National Institute for Public Health
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Impact assessment of the Dutch Soil Quality Decree on Groundwater

RIVM report 607711014/2013

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Colophon

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Abstract

Since the industrial revolution, Dutch soils have gradually been diffusely contaminated by human activities like industry, agriculture and road traffic. Nevertheless, most soils comply with the threshold levels of the Dutch Soil Quality Decree. However, in the long term (several hundreds of years) underneath (diffusely) contaminated soils the increasing concentrations of heavy metals in groundwater may become a risk. These substances can leach from the upper soil and gradually contaminate the groundwater. The National Institute for Public Health and the Environment recommends that for sustainable groundwater management these long-term effects are taken into account. Special attention is needed for the concentrations of cadmium, nickel and zinc.

It is unrealistic to undo the impact of human activities on soils. However, it is important for spatial planning to reckon with the effects of soil contamination on groundwater – for example, when diffusely contaminated soils are being re-used. For sustainable groundwater management the groundwater function (ecosystemservice) should not deteriorate as a result of these effects – for example, when groundwater is used for drinking water production or when groundwater feeds a sensitive surface water ecosystem. At locations with residential or industrial activities, higher metal soil concentrations are allowed in accordance with use.

For the model calculations the worst case scenarios from the Dutch Soil Quality Decree are simulated. In these scenarios soils have the maximum concentrations allowed (the so-called Maximum Values). The National Institute for Public Health and the Environment recommends refining the model scenarios to gain insight into the specific situations in which these increased concentrations in groundwater can occur. It is also recommended that the model be improved so that it can be used to address general questions concerning the relationship between heavy metal impact on soils and groundwater quality – for example, in the case of sustainable spatial planning and the re-use of contaminated soils and waste products.

Rapport in het kort

De bodem in Nederland is sinds de industriële revolutie geleidelijk aan licht vervuild geraakt door menselijk handelen, zoals industrie, landbouw en verkeer. Toch voldoen de meeste bodems aan de normen volgens het Besluit bodemkwaliteit. In bodems met verhoogde gehalten kunnen op de zeer lange termijn (enkele honderden jaren) de concentraties van zware metalen in het grondwater toenemen en een risico vormen. Deze stoffen kunnen namelijk vanuit de bodem weglekken en op termijn het grondwater vervuilen. Het RIVM adviseert daarom voor duurzaam grondwaterbeleid rekening te houden met deze langetermijnontwikkelingen. Hierbij is vooral aandacht nodig voor de concentraties cadmium, nikkel en zink.

Het is niet haalbaar om de menselijke invloed op de bodem terug te draaien. Wel is het van belang om bij ruimtelijke ontwikkeling rekening te houden met de effecten van de vervuiling op het grondwater, bijvoorbeeld als ‘licht verontreinigde bodems’ worden hergebruik. Voor duurzaam beheer van het grondwater mag de functie die het grondwater heeft (ecosysteemdiensten) niet te lijden hebben onder deze effecten. Dit geldt bijvoorbeeld voor grondwater dat als drinkwater wordt gebruikt of als voeding dient voor kwetsbare ecosystemen. Daar waar de bodem gebruikt wordt om te wonen of voor industriële activiteiten zijn hogere metaalconcentraties in de bodem toegestaan.

Voor de modelberekeningen zijn worst case-situaties uit het Besluit bodemkwaliteit doorgerekend. Dit zijn situaties met de maximale concentraties zware metalen in de bodem die wettelijk zijn toegestaan (de ‘Maximale waarden’). Het RIVM adviseert om de modelresultaten voor cadmium, nikkel en zink te verfijnen om inzichtelijk te krijgen in welke specifieke situaties deze stoffen in verhoogde concentraties in het grondwater voorkomen. Daarnaast wordt geadviseerd om het model verder uit te bouwen tot een algemeen model, waarmee vragen kunnen worden beantwoord over de relatie tussen bodembelasting en grondwaterkwaliteit. Voorbeelden zijn duurzame gebiedsontwikkeling en hergebruik van grond- en afvalstoffen.

Contents

Summary

In 2008 a new Soil Quality Decree (SQD) came into force in the Netherlands (Boekhold, 2008). This SQD presents new limits for soil background concentrations and contamination. The new SQD marks a change in soil policy from protection and sanitation towards sustainable use and re-use of contaminated soils (but still addressing sanitation in cases of severe soil contamination).

Considering that the SQD envisages sustainable soil management, the groundwater below such soils should also develop in a sustainable manner. This implies that groundwater quality should not deteriorate for future generations. This research addresses the question of how groundwater composition changes below soils which are managed under the SQD.

In an earlier study it was decided to assess the risk of leaching of diffuse contamination to groundwater using a model with a state-of-the-art multi-surface speciation model combined with a transport model (Spijker et al., 2009).This study revealed two shortcomings of the modelling approach to assess the effects on groundwater under SQD-managed soils. First, the chosen endpoint of the modelling, the Maximum Permissible Addition (MPA) risk level, was criticised for not being representative of current groundwater concentrations. Often the MPA values were below ambient groundwater concentrations. Second, the model appeared very sensitive towards the pH and organic matter input parameters. While input values for pH are well known, for organic matter these were largely unknown. Specifically, the reactivity of the different organic matter fractions, solid and dissolved, was little understood.

Moreover, in the study of Spijker et al. (2009) a prediction of leaching towards groundwater was made for only three soil profiles (sand, peat and clay), regarded as representative of Dutch soils. With only three soil profiles it was not possible to give an indication of the variability of leaching over a large spatial area, like the area of the Netherlands.

This study aims to improve the model with regard to both shortcomings: to consider pH and organic matter and to apply the model on a wider spatial scale. We aimed at a better parameterisation of organic matter reactivity and a more representative estimate of endpoint (i.e. groundwater) concentrations.

We predicted groundwater concentrations below soils with assumed concentrations of As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Sn, V and Zn at the level of the Maximum Values for agricultural, residential or industrial soil use, as defined in the SQD, and we created a model to calculate the groundwater concentrations which result from leaching of the aforementioned elements.

We evaluated the model and showed the suitability of the multi-surface model to predict the solubility of most metal cations in soils, with the exception of Sb. The precision of the predictions is highest for metals with a moderate to strong affinity for binding with organic matter. Generally the model performance for oxyanions is lower than for metal cations. The results of hindcast modelling give confidence in the ability of the model to simulate the transport of metals adequately on long timescales on the basis of equilibrium chemistry.

The modelled scenarios were based on soil profiles from the STONE soil schematisation of the Netherlands. In this schematisation, Dutch soils are divided into 456 plots, each with its own soil profile. In each soil profile in the upper 50 cm, the concentrations of elements were set at the level of one of the Maximum Values in the various simulations. Three soil profiles, representative of sand, peat and clay soils, were studied in detail. Twenty soil profiles, from the 20 largest plots in the STONE schematisation, were studied at an aggregated level. All 456 soil profiles, covering the whole area of the Netherlands, were studied using maps showing binned results.

Leaching from the soil was assessed in three ways. First, breakthrough curves showing the change in groundwater concentration after several time spans at several depths were studied from the three representative soil profiles. Second, for the 20 soil profiles from the largest plots, aggregated concentration ranges were studied. Third, for all 456 profiles, the results were studied spatially using maps. For all the soil profiles the maximum average concentration was calculated from the average concentration over a 1 metre depth range for each time step. Then, for all the time steps, the maximum of these maximum average values was determined. These maximum concentrations were calculated after 1, 100, and 500 years and for 1 metre (100–200 cm) and 5 metre (500–600 cm) depths.

Three indicators were used to compare the maximum average concentration with a threshold value. The first indicator was based on the MPA. This MPA is a risk level and is used in risk assessments as the ‘no effect’ level for an added concentration for substances that also occurs naturally. The second indicator was based on the 95th percentile of current groundwater concentrations. This percentile was derived in this study. The third indicator compared the maximum average concentrations as results of soils with concentrations up to of the Maximum Value Residential and the Maximum Value Industrial with the Maximum Value Agricultural. This last indicator presents the predicted changes in groundwater as a result of residential and industrial soil use compared with ‘clean’ soil, as defined in the SQD, despite the fact that this ‘clean’ soil has an accepted diffuse anthropogenic imprint of contaminants.

In this report, we argue that the MPA is not very useful as a reference to compare shallow groundwater concentrations that result from curative soil management of historically diffuse contaminated soils. The major reason is that it is hard to differentiate between the natural background concentration and the anthropogenically added part within the ambient groundwater concentrations. These ambient groundwater concentrations are often above the MPA level already.

In a comparison between the results of scenarios based on soils with concentrations at the level of the Maximum Value Agricultural and the current groundwater concentrations, the elements Cd, Co, Cu, Ni and Zn can be considered mobile at the time range of 500 years. Cadmium, Co, Cu and Ni show mobility related to soil type. Cadmium, Mo, Ni and Zn are also found at greater depths (5 m) and are more mobile than the others.

For the scenarios with Maximum Value Residential and Maximum Value Industrial, Cd, Ni and Zn show enrichment when compared to current groundwater concentrations. Lead also shows elevated concentrations in peat and clay areas but this is due to the relatively low, and possibly biased, current groundwater concentrations together with an overestimation of concentrations from the model.

In a comparison of the maximum average concentrations of the scenarios having the Maximum Value Residential and Maximum Value Industrial with those having the Maximum Value Agricultural (i.e. ‘clean’ soils), higher concentrations occur for Cd, Co, Ni and Zn.

The results for Mo, Sb and Sn are regarded as unreliable due to modelling artefacts.

