, which varies considerably in terms of metal loading rates, is not taken into account. A conceptual problem is that the data from groundwater are probably not representative for the water that leaves the soil by lateral flow. Another problem might be that the heavy metal fluxes are not constant through-out the year. During wet periods with high groundwater levels the heavy metal concentrations will be determined by soil horizons closer to the surface contained higher copper contents.

The results indicated that, despite these obvious shortcomings, metal leaching can be considered as a significant contribution to the total metal load in surface waters.

The second approach is to use copper concentration in the soil solutions in combination with a hydrological description of the water fluxes going to the surface water and deeper groundwater. The copper concentrations can also be calculated based on the total copper content of soils using well-known transfer functions based on pH, CEC and other explaining parameters. This approach has been recently used (Römkens et al., 2003; Bonten & Römkens, 2004) to calculate to total copper flux from soil to surface waters in the Netherlands. This was done on the basis of a description of the Netherlands in approximately 6000 units with certain pH, and copper, organic matter and clay contents for the soil layers and a hydrological description of these units. As an illustration of the possibilities, shortcomings and results of such an approach, the study by Römkens et al. (2003) is explained in some more detail in paragraph 4.4.

A third approach is to use a dynamic approach (chapter 3.2) in which the copper fluxes to and from the soil can vary. As explained before (chapter 4.1) such an approach is hampered by the lack of a knowledge of the DOM transport. Therefore one might assume constant partition coefficients but this limits the dynamic approach because all factors that influence the DOM concentrations (changing land use, changing types of manure) can therefore not be assumed to be dynamic.

4.4 Modelling copper leaching from soils to surface waters: outline of an approach currently used in the Netherlands

4.4.1 Background

Leaching of metals from soils to surface waters has not been considered an important process that contributes significantly to the total load of metals in surface waters. However, in many rural areas in the Netherlands levels of heavy metals like Cu, Ni and Cd exceed current threshold levels. Based on crude estimates (Römkens et al., 2002) however, the assumption that leaching can be neglected was questioned. Therefore a more detailed study was funded to quantify the total leaching flux from soil to surface waters. These estimates will be incorporated in the annual report by the CCDM (Coordinatie Commissie Doelgroep Monitoring). This committee is responsible for the quantification of all relevant emissions of harmful substances and nutrients to various compartments of the environment.

4.4.2 Approach

The aim of the project is to calculate copper (as well as other metals) leaching from soil based on a regional scale.

This requires the following inputs:

1. An appropriate (as far as scale is concerned) distribution of spatial units. The ultimate size of the units depends on, among others, the available information (in terms of on which scale level the information is available).
2. For each unit a hydrological schematisation. Flux of water to groundwater, lateral fluxes towards nearby surfaces water (ditches, brooks, channels) and fluxes within the soil profile and uptake by crops are needed.
3. A chemical characterisation of soils within each units. Important properties that are needed include pH, organic matter, clay content, and of course the heavy metal content for each diagnostic horizon down to the parent material
4. A model concept to calculate the solubility of metals in each soil horizon. Based on the concentration in solution the metal flux from each horizon can be calculated using the hydrological information. The choice of the model concept depends on the availability of soil parameters at the regional level. This means that no information on composition of soil solutions (e.g. macro ions) can be used.

It was decided to use the concept developed by RIVM, RIZA and ALTERRA (STONE) that was used to calculate fluxes of nutrients. In this concept, the Netherlands are divided in 6405 different units of variable size depending on the heterogeneity of the land, land use, and hydrology (Kroon et al., 2001). Each unit is characterised by its own hydrological conditions (all fluxes mentioned under point 2 are calculated using the model SWAP, (Kroes et al., 1999) and a schematisation of major soil properties including the ones required in the chemical model. What was not included yet was the schematisation of heavy metals for each soil layer. Based on the existing map of the Netherlands for heavy metals which was created at a 500 x 500 m grid level, metal contents for Cu (as well as Zn, Cd and Pb) were derived for each STONE plot (Brus et al., 2002). These maps however only cover the topsoil and characterisation of the sub-soil layers was based on data from a recent inventory of soil profiles (data not published as of now). In this inventory more than 60 soil profiles from the major soil types and forms of land use were studied. Analysis included the heavy metals.

In figure 4.4 a schematic representation is given of the model concept.