1 Introduction

In 2008 the new Soil Quality Decree (SQD) in the Netherlands came into force (Boekhold, 2008, VROM 2007). This SQD presents new limits for soil background concentrations and contamination. Threshold levels for contaminated soil levels are made dependent on land use, i.e. residential or industrial. The thresholds for contaminated situations are risk based. The so-called added risk approach was used, in which an acceptable risk level was derived based on exposure scenarios and this risk level was added to a background concentration to obtain the threshold. The new SQD is a change in soil policy from an emphasis on protection and sanitation to an emphasis on sustainable use and re-use of contaminated soils (but maintaining a focus on sanitation in cases of severe soil contamination).

In former soil policies in the Netherlands the risk levels or threshold levels were also assessed for the risk of leaching into groundwater using a simple partition model (Crommentuijn et al., 2000). In the current SQD such an assessment is not part of the risk assessment. Considering that the SQD envisages sustainable soil management, the groundwater should also develop in a sustainable manner. This implies that the groundwater quality remains at a level that ensures that the possibilities for future groundwater use are not restricted.

An indicative study to provide some insight into the impact of enriched soil concentrations on groundwater was performed at the same time as the threshold levels of the SQD, the so-called Maximum Values (MV), were derived (Dirven et al., 2007; Appendix 9). This study indicated that the new MV in soil could result in the risk limits in groundwater due to leaching from soil being exceeded, violating the aim of the SQD, namely sustainable soil management.

With the creation of the SQD a risk assessment was also executed, which should lead to criteria for leaching from construction products (Verschoor et al., 2006). In this study leaching through soil into groundwater was assessed including an assessment with a multi-surface speciation model. This also showed the potential to use such models to give an estimate of changes in groundwater concentrations as a result of diffuse metal inputs.

Therefore, it was decided to assess the risk of leaching of diffuse contamination into groundwater using the state-of-the-art multi-surface speciation model (Spijker et al., 2009). Leaching from soils at the level of the Maximum Values specified by the SQD was estimated for the first metre of groundwater and compared with the Maximum Permissible Addition (MPA) risk level. The conclusions of the study were that for most of the assessed substances the MPA was exceeded in soil with concentrations at the level of the MV Residential. However, due to modelling uncertainties and uncertainties in input parameters it was not possible to indicate to what extent or at which spatial scale these exceedances would occur in actual soil–groundwater systems.

The study by Spijker et al. (2009) revealed two shortcomings of the modelling approach with a multi-surface speciation model to obtain an impact assessment for the effects on groundwater for soils managed under the SQD. First, the chosen endpoint of the modelling, the MPA, was criticised for not being representative of current groundwater concentrations. Often the MPA values were below known groundwater concentrations. Second, the model appeared highly sensitive to the pH and organic matter input parameters. While input values for pH are well known, for organic matter these were largely unknown. Specifically the reactivity of the different organic matter fractions, solid and dissolved, were very uncertain.

Also in the study of Spijker et al. (2009) a prediction of leaching into groundwater was made for only three soil profiles (sand, peat and clay), regarded as representative of Dutch soils. With only three soil profiles it was not possible to give an indication of the variability of leaching over large spatial areas, such as the whole of the Netherlands.

This study aims to improve the model in respect of both shortcomings and to apply the model on a wider spatial scale. We aim at a better parameterisation of organic matter reactivity and a more representative estimate for the model endpoint (i.e. groundwater) concentration. To fulfil our overall aim this study has the following objectives:

1. to characterise nationwide groundwater concentrations to obtain a representative value for the upper bound of variability of these groundwater concentrations;
2. to measure representative values for the reactive fractions of solid and dissolved organic matter in Dutch soils;
3. to obtain input parameters which can be applied on a wide spatial scale;
4. to define an endpoint representative of the current situation which is used for the impact assessment in Dutch soils;
5. to evaluate (validate) parts of the model to obtain insights into model uncertainties.

Using these objectives we will provide insight into the consequences for groundwater below soils which are managed using the SQD.

This study fulfils the request by the Soil Protection Technical Committee (TCB) to obtain insight into the effects of soil managed under the SQD on groundwater (Technische Commissie Bodembeheer, 2012). The TCB particularly refers to the uncertainties in the modelling of these effects on groundwater.

In this report we give a short overview of the soil and groundwater system of the Netherlands (Chapter 3). In Chapter 4 we show how we obtain and model the data necessary as input in the multi-surface speciation model, and the derivation of representative groundwater concentrations which are used as the endpoint of the model. Chapter 5 explains the model set-up and Chapter 6 summarises some evaluation and validation studies of the model. The results of the modelling using the data from the previous chapters is given in Chapter 7. The report concludes with a summary (Chapter 8) and recommendations for further work (Chapter 9). Detailed results are presented in Appendix A.

Chapter 2 presents the relevant consequences of the model results for Dutch soil policy. This study was commissioned by the Dutch Ministry of the Environment and Infrastructure, at whose request Chapter 2 is in Dutch.

2 Uitgebreide samenvatting resultaten voor het bodembeleid

2.1 Doel en beleidsmatige vraagstelling

Dit Engelstalige rapport beschrijft de opzet, evaluatie en resultaten van een modellering van uitloging van metalen en metalloïden uit bodems naar het grondwater. Deze studie had de volgende doelen:

1. het bepalen van representatieve concentraties van metalen en metalloïden in het ondiepe (eerste meter) grondwater;
2. het bepalen van representatieve waarden voor bodemparameters die de uitloging van metalen en metalloïden bepalen, zoals reactiviteit van opgelost organische koolstof, gehalten aan oxiden en reactiviteit van metalen en metalloïden;
3. het verbeteren van het bestaande modelinstrumentarium voor het modelleren van de uitloging van metalen en metalloïden uit de bodem, inclusief de onzekerheid van deze modellen.

In het Besluit Bodemkwaliteit (Bbk) wordt een duurzame kwaliteit van bodem en grondwater beoogd. Een beleidsmatig uitgangspunt is dat de grondwaterkwaliteit die hoort bij de huidige kwaliteit van een binnen het Bbk duurzaam beheerde bodem opgevat wordt als duurzame kwaliteit. Daarnaast bepaalt de Kaderrichtlijn Water dat er geen onacceptabele toevoeging van stoffen aan het grondwater mag plaatsvinden. Beleidsmatig is daarom de vraag gesteld of het Bbk ook daadwerkelijk beschermend is voor het grondwater. Met het verbeterde modelinstrumentarium zijn de consequenties inzichtelijk gemaakt van de uitloging naar het grondwater uit bodems beheerd volgens het Bbk. Deze bodems hebben concentraties van stoffen (metalen en metalloïden) op het niveau van de Achtergrondwaarde.

Naast de beleidsmatige vraag is er ook een aantal onderliggende inhoudelijke vragen gesteld met betrekking tot de modellering van de uitloging van anorganische stoffen uit de bodem. Deze onderliggende inhoudelijke vragen worden in het Engelstalige rapport besproken en vallen buiten de discussie in dit hoofdstuk.

De huidige kwaliteit van een schone bodem wordt gedefinieerd door de Achtergrondwaarde. In dit rapport wordt de term ‘Achtergrondwaarde’ (met hoofdletter) gebruikt voor de achtergrondwaarde uit het Besluit bodemkwaliteit. Dit is de kwaliteit van die wordt aangetroffen in zogenaamde ‘onbelaste’ bodems, bodems waarvoor geen directe bron van vervuiling aanwezig is. Echter, door diffuse belasting zijn de concentraties in de bodem gedurende de afgelopen eeuw wel door de mens beïnvloed. Die invloed heeft geleid tot verhoogde concentraties van sommige metalen (zoals Cd, Cu, Ni, Zn, Pb).

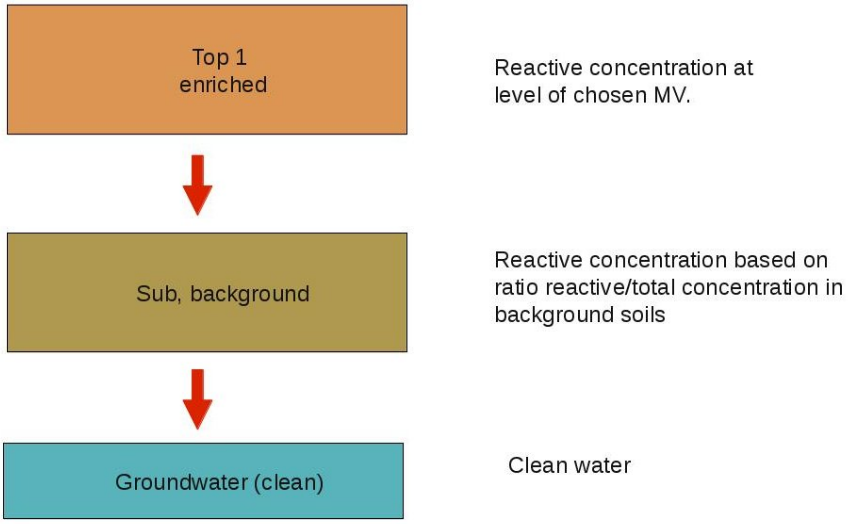
Daarnaast gebruiken we in dit rapport de term achtergrondwaarde (zonder hoofdletter) voor gemeten achtergrondconcentraties in bodem en grondwater.

In deze studie hebben we de uitloging van stoffen uit de bodem naar het grondwater voorspeld. De (toekomstige) grondwaterconcentraties zijn vergeleken met de huidige grondwaterconcentraties. Voor bodems met bodemconcentraties op het niveau van de Maximale Waarden Wonen en Industrie zijn de concentraties vergeleken met grondwaterconcentraties zoals die zich in de toekomst kunnen ontwikkelen.