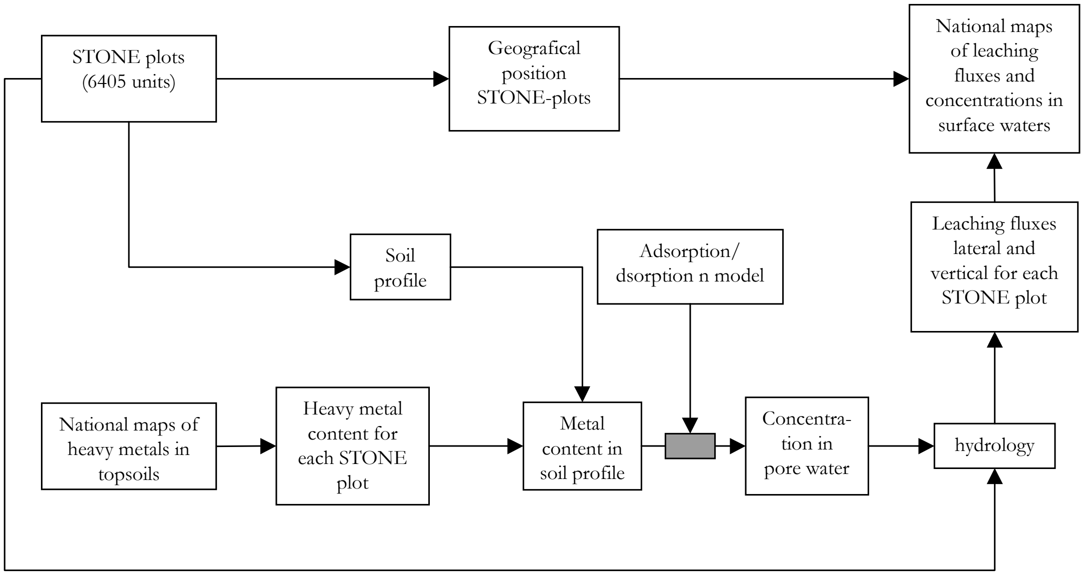

Figure 4.4 schematic representation of steps to calculate the total emission of heavy metals from soils to surface waters

For each soil layer from all plots the solution concentration of copper was calculated using so-called transfer functions. These empirical relations are able to calculate the dissolved metal concentration (as well as the free metal activity) from soil properties like pH, organic matter, clay content and the reactive heavy metal content (Römkens et al., 2004) according to eq. 1:

$$\text{Log } Me_{aq} = n \log[Me] + A_0 + A_1 \log OM + A_2 \log clay + A_3 \log FeAlox + A_4\,\text{pH} + A_5 \log DOM \qquad [1]$$

with

Me_{aq} :	concentration in the soil solution (mg L^{-1})
n:	Freundlich non-linearity coefficient
A_0 - A_5	regression coefficients
$[Me]$:	reactive metal content in the soil (in mg kg^{-1})
OM:	organic matter content of the soil (in %)
$clay$:	clay content of the soil (in %)
$FeAlox$:	oxalate extractable Fe and Al content (in mmol kg^{-1})
pH	pH soil solution or pH $CaCl_2$ (0.01 M)
DOM	Dissolved Organic Matter content in solution (in mg C L^{-1})

In table 4.4 an overview of the coefficients are given. For comparison also coefficients for other metals (Cd, Ni, Pb and Zn) are included.

Table 4.4 Coefficients of the partition equation for copper and other metals

Metal	n	A_0	A_1	A_2	A_3	A_4	A_5	R^2	SE(Y)
Cadmium	0.50	-1.30	0.43	0.12	0.32	0.25	-0.04	0.78	0.30
Copper	0.67	0.79	0.47	0.12	0.37	0.12	-0.31	0.67	0.34
Nickel	0.62	-0.77	0.68	0.39	0.06	0.26	-0.08	0.88	0.27
Lead	1.11	1.00	0.61	0.09	0.65	0.22	-0.43	0.58	0.63
Zinc	0.75	-1.13	0.38	0.26	0.23	0.44	-0.13	0.83	0.39

The preference for copper (and lead) to form soluble complexes with DOM is reflected in the strong contribution of parameter A5 (coefficient for DOM). Compared to metals like Cd and Ni the effect of DOM on the solubility of copper is much larger.

In many cases DOM is not available but reliable estimates can be obtained based on pH and organic matter. In the current model approach a dilute acid extraction is used to obtain the reactive copper content. The idea behind this is that the total copper content of the soil does not reflect the amount of copper that controls the concentration in the soil solution.

4.4.3 Results for copper

Estimates of the total load of copper that leaves the soil by leaching to surface waters ranges from 30 to 44 tons per year. The differences is due to a different way of up-scaling the results. Initially (estimate of 30 tons) representative units were used and an scaling factor was used to convert it to a total surface are. In a more recent calculation (Bonten and Römkens, 2004), all 6405 units were used an no up-scaling was necessary. The results of this study were used to construct national images of copper concentrations in the upper groundwater as well as estimates of fluxes to surface water (figure 4.5)

Compared to inputs, leaching is small. Inputs of copper to agriculture soils are estimated at 700 tons per year. However, compared to other emissions to surface waters, leaching contributes quite significantly to the total load.

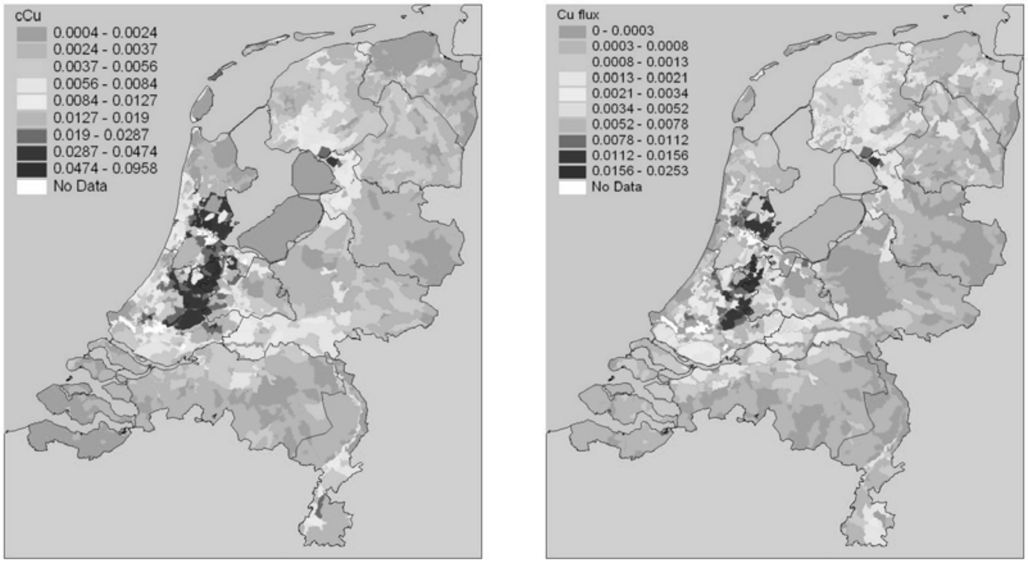

Figure 4.5 National overview of copper concentrations in freatic groundwater draining to surface waters (left, in mg L^{-1}) and calculated copper flux (right, in ton yr^{-1} per geographic unit)

Table 4.5 Overview of calculated concentrations in groundwater (-5 m, C-vert.) and water draining to surface waters (C-lat. concentration in mg L^{-1})

	C-vert	C-lat
All soils		
5%	0.1	0.7
50%	0.4	2.8
95%	1.7	16.9
Soil type	median	median
clay	0.31	3.0
sand	0.34	1.7
peat	0.65	4.9
loess	0.40	9.5

The data in Table 4.5 indicate that the modelled values for the freatic groundwater (C-lat.) are in agreement with those presented in figure 4.2 (overview of measured data in freatic groundwater in similar soil types). Only the median value for sand (1.7 μg L^{-1}) seems to be lower than measured values. Also modelled values for deeper groundwater (C-vert.) confirm that differences between soil types are still limited. Differences in modelled values for the concentrations in deeper groundwater (C-vert.) between grassland, arable land and nature were insignificant (data not shown here). It should be stated however that the model was developed for regional or even national applications. The match between locally measured data and model predictions for that same site has not been tested yet. This has proven to be very difficult since not all site specific parameters (soil properties, metal content) are available.

5 Conclusions and recommendations for further research

Role of DOM

Copper leaching from soils to ground- and surface waters is controlled largely by speciation of copper and more specifically by binding of copper to DOM. To predict leaching of copper from soils to ground- and surface waters information is needed on:

1. Release of copper from soil by DOM (both production of DOM and mobilisation of copper)
2. Transport and retention of Cu bound to DOM through soil and aquifer material

Extensive information on the interaction between copper and various types of dissolved organic material exists. Using available techniques (either Donnan membrane cells, Diffuse Gradient in Thin Films (DGT), voltametry or Ion Selective electrodes) speciation of copper can be measured at relevant levels under field conditions.