2.2 Basisprincipe van de modellering

De basisprincipes van dit onderzoek zijn gelijk aan die van de voorgaande studie (Spijker e.a., 2009). De principes zijn grotendeels gelijk aan die van het afleiden van de emissiegrenzen van de bouwstoffen (Verschoor e.a., 2006). Het conceptueel model, zie Figuur 2.2.1, dat is gebruikt bestaat uit een bodemprofiel met drie lagen:

1. de toplaag ('top layer') is de bodemlaag met concentraties op het niveau van de Achtergrondwaarde;
2. de sublaag ('sub layer') is een schone bodemlaag met concentraties op het niveau van de natuurlijke achtergrond. Deze concentraties liggen lager dan de Achtergrondwaarde, welke zijn gebaseerd op 95 percentiel van diffuus verontreinigde bodems;
3. de grondwaterlaag ('groundwater') is een schone bodem- en grondwaterlaag met concentraties in de vaste fase op het niveau van de natuurlijke achtergrond.



Figuur 2.2.1: Conceptueel model met bodemlagen (rechthoeken) en watertransport (rode pijlen)

Voor de toplaag wordt voor iedere Maximale Waarde de toegevoegde hoeveelheid aan metalen ten opzichte van de natuurlijke achtergrond berekend door de natuurlijke achtergrondconcentratie van de Maximale Waarde af te trekken. Deze toevoeging wordt als reactief verondersteld. Het reactieve deel van de concentratie doet vervolgens mee in de bodemchemische processen zoals uitloging en uitwisseling tussen de vaste fase en de vloeistoffase.

Een modelscenario bestaat uit een bodemprofiel met een toplaag op het niveau van de Achtergrondwaarde, Wonen, of Industrie. Per bodemprofiel kunnen dus drie scenario's doorgerekend worden. Omdat de rekentijd en de tijd voor de interpretatie per bodemprofiel aanzienlijk is, is er gekozen om de gegevens op drie schalen te beoordelen:

De eerste schaal betreft drie standaard bodemprofielen die in detail bestudeerd zijn. Deze bodemprofielen zijn gelijk aan de bodemprofielen uit voorgaande studies (Spijker e.a., 2009, Verschoor e.a., 2006). De bodemprofielen zijn in de voorgaande studies gekozen als 'gemiddelde' profielen voor de drie bodemtypen zand, veen en klei (Verschoor e.a., 2006). Vanwege de vergelijkbaarheid zijn dezelfde profielen ook in deze studie gebruikt.

De tweede schaal betreft, naast de drie standaardprofielen, de 20 meest voorkomende bodemprofielen. De gegevens van deze profielen zijn per bodemtype (zand, veen, klei) bestudeerd.

De derde schaal betreft alle bodemprofielen tezamen. Ook deze zijn geaggregeerd naar bodemtype en worden door middel van kaarten of overzichtsfiguren beoordeeld. Deze profielen zijn alleen doorgerekend voor de Achtergrondwaarde.

2.3 Belangrijke aannames

Door middel van modelberekeningen zijn de consequenties van de Maximale Waarden voor het grondwater berekend. Voor het modelleren zijn, zoals bij iedere modelstudie, een groot aantal aannames gedaan en vereenvoudigingen ten opzichte van de werkelijkheid doorgevoerd. Voor het interpreteren van de resultaten zijn de volgende aannames en vereenvoudigingen van belang:

- De bodemconcentraties van de zware metalen/metalloïden uit het Besluit Bodemkwaliteit zijn in de eerste halve meter van de bodem allemaal gesteld op de Maximale Waarden. Dit is de worst case-situatie die nog is toegestaan vanuit het besluit. In werkelijkheid zal deze situatie uitzonderlijk zijn, ervaring leert dat een bodem meestal is verontreinigd met enkele metalen/metalloïden.
- Voor de bodemconcentraties op het niveau van de Maximale Waarden geldt de toegevoegd-risicobenadering. Het risico wordt bepaald door het deel van de concentratie dat door menselijke activiteiten is toegevoegd ten opzichte van de natuurlijke achtergrond. Deze natuurlijke achtergrond is gebaseerd op de mediane (50 percentiel) concentraties, gecorrigeerd voor bodemtype, uit de Geochemische Bodematlas van Nederland. Deze concentraties zijn in het algemeen lager dan de antropogeen beïnvloedde achtergrondwaarden, of Achtergrondwaarde en Natuur, uit het Bbk. Deze laatste zijn gebaseerd op een 95-percentielniveau. De toegevoegde concentratie wordt berekend door de natuurlijke achtergrond af te trekken van de Maximale Waarde. Deze toegevoegde concentratie wordt als chemisch reactief verondersteld en zal gaan uitlogen. Op basis van eerdere studies (zie o.a. Spijker e.a., 2011, Spijker, 2012) weten we dat voor diffuus licht verontreinigde niveaus deze aanname voor een aantal stoffen (Cu, Pb, Zn, Cd) goed opgaat. Voor hogere verontreiniging niveaus, zoals de Maximale Waarde Industrie, of voor stoffen zoals Sn en Sb geeft deze aanname een overschatting.
- Voor de uitloging is een vereenvoudigde hydrologie gebruikt. De belangrijkste consequentie hiervan is dat de doorbraaktijd van concentraties een benadering is. De doorbraaktijden van de stoffen moeten vooral in relatie tot elkaar worden beschouwd. De absolute tijd is afhankelijk van de lokale hydrologie en deze is voor de eenvoud gelijkgesteld tussen de verschillende scenario's. Bijvoorbeeld Ni heeft een lagere doorbraaktijd dan Pb, dat betekent dat Ni ook mobieler is dan Pb (onder de gemodelleerde omstandigheden). De neerwaartse waterflux is voor iedere bodemkolom gelijk en gesteld op een neerslagoverschot van 300 mm/jaar. In werkelijkheid zal dit verschillen. Ook wordt er geen rekening gehouden met afspoeling of drainage naar oppervlaktewater.
- De hydrologie is verder geschematiseerd door de concentraties in het grondwater te berekenen als een gemiddelde concentratie in een laag grondwater van 1 meter dik. De diepte van deze lagen zijn 1 meter onder

maaiveld (laag 1-2 m diep) of 5 meter onder maaiveld (laag 5-6 m diep). De laag van 1 meter onder maaiveld komt overeen met eerdere studies naar uitloging (Verschoor, 2006, Spijker e.a., 2009). In een grondwaterlaag vindt nog wel neerwaarts transport plaats, gelijk aan de bovengrond, maar geen processen zoals verdunning. Het ontbreken van verdunning is een redelijke aanname bij diffuus aanwezige concentraties maar een overschatting bij lokale verontreinigingen.

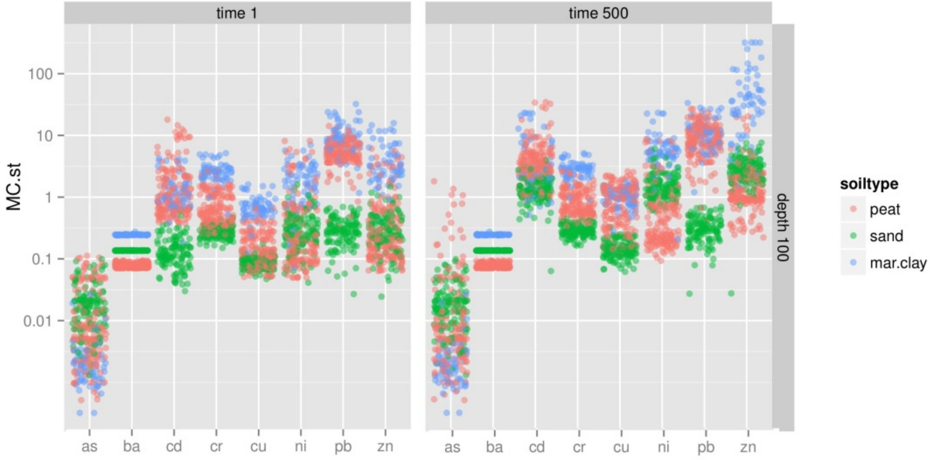
- Het model gaat uit van een licht aeroob milieu, dus zuurstofhoudend. Veranderingen in het redoxniveau (eenvoudig gezegd, overgangen naar zuurstofloos milieu) kunnen op dit moment nog niet goed gemodelleerd worden. Het aangehouden redoxniveau is vooral representatief voor zandgronden. Profielen in klei- en veengronden kunnen meer zuurstofloos zijn. Het redoxniveau wordt in de hele gemodelleerde bodemkolom min of meer constant gehouden terwijl in werkelijkheid het zuurstofgehalte met de diepte zal afnemen. Hierdoor kan de mobiliteit van de meeste metalen waarschijnlijk licht worden overschat. Voor As geldt dat de mobiliteit waarschijnlijk wordt onderschat.
- De modeluitkomsten worden vergeleken met grondwaterconcentraties zoals die in het bovenste grondwater worden aangetroffen. Hierbij is beleidsmatig gekozen om het 95 percentiel als criterium te gebruiken, analoog aan de keuze van het 95 percentiel bij bodem. Omdat een normale 95 percentiel meestal erg onzeker is in situaties van diffuse verontreiniging, is gekozen voor een robuuste 95 percentiel op basis van de spreiding in de mediaan (MAD, median absolute deviation). Dit criterium noemen we het MAD-criterium, afgekort MC (zie paragraaf 4.4.1). Het MC is afgeleid uit de data van het Landelijk Meetnet Mestbeleid (LMM) en omvat gegevens uit het landbouwareaal van Nederland. Uit de gegevens van het LMM blijkt dat concentraties van metalen en metalloïden in zandgebieden relatief hoger zijn dan in klei- en veengebieden (zie Tabel 4.4.2.1). In deze studie toetsen we de uitgeloogde concentraties uit een bodemtype, zand, veen, of klei aan de MC-waarde die hoort bij dat bodemprofiel. Dat betekent dat bij toetsing van de uitloging het toetscriterium voor klei en veen lager is dan bij zand.

2.4 Resultaten

In hoofdstuk 6 van dit rapport zijn de resultaten in detail besproken. In dit hoofdstuk lichten we alleen die resultaten eruit die van belang kunnen zijn voor het bodembeleid.

2.4.1 Resultaten uitloging op het niveau van de Achtergrondwaarde

Op het niveau van de Achtergrondwaarde zijn de resultaten van belang omdat dit inzicht geeft in de uitloging onder diffuse belasting. Deze uitloging zou op korte tijdschalen in dezelfde orde van grootte moeten liggen als de grondwaterconcentraties. Uitloging van de Achtergrondwaarde geeft ook inzicht in hoe de grondwaterconcentraties kunnen veranderen over lange tijdschalen als gevolg van deze diffuse belasting.



Figuur 2.3.1: Resultaten van de 356 scenario's. Concentraties van metalen/metalloïden zijn weergegeven als log-ratio van de piekconcentratie gedeeld door de bodemtype specifieke MC (y-as: MC.st). Piekconcentraties zijn berekend op 1 meter diepte, na 1 en na 500 jaar. De kleuren van de punten geven het bodemtype weer. Voor verdere uitleg zie tekst.

Voor de Achtergrondwaarde zijn 356 scenario's doorgerekend. Deze scenario's gingen uit van een bodem met alle concentraties op het niveau van de Achtergrondwaarde, een niveau wat verondersteld wordt overeen te komen met het 95 percentiel van de concentraties in de Nederlandse bodem (en hoger dan de natuurlijke achtergrond). Voor het bodemprofiel zijn de bodemprofielen uit de STONE-database gebruikt (zie hoofdstuk 4).

In Figuur 2.3.1 is de uitloging van ieder metaal/metalloïde voor ieder afzonderlijk scenario weergegeven als punt in een puntenwolk. Deze figuur is een uitsnede van Figuur 7.16.1.1 in hoofdstuk 7. De hoogte van de punt langs de y-as geeft de log-ratio aan van de overschrijding van de MC, de berekende concentratie ten opzichte van de actuele achtergrond. De punten zijn horizontaal gespreid om de verdeling van de punten goed weer te kunnen geven en om weer te kunnen geven hoe de punten van de verschillende bodemtypen ten opzichte van elkaar liggen.

Voor de toetsing aan de achtergrondconcentratie grondwater zijn twee grenzen aangehouden: 1 x MC en 10 x MC. Als een waarde onder de 1 x MC valt, dan valt deze waarde binnen de variatie van concentraties in het huidige grondwater. Tussen 1 x MC en 10 x MC overschrijdt de voorspelde concentratie binnen een ordegrootte het 95 percentiel van de huidige grondwaterconcentraties. Een waarde die we acceptabel achten gezien de onzekerheden in het model.

Naast de absolute toetsing aan de MC wordt er ook gekeken hoe de uitloging van de metalen/metalloïden zich in de tijd ontwikkelt. Als binnen 100 jaar de overschrijding van de MC toeneemt, dan is er onder de vigerende Achtergrondwaarde nog geen stand still bereikt en voorspelt het model dat de grondwaterconcentraties in de komende decennia nog zullen toenemen.

Op basis van de in volgende hoofdstukken gepresenteerde gegevens en de resultaten uit Figuur 2.3.1 blijkt dat op het niveau van de Achtergrondwaarde de uitloging van de metalen Ni, Cd en Zn nog kan leiden tot verhoging van de concentraties van deze stoffen in het grondwater. Voor Zn gaat het om overschrijdingen groter dan 10 x MC. Voor Ni en Cd gaat het om overschrijdingen tussen 1 x MC en 10 x MC.

Lood en, in iets mindere mate, Zn laten voornamelijk waarden groter dan 10 x MC zien in klei- en veengebieden. Bij de interpretatie van deze (hoge) overschrijdingen is het ten eerste van belang om in acht te nemen dat de MC's in deze gebieden (veel) lager zijn dan in de zandgebieden. Ten tweede moet rekening worden gehouden met de aangenomen infiltratiesnelheid naar het grondwater, deze is 300 mm/jaar en zonder oppervlakte-afstroming. Dit geeft in klei- en veengebieden met lage infiltratiesnelheden en veel oppervlakkige afstroming een overschatting van de uitgeloogde concentratie. Voor Pb geldt dat, op basis van de validatie in hoofdstuk 5, de Pb-concentratie ook door het model overschat wordt. Daarnaast is voor Pb in het scenario na één jaar ook al overschrijding van de MC te zien. Dat betekent dus dat in de evenwichtsberekeningen van het model er voor een bodem op het niveau van de natuurlijke achtergrond al grondwaterconcentraties worden berekend boven de MC.

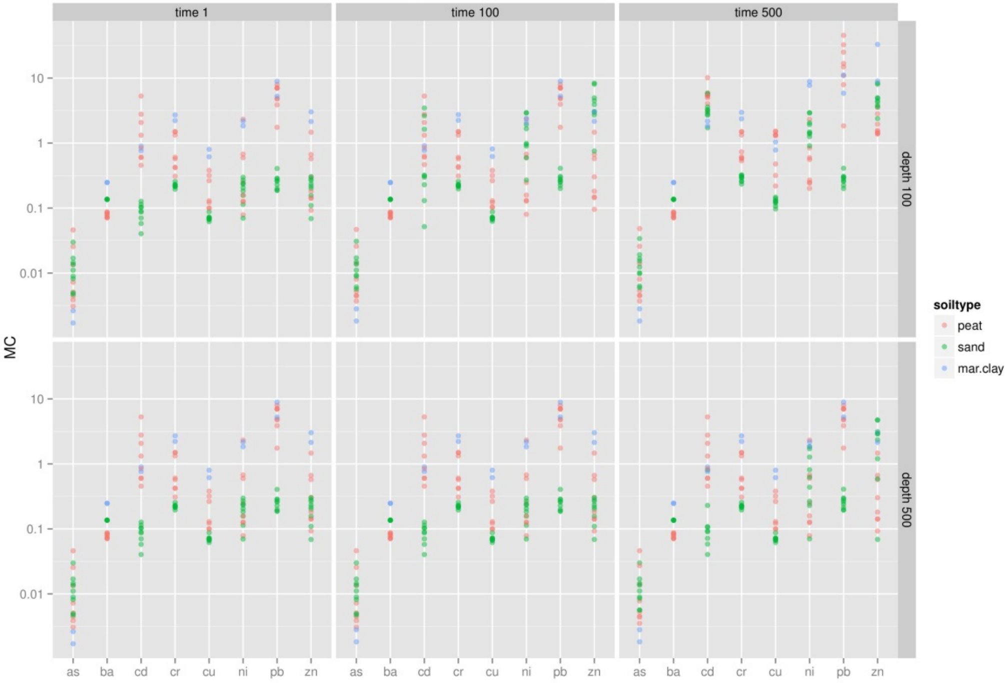
De voorspelde stijging van Cd, Ni en Zn op zandgronden blijft binnen de grens van 10 x MC. Deze resultaten wijzen erop dat de bodem, vanuit het Bbk toegelaten als 'schone grond', nog wel het grondwater kunnen beïnvloeden. Voor Ni en Zn zijn de invoerconcentraties hoog ten opzichte van het bestaande 95 percentiel in zandgronden. Deze hoge invoerconcentraties zijn een resultaat van de toepassing van de bodemtypecorrectie. Deze bodemtypecorrectie geeft voor Ni en Zn een overschatting van de werkelijke achtergrondwaarde in zandgronden (zie Spijker, 2012).Voor Cd is de invoerconcentratie realistisch.

De voorspelde uitloging van de elementen Cd, Ni en Zn is zeer gevoelig voor competitie met andere kationen die voorkomen in het bodemvocht en het grondwater, zoals Ca^{2+}, zeer bepalend kunnen zijn voor de uitloging. In het huidige model is de aangenomen Ca^{2+}-concentratie gebaseerd op data van Dijkstra e.a. (2004) en is relatief hoog. Als deze Ca^{2+}-concentratie een factor 10 lager wordt gesteld, een waarde die op basis van nieuwe gegevens realistischer lijkt voor de Nederlandse bodem, dan worden de piekconcentraties van Cd, Ni en Zn ongeveer een factor 2 tot 10 lager.

2.4.2 Resultaten uitloging op het niveau van de Maximale Waarden Wonen en Industrie

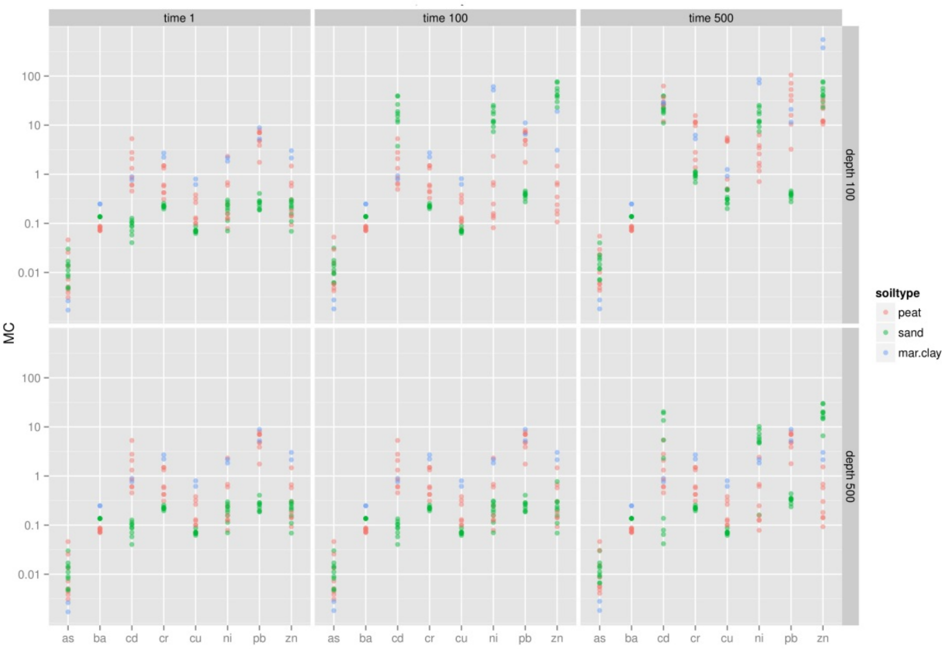
In Figuur 2.4.2.1 zijn de voorspelde piekconcentraties ten opzichte van de achtergrondconcentraties in het grondwater (MC) weergegeven door middel van de ratio tussen de piekconcentratie en de MC. Vanwege de rekentijd zijn hiervoor 20 scenario's geselecteerd met in oppervlakte de meest voorkomende bodemprofielen. Voor 5 van deze 20 scenario's was het niet mogelijk om grondwaterconcentraties te berekenen (zie hoofdstuk 6). In het figuur is ook de situatie na één jaar weergegeven, deze situatie is te vergelijken met een nul-situatie. Verandering in de tijd (na 100 en 500 jaar) kunnen worden vergeleken met deze nul-situatie.