However the *release* and *degradation* of DOM are far less explored. Usually DOM is extracted from soil or obtained from leachates or extracts but little information is available on the controls of DOM release and its impact on the composition in different soils. Apart from release by soil micro organisms also plants can influence the composition of DOM in the rooting zone.

Differences in DOM resulting from differences in source materials is still poorly quantified other than in terms of total charge or fluorescence spectroscopy signals. Also conflicting evidence has been presented as to whether differences in DOM in different soils or from different plant material are significant.

Furthermore the impact of microbiological processes is in the process of releasing DOM from soil remain virtually unknown. Also the role in *degradation* of DOM once in the soil solution remains unsolved. Usually DOM retention in sorption studies is measured as the difference between input and output solution concentration. In real soils, the observed decrease in the concentration of DOM (and copper attached to it) is the sum of physical adsorption processes and microbiological degradation (McCracken et al., 2002) although pure adsorption controlled systems have been documented as well (Guggenberger et al., 1998).

It is clear that under natural conditions DOM consists of different size and chemical fractions with different affinities for copper. In modelling concepts these differences are only considered marginally. Most modelling concepts consider one type of DOM (or a constant ratio between HA and FA).

Especially the differences in characteristics in DOM from the upper soil layer and DOM in groundwater is of crucial importance to assess whether or not for example application of manure or sludge (containing large amounts of rather soluble organic compounds) has (or will have) an impact on deeper groundwater. If these organic compounds can be degraded in the upper soil layer, the carrying capacity is limited and changes in the quality of groundwater will be slow. The fact that both DOM and copper levels in the freatic groundwater in areas with intensive animal husbandry are higher (albeit only a factor of 1.5 to 2) compared to areas with extensive animal husbandry seems to indicate that manure-born DOM remains stable enough to cause an increase in the total dissolved levels of copper in the groundwater.

Characterisation of 'reactive' copper content in soils and aquifers

Apart from the need to improve our understanding of the nature of DOM, also the characterisation of the total reactive copper pool in the soil requires more attention. AS of now still no consensus exists on how to measure the 'reactive' fraction in soils, i.e. that part of copper that can be considered to be in equilibrium with the surrounding pore water. Currently best estimates are based on dilute acid or EDTA extractions. However, changes in the reactivity upon depletion (or enrichment) of the copper pool in soil are not considered in most models. For example, in the model approach described in paragraph 4.4 it is simply assumed that copper added to the soil in time is added to the reactive fraction.

In most cases the total copper content is used for model calculation. The difference between the total copper content and the reactive part of this not only depends on the form in which copper has been (or will be added) but also on the soil type. For modelling purposes an empirical relationship has been derived between the amount of copper extracted by Aqua Regia (considered a measure of the total copper content although this is not always correct) and the reactive fraction as measured in a 0.43 N HNO_3 extract (Römkens et al., 2004). This was done on data from many soils in the Netherlands and it is clear that the geochemical nature of Dutch soils (mainly sediments from major rivers, glaciers and wind deposits) can be very different from that of soils in areas with different geological parent material.

Approaches to model copper leaching from soils: perspectives and limitations

Current modelling approaches are able to calculate dissolved copper levels in soils rather well considering the wide range of processes that affect the solubility and speciation. Either (semi) mechanistic or empirical relationships can be used to predict the free metal ion activity or the total dissolved concentration. However, site specific input is still needed to obtain a close match between locally measured data en model predictions.

To model copper leaching on a regional or national scale, input has to be obtained from databases or soil maps with a limited resolution. Although these more or less generic predictions of dissolved copper levels in the upper or deeper groundwater seem to be in agreement with measured data, the match with local data has not been confirmed yet other than by comparison of average values.

It cannot be expected however that input data (soil properties, metal content in the soil) with a limited variation on a small scale, local differences in copper levels in groundwater can be predicted. One conclusion therefor is that lack of appropriate data is of greater importance in order to improve model predictions than the quality of the models itself.

Major limitations in this respect include:
1. data on the reactive copper content in the subsoil,
2. data on the amount and characteristics of DOM as well as solid organic matter in the subsoil.

Despite these obvious limitations, the models appear to be suited for predictions of changes in the copper concentration in different combinations of soil type and land use and as such of value to evaluate whether or not current (or future) forms of land use and, for example, intensity of agriculture will lead to unacceptable levels in ground- and surface waters.

Both data and model calculations show that differences in copper concentrations due to differences in land use or soil type in deeper groundwater are still small. This implies that the impact of anthropogenic activities on the levels of copper in groundwater seems yet to be limited to the upper groundwater.

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