Uit Figuur 2.4.2.1 blijkt dat na 100 jaar de concentraties van de stoffen Cd, Ni en Zn sterk zijn toegenomen in het grondwater onder zandgronden. Zaten de concentraties van deze stoffen nog onder de grens van 1 x MC in de nul-situatie, na 100 jaar zijn voorspelde overschrijdingen te zien tussen de 1 x MC en 10 x MC. Na 500 jaar zijn voor Pb op veengronden en voor Zn op kleigronden overschrijdingen van meer dan 10 x MC te zien. Echter, bij de interpretatie van de deze waarden op klei en veen gelden dezelfde opmerkingen als in de vorige paragraaf, namelijk dat de MC in klei en veen relatief laag is en dat de watertransportsnelheid relatief hoog is voor deze bodemtypes.



Figuur 2.4.2.1:Rresultaten van de scenario's met een bodemconcentratie op het niveau van de Maximale Waarde Wonen. Concentraties van metalen/metalloïden zijn weergegeven als ratio van de piekconcentratie en de bodemtype specifieke MC. Piekconcentraties zijn berekend in de bodemlagen van 100-200 cm diepte (depth 100) en 500-600 cm diepte (depth 500) na 1, 100 en na 500 jaar (respectievelijk time 1, time 100, time 500). De kleuren van de punten geven het bodemtype weer.

In Figuur 2.4.2.2 zijn dezelfde scenario's te zien als in Figuur 2.4.2.1 alleen dan op het niveau van de Maximale Waarde Industrie. Ook hier geldt dat de voorspelde uitloging van de stoffen Cd, Ni en Zn in zandgronden de MC gaat overschrijden. De mate van overschrijding is door de hogere Maximale Waarde echter gestegen van kleiner dan 10 x MC naar 10-100 x MC. Lood en Zn op klei- en veengronden vertonen ook toegenomen concentraties, echter ook hier moeten deze stoffen voorzichtig beoordeeld worden door de relatief lage MC en de relatief hoge transportsnelheid voor klei en veen.

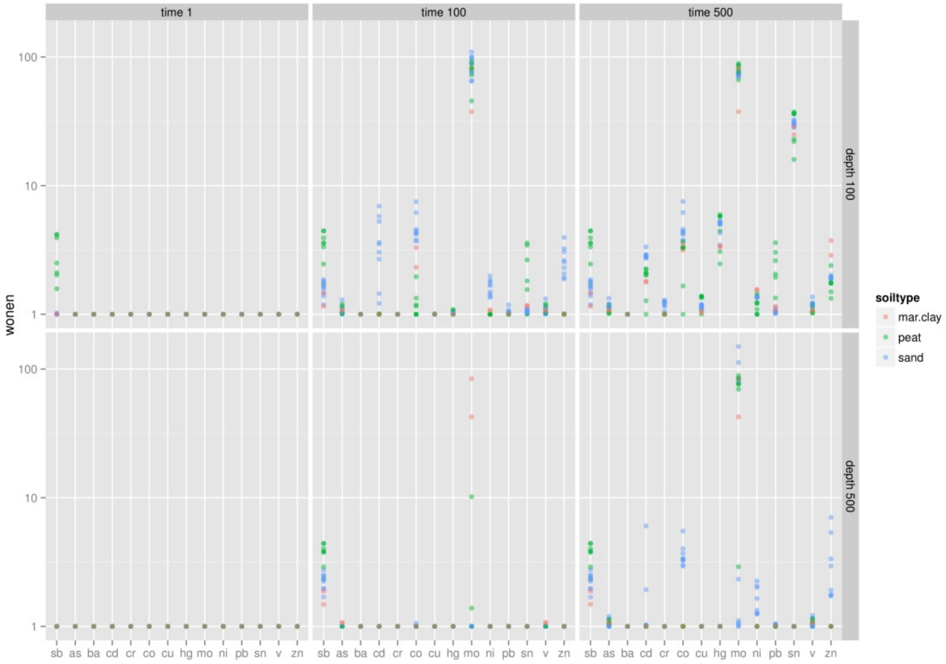


Figuur 2.3.2.2: Resultaten van de scenario's met een bodemconcentratie op het niveau van de Maximale Waarde Industrie. Concentraties van metalen/metalloïden zijn weergegeven als ratio van de piekconcentratie en de bodemtype specifieke MC. Piekconcentraties zijn berekend in de bodemlagen van 100-200 cm diepte (depth 100) en 500-600 cm diepte (depth 500) na 1, 100 en na 500 jaar (respectievelijk time 1, time 100, time 500). De kleuren van de punten geven het bodemtype weer.

2.4.3 *Resultaten uitloging bij duurzaam bodembeheer*

De voorspelde toename van de concentratie in het grondwater door uitloging uit de bodem vindt dus ook plaats bij bodems op het niveau van de Achtergrondwaarde. Daarom zijn de voorspelde grondwaterconcentraties als gevolg van de Maximale Waarden Wonen en Industrie vergeleken met de voorspelde grondwaterconcentraties als gevolg van de Achtergrondwaarde. De ratio tussen de grondwaterconcentratie die hoort bij de Maximale Waarden Wonen en Industrie met de grondwaterconcentratie als gevolg van de Achtergrondwaarde, op dezelfde diepte en tijd, geeft de mate aan waarin de grondwaterconcentraties toenemen ten opzichte van deze achtergrond.

Figuur 2.4.3.1 laat de ratio's zien van de Maximale Waarde Wonen. Op basis van de ratio's op 100 cm diepte en na 100 jaar is duidelijk dat de voorspelde concentraties van de elementen Sb, Cd, Mo, Co, Ni, Sn en Zn toe zullen gaan nemen. Verschillen tussen bodemtypen zijn ook zichtbaar. Bijvoorbeeld Cd, Co, Ni en Zn vertonen toenemende ratio's in zand terwijl Sb en Sn de hoogste ratio's vertonen in veen en klei. Ook in de diepere laag (500 cm) en na 500 jaar nemen de concentraties van Sb, Cd, Co, Mo, Ni en Zn toe, vooral in zandgronden.

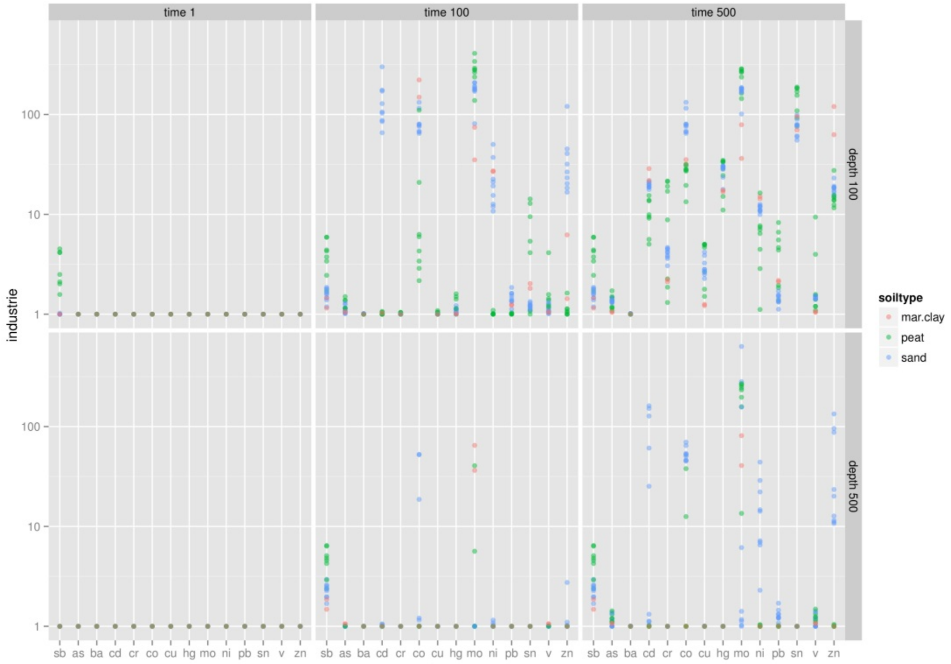


Figuur 2.4.3.1: De ratio van de grondwaterconcentratie onder bodems op het niveau van de Maximale Waarde Wonen met die van bodems op het niveau van de Achtergrondwaarde (y-as) voor 14 elementen (x-as). Voor ieder element zijn de resultaten van de set van 20 standaardscenario's (n = 15) op het niveau van de Maximale Waarde Wonen weergegeven als punt, waarbij het bodemtype de kleur van de punt bepaalt (mar.clay: klei; peat: veen; sand: zand). Elk paneel in de figuur geeft een combinatie van een tijdspanne en diepte. Kolommen tonen tijdspanne van 1, 100 en 500 jaar. Rijen geven dieptes aan van 100-200 cm (depth 100) en 500-600 cm (depth 500).

In Figuur 2.4.3.2 zijn de ratio's te zien met de Maximale Waarde Industrie. De ratio's van Cd, Co en Mo zijn binnen 100 jaar met een factor 10 tot 100 gestegen in vergelijking met de situatie met schone bodems (Achtergrondwaarde). Voor Ni, Sn en Zn zijn deze ratio's een factor 10 gestegen.

Na 500 jaar, op 100 cm diepte, zijn de ratio's van Cd en Co veel lager dan na 100 jaar. Dit wordt veroorzaakt doordat ook het referentiescenario, de uitloging uit bodems met een Achtergrondwaarde en de resulterende grondwaterconcentratie, ook in de tijd verandert.

In het diepere grondwater, op 500 cm diepte, na 500 jaar is ook een duidelijke toename van de voorspelde grondwaterconcentraties te zien. Ook hier vertonen Cd, Mo en Zn ratio's van 10 tot 100 keer hoger dan de achtergrondsituatie. Cobalt en Ni zijn ongeveer een factor 10 hoger dan de achtergrondsituatie. Antimoon wordt in deze discussie buiten beschouwing gelaten, het model kan deze waarden nog niet betrouwbaar voorspellen. (zie hoofdstuk 7).



Figuur 2.4.3.2: Resultaten van de 20 standaardscenario's met bodemconcentraties op het niveau van de Maximale Waarde Industrie. Voor verdere beschrijving zie onderschrift Figuur 2.4.3.1.

2.5 Discussie en conclusies

Uit de analyse blijkt dat voor bodems op het niveau van de Maximale Waarden Wonen en Industrie de voorspelde uitloging van de elementen Cd, Co, Ni, Mo, Sb, Sn en Zn leidt tot grondwaterconcentraties die een factor 10 tot 100 hoger liggen dan de grondwaterconcentraties onder bodems met een Achtergrondwaarde. Bij deze resultaten moeten de volgende kanttekeningen geplaatst worden:

1. De modellering van Sb is erg onzeker doordat de wetenschappelijke kennis over het gedrag van dit element onvoldoende is. De voorspellingen van het model voor dit element we daarom te weinig betrouwbaar.
2. De Maximale Waarden Wonen en Industrie voor Mo liggen bodemchemisch gezien op een extreem hoog niveau waarbij vorming van minerale neerslagen plaats kan vinden. Deze neerslagvorming is om inhoudelijke redenen in het model uitgezet (zie paragraaf 7.9), met als gevolg zeer hoge Mo-concentraties in het grondwater. Deze voorspelde concentraties van Mo vinden we daarom ook weinig betrouwbaar.
3. Uitgangspunt bij de modellering is dat de toegevoegde concentratie van het metaal/metalloïden reactief is. Voor Sn betekent deze aanname dat de berekende invoerconcentratie behorend bij de Achtergrondwaarde al een factor 10 tot 100 boven de werkelijk gemeten reactieve concentratieniveaus in de Nederlandse bodems ligt.

In het model worden ook concentraties aangenomen voor veel voorkomende ionen in het poriewater, zoals Ca^{2+} en SO_4^{2-}. Deze concentraties zijn relatief hoog en gedurende het onderzoek bleek dat deze concentraties een factor 10 omlaag kunnen. Dat betekent ook dat er minder competitie is met andere (kat)ionen met als gevolg een lagere uitloging van de beschouwde metalen/metalloïden. Dit leidt voor de meeste van deze stoffen tot grondwaterconcentraties die ongeveer één ordegrootte lager zullen liggen.

Naast het vergelijken van veranderingen in voorspelde concentraties op basis van ratio’s moet ook gekeken worden naar de absolute concentraties in grondwater. Voor de Maximale Waarden Wonen en Industrie van Sn overschrijden de voorspelde grondwater concentraties op 1 meter diepte alleen de MTT bij veenbodems na 500 jaar. De elementen Cd, Co, Ni en Zn overschrijden in veel scenario's de MTT en de concentraties in het grondwater nemen in de tijd ook toe.

2.6 Advies voor het bodem- en grondwaterbeleid

In deze studie is een grote hoeveelheid kennis, data gecombineerd met modellering van stofgedrag in de bodem. De resultaten van deze studie omvatten niet alleen modelresultaten maar ook veel nieuwe kennis die ingezet kan worden bij het ontwikkelen van bodem- en grondwaterbeleid. De hieronder genoemde aanbevelingen, benadrukt in cursief, richten zich op het toepassen van deze nieuwe kennis.

Op basis van de voorspellingen van het huidige model is te verwachten dat bij de Maximale Waarden Wonen en Industrie grondwaterconcentraties voor Cd, Co, Ni en Zn toe kunnen nemen ten opzichte van de Achtergrondwaarde. Van deze vier stoffen zijn Cd, Ni en Zn bekend als stoffen die regelmatig worden aangetroffen in verhoogde concentraties in bodem en grondwater. *Wij adviseren om de voorspelde uitloging van Cd, Ni en Zn nader te onderzoeken aan de hand van een meer specifieke (hydrologische) opzet van het mode en praktijkgegevens, en te onderzoeken in welke praktijksituaties deze stoffen daadwerkelijk in verhoogde concentraties in het grondwater voor kunnen komen.* Vervolgens kan beter beoordeeld worden of deze verhoogde concentraties risico inhouden voor het ecosysteem of voor ecosysteemdiensten. Op basis hiervan kan ook beoordeeld worden of aanpassing van het generieke bodembeleid wenselijk is, of dat locatiespecifiek beleid in kwetsbare gebieden de voorkeur verdient. In het locatiespecifieke bodembeleid kan bijvoorbeeld vastgelegd worden welke functies het grondwater heeft voor de lokale ecosysteemdiensten. Door terug te rekenen van gewenste grondwaterconcentratie naar bodemconcentratie kan een lokale Maximale Waarde worden vastgesteld.

De Maximale Waarden worden gecorrigeerd met de bodemtypecorrectie. In Spijker (2012), op basis van nieuwe inzichten, is een aantal tekortkomingen geconstateerd van deze correctie. Daarnaast vermeldt Spijker (2012) een mogelijke oplossing van deze tekortkomingen. Het gebruik van de bodemtypecorrectie leidt bij Ni en Zn tot hogere concentraties voor de Achtergrondwaarde in klei-arme zandgronden ten opzichte van de natuurlijke achtergrond. Deze relatief hoge Achtergrondwaarde leidt ook tot een hogere uitloging. *Wij adviseren om aanpassingen van de bodemtypecorrectie in het Besluit Bodemkwaliteit en elders in het beleid door te voeren*. Daarbij kan ook aandacht besteed worden aan de correctie van de Achtergrondwaarde in arme zandgronden met lage natuurlijke metaalconcentraties.

In deze studie zijn de gemodelleerde grondwaterconcentraties vergeleken met drie eindpunten: de huidige grondwaterconcentraties, de Maximale Toelaatbare Toevoeging (MTT) en de voorspelde grondwaterconcentratie behorend bij de Achtergrondwaarde. Voor het ontwikkelen van het grondwaterbeleid is het belangrijk de verschillen tussen de eindpunten te kennen. De huidige grondwaterconcentratie is de concentratie die men nu aantreft in het grondwater. Uitgaande van het stand still-principe, of het 'prevent en limit'-principe uit de Kaderrichtlijn Water zal op korte termijn (enkele tot tientallen jaren) deze concentratie niet mogen stijgen. De modelvoorspellingen in dit rapport wijzen er echter wel op dat op de lange termijn (tientallen tot honderden jaren) deze concentratie voor sommige stoffen, zoals Cd, Ni en Zn, wel gaan toenemen door de uitloging uit de diffuus verontreinigde bovengrond. De grondwaterconcentraties die horen bij de uitloging op lange termijn zijn de gemodelleerde grondwaterconcentraties als gevolg van de Achtergrondwaarde. Voor deze grondwaterconcentraties geldt dat naast temporele veranderingen ook gekeken moet worden naar de risiconiveaus, zoals bepaald door het MTT. Grondwater heeft een functie binnen diverse ecosysteemdiensten gerelateerd aan bijvoorbeeld natuur, drinkwater en landbouwproductie. Overschrijding van een risiconiveau zou kunnen betekenen dat bepaalde ecosysteemdiensten (of functies) in gevaar komen. *Wij adviseren om bij het ontwikkelen van grondwaterbeleid rekening te houden met de voorspelde korte en lange termijn ontwikkelingen van de grondwaterkwaliteit.*

Deze studie toont aan dat het voor de metalen Ba, Cd, Co, Cr, Cu, Ni, Pb, Sn, V en Zn mogelijk is om een goede inschatting te maken van de uitloging uit de bodem naar het grondwater. De resultaten van Hg zijn in de modelevaluatie niet getoetst. Voor Mo is dit ook mogelijk op het niveau van de Achtergrondwaarde. De voorspelling van As zou verbeterd kunnen worden door aanpassingen in de parameterisatie van het model. Voor Sb is het nog niet mogelijk om het stofgedrag goed te voorspellen. Bij het opstellen of aanpassen van duurzaam bodembeleid is het mogelijk om de impact van het bodembeleid op grondwater te voorspellen. Met het model is het ook mogelijk om de uitloging uit bouwstoffen, (grote) bodemtoepassingen of andere bronnen te beoordelen. In de kamerbrief 'Groene Groei' (Kamerbrief, 28 maart 2013) worden diverse ontwikkelingen beschreven voor een duurzame ontwikkeling binnen de maatschappij, waaronder de circulaire economie. Hergebruik van grond- en afvalstoffen is daar onderdeel van. Bij de beoordeling van hergebruikstoffen, zoals nu al in het bouwstoffenbeleid toegepast wordt, is een goed beoordelingsmodel een vereiste. *Wij adviseren om de kennis die is opgedaan in deze studie te gebruiken om de doelen rond hergebruik van materialen en ambities rond de circulaire economie in relatie te brengen met het te ontwikkelen duurzame bodem- en grondwaterbeleid.*

De basisgegevens voor deze studie, voor zowel bodem als grondwater, zijn gebaseerd op gegevens uit het landelijk gebied van Nederland. Specifieke gegevens over stedelijke gebieden waren in deze studie niet voorhanden. De belangrijkste oorzaak hiervan is het gebrek aan goede (wetenschappelijke) gegevens over bodemeigenschappen en de huidige kwaliteit van het stedelijk grondwater. Ook de hydrologie en het transport van metalen in steden is anders dan in het landelijk gebied. *Wij adviseren om onderzoek naar gedrag van stoffen in het stedelijk bodem- en grondwatersysteem te stimuleren en aan te laten sluiten op de kennis uit dit onderzoek*. Dit betekent niet dat er gedetailleerd onderzoek nodig is in stedelijk gebied. Het gaat vooral om gegevens waarmee de resultaten van deze studie in het perspectief van de stedelijke omgeving geplaatst kunnen worden. Gegevens over de bandbreedtes van concentraties van metalen en metalloïden in de stedelijke bodem en het grondwater samen met bodemkenmerken (zoals pH, organisch stof, korrelgrootteverdeling, ijzergehalten) van de stedelijke bodem zijn al een goede eerste stap. Daarmee wordt het ook mogelijk om de impact van het stedelijk bodembeheer (en andere stedelijke bronnen) op het grondwater inzichtelijk te maken.

Vanuit technisch oogpunt is het model een goed werkend prototype. *Wij adviseren om het model verder uit te laten bouwen tot een meer algemeen toepasbaar model voor het beantwoorden van vragen over de relatie tussen bodembelasting en grondwaterkwaliteit en voor het stellen van randvoorwaarden voor duurzaam bodembeheer.* Hiermee is het mogelijk om instrumenten ('tools') te maken voor het bodem- of grondwaterbeleid en deze kunnen ook gebruikt worden als basis voor een grondwatermodule in de RisicoToolbox Bodem. Hiermee kan dan bepaald worden welke grond gevoelig is voor uitloging en wat de verwachte toekomstige grondwaterconcentraties kunnen worden. Vervolgens kunnen decentrale overheden bepalen of deze concentraties kunnen worden geaccepteerd of niet.

2.7 Aanbevelingen voor nader onderzoek

Tijdens deze studie is een aantal technische verbeterpunten geconstateerd. Van sommige aannames in het model is het mogelijk om deze meer in overeenstemming te brengen met de werkelijkheid. Keuzes met betrekking tot de achtergrondconcentratie van belangrijke ionen zoals Ca^{2+} en SO_4^{2-}, mate van reactiviteit en aanwezigheid van combinaties van metalen kunnen al aangepast worden. Wij bevelen aan om de resultaten van deze studie nogmaals uit te rekenen met de aangepaste aannames (zie Bijlage C).

Bij de voorgestelde herberekening van de resultaten kan ook aandacht besteed worden aan beschikbare computerfaciliteiten. Hierdoor zal het mogelijk worden om ook een landsdekkend beeld te berekenen voor de Maximale Waarden Wonen en Industrie. Deze twee maximale waarden kunnen nu voor een beperkt aantal scenario's afgezet worden tegen de Achtergrondwaarde. Als een landsdekkend beeld beschikbaar komt voor alle maximale waarden, dan ontstaat er een meer betrouwbaar beeld van de impact van de Maximale Waarden op het grondwater. Daarnaast kunnen ook kaarten gepresenteerd worden van deze impact.

Daarnaast kan aandacht besteed worden aan het gebrek aan resultaten van scenario's van kleigronden met hoge pH-waarden. Deze scenario's zijn nu verworpen doordat het model niet tot een goede oplossing kan komen. Hoewel de noodzaak voor het uitrekenen van deze scenario's beperkt is, er wordt nauwelijks uitloging verwacht, is het wel gewenst gezien de mogelijke ontwikkeling van toekomstige instrumenten. In deze studie zijn een groot aantal modelparameters voor de verschillende bodemtypes gelijk gehouden in verband met de vergelijkbaarheid. Door de modelparameters voor kleigronden aan te passen zal het mogelijk zijn om ook voor deze bodems de uitloging te berekenen.

Een herhaling van de berekeningen van het aangepaste model, waarin bovenstaande aanbevelingen worden meegenomen, vergt veel rekentijd en computerfaciliteiten, maar een beperkt aantal mensuren.

3 Description of the soil and groundwater system in the Netherlands and its relevance for soil policy.

3.1 Concise description of the soils of the Netherlands

A concise description of the soils of the Netherlands aimed at soil geochemistry can be found in Van Der Veer (2006, Chapter 2). The following text is an edited excerpt from this description:

The current land surface of the Netherlands (excluding inland water) amounts to 33,873 km^2, which supports a population of about 16 million inhabitants. About 70% of the land surface is used for agricultural purposes, while some 17% consists of built-up areas. The remaining 13% is used as managed forest and nature reserves.

The soil parent material in the Netherlands consists of Pleistocene sediments, which are mainly found in the elevated northern, eastern and southern parts of the Netherlands, and Holocene sediments, which are mainly confined to the low-lying coastal areas in the southwest, west and north. Whereas the Pleistocene deposits are made up of coarse river deposits and various glacigenic deposits that are largely overlain by locally reworked eolian sediments, the Holocene deposits consist of clayey marine and fluvial sediments alternated with extensive peat layers. On the basis of the lithogenesis of the topsoil layer, five parent material districts are distinguished; sand, loess, peat, marine clay and fluvial clay districts (see Figure 3.1.1).

The morphology of the Pleistocene area, which was shaped by glaciers, consists of sand plains covering river sediments (relief <1 m), and ice-pushed ridges with altitudes up to 105 m above sea level. According to Frapporti et al. (1993) the sandy Pleistocene formations contain generally over 90 wt-% quartz, about 5 wt-% K-feldspar, less than 1 wt-% of heavy minerals (e.g. epidote, hornblende, garnet), and locally pyrite. Most sandy formations also contain carbonate minerals, generally between <2% and 20%. In more elevated areas (cover sands and ice-pushed ridges) the carbonate minerals have been leached out (Frapporti et al., 1993).

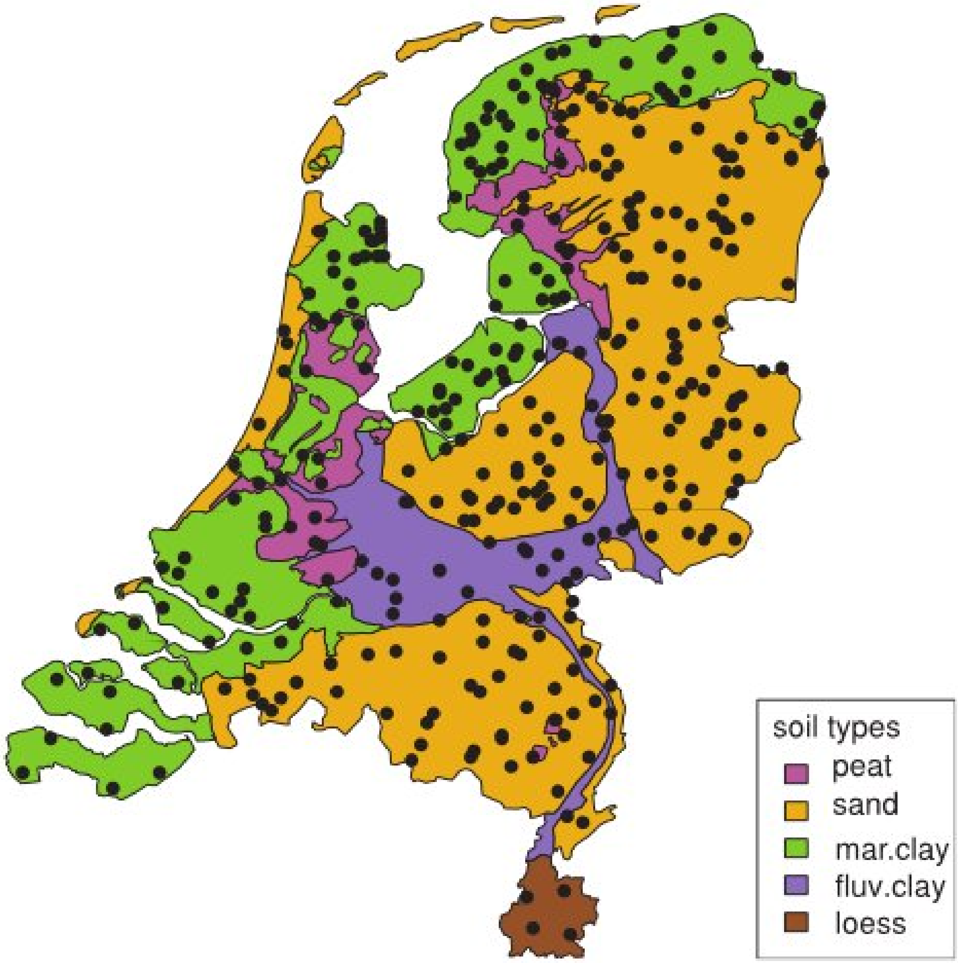


Figure 3.1.1: Simplified soil map. Dots show the sampling locations from the Dutch Geochemical Atlas (Van Der Veer, 2006: Mol et al., 2012).

Soil formation started around the end of the Pleistocene in the Pleistocene deposits (sand and loess), but much later in the Holocene deposits (marine and fluvial clays and peat). During the Holocene, the climate has been fairly constant and classifies as a moderate sea climate. Average daily temperatures range between 2 degrees Celsius in January and 16 degrees Celsius in July and the yearly precipitation varies between 400 mm and 1,200 mm. Due to the 0 restricted evapotranspiration, there is an average precipitation excess of ~300 mm, resulting in a net leaching of the soils. See Van Der Veer (2006) for further details.

3.2 Concise description of the Dutch groundwater system

The hydrogeology of the shallow groundwater aquifers can roughly be divided between the Pleistocene and Holocene areas. Most aquifers are shallow, with a mean groundwater level within the first two metres. The Holocene deposits are in general below sea level, with upward groundwater seepage as a result. The Pleistocene areas are above sea level and the areas with a higher altitude (a few tens of metres above sea level) can have groundwater levels of a few metres below the surface.

The Pleistocene deposits form the major fresh water aquifers in the Netherlands. These aquifers are recharged by precipitation, while being discharged through a natural drainage system of rivers and brooks, and an artificial system of ditches and canals. Large-scale reallotment of farmland, accompanied by the excavation of deep ditches, irrigation and groundwater abstraction for drinking water and industry, have a great impact on the hydrological situation (Frapporti et al., 1993).

Groundwater below Holocene deposits is often brackish. The sediments are deposited in a peat and salt marsh environment consisting of clay cover and cut by sand-and clay-filled erosion channels. Maximum carbonate content in marine deposits is around 10 wt-% CaO (Mol et al., 2012). Large areas have been reclaimed from the sea and are surrounded by dikes to prevent inundation. These areas are below sea level, down to about 6 m, and as a result high upward groundwater seepage rates occur in these areas.

4 Materials and methods: natural background concentrations, reactive concentrations and concentrations in groundwater

The model used for this study (described in the next chapter) uses geochemical soil data as input, and the modelling results are compared with groundwater concentrations. This chapter describes how the geochemical soil and groundwater data are obtained. This includes modelling of the geochemical data to get to the input values needed for the model described in Chapter 5.

For the modelling we use the principle of the added risk approach. In this approach a distinction is made between natural background concentrations and the anthropogenic added concentration. The risk level associated with the added concentrations is the Maximum Permissible Addition (MPA). For more information see Section 5.2.1.

4.1 Assessment of natural baseline concentrations and enrichment in rural areas

In this section we show how we estimate natural background concentration and anthropogenic enrichment. Since natural background concentrations vary spatially, we use the concept of a baseline, which describes these varying concentrations for geochemically undisturbed soils. We then show how to derive the anthropogenic enrichments, which are defined as the difference between the actual concentrations and the natural baseline concentrations. Finally, we show the relation between this enrichment and reactivity.

4.1.1 Baseline model

The aim of the baseline model is to describe the natural variability between the bulk geochemistry and trace elements in a simple statistical manner. The baseline model is based on geochemically unaltered subsurface sediments (80120 cm depth). This approach resembles the model currently used in the Soil Type Correction mentioned in the SQD. However, the baseline model is not based on clay size fraction, like the Soil Type Correction, but on Al_2O_3. Some authors have already pointed out that there is a close relation between trace elements and bulk geochemistry. Spijker (2005) and Van Gaans et al. (2007) have shown that for the marine clayey soils in the southwest of the Netherlands a strong relation exists between trace element geochemistry and Al_2O_3 as measured by X-ray Fluorescence (XRF). Spijker (2005) used a relation where the trace element content was expressed as a function of Al_2O_3, using an ordinary least squares linear regression model. Van der Veer (2006) showed that the same method of regression as used by Spijker (2005) applies to all major soil types in the Netherlands. Therefore, Al_2O_3 was chosen as the predicting variable for the baseline model.

Organic matter is not part of the model. Van der Veer (2006) showed that organic matter content is partly related to mineral organoclay aggregates in soil. This means that a part of the variability of trace elements with organic matter is explained by variability in clay content, which is covered by variability in Al_2O_3. Spijker et al. (2008) showed that adding organic matter as a variable to the baseline model does not improve the estimation of natural background concentration; hence organic matter was excluded from the model.

The baseline model is a robust regression model using the Least Quantiles of Squares (LQS) algorithm (Leroy and Rousseeuw, 1986). Based on the results of Spijker (2005) and Van der Veer (2006), the following linear model was used for the LQS regression:

$$C = \beta_0 + \beta_1 C_{\mathrm{Al}} + \varepsilon \tag{4.1}$$

Where C is the estimated total trace element concentration, using C_{Al} expressed as Al_2O_3 in wt-%. The regression parameters $\beta_{0,1}$ are calculated using the LQS method mentioned above. The regression error ε gives the residual variance, which represents the variation not explained by the variability in Al content.

According to Leroy and Rousseeuw (1986) the linear interval of 2.5ε is similar to the range of the normally distributed residuals. Since the LQS method does not assume normality of the data, no values determining the significance of the regression are derived.

Spijker (2012) showed that the baseline model gives a good prediction of variability in natural background concentrations. Baseline models (Figure 4.1.1.1) were created for As, Ba, Be, Cd, Cr, Cu, Pb, V, Zn, Ni, Sb and Sn. The model parameters can be found in Spijker (2012). This figure shows how accurate the prediction of the baselines is. A model was created for each distinct soil lithology in the Netherlands (peat, sand, fluvial clays and marine clays) and a generic model was created for all the four soil lithologies together. A map of lithologies and the spatial concentrations of Al_2O_3 are shown in Figure 4.1.1.2.

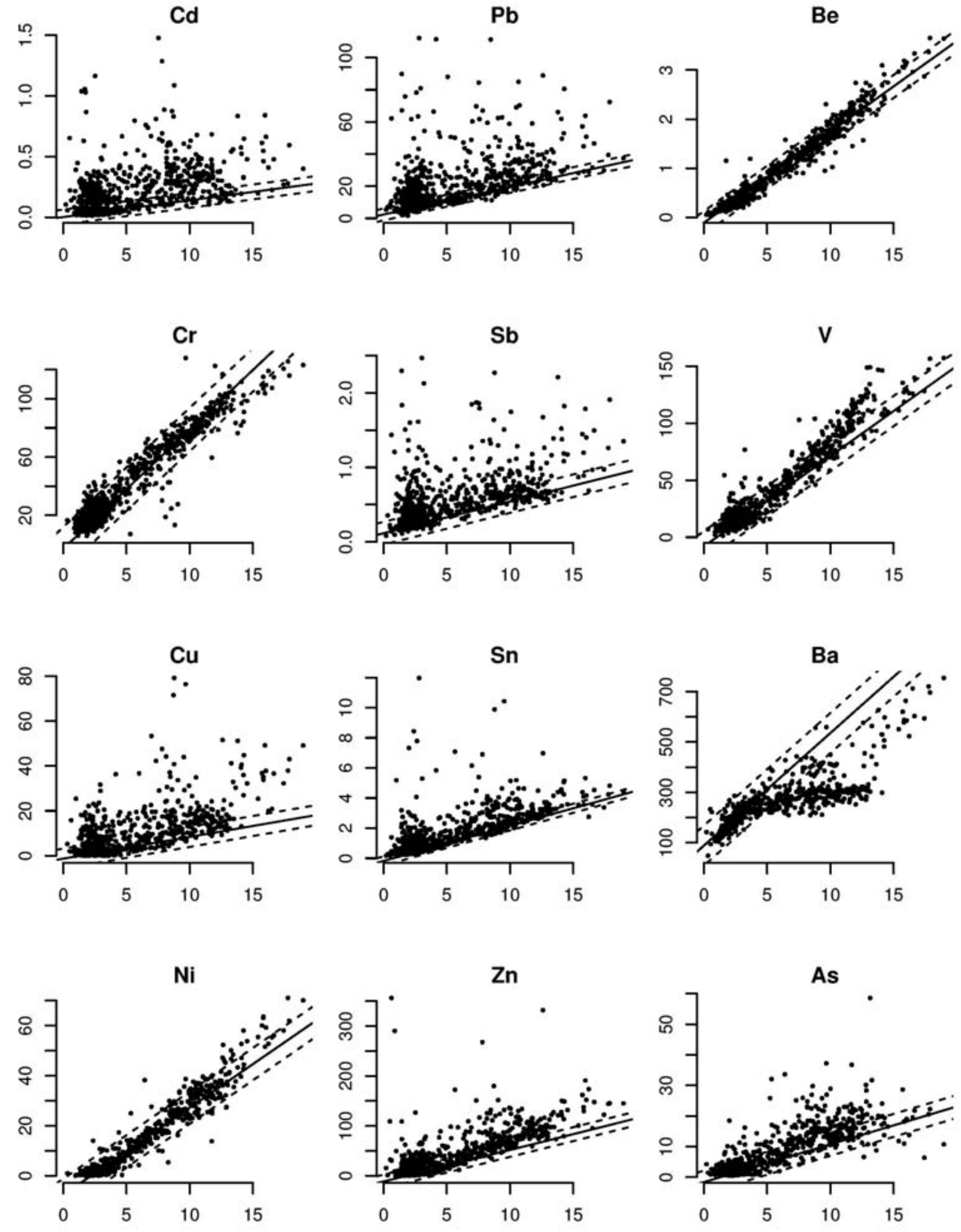


Figure 4.1.1.1: Plots of each element (y-axis) against Al_2O_3 (x-axis). Element concentrations are in mg/kg, Al_2O_3 concentration is in wt-%. The black dots are subsoil concentrations. The lines denote the generic regression model: the solid line is the LQS regression line, the dashed lines are the regression error (2.5ε). From Spijker (2012).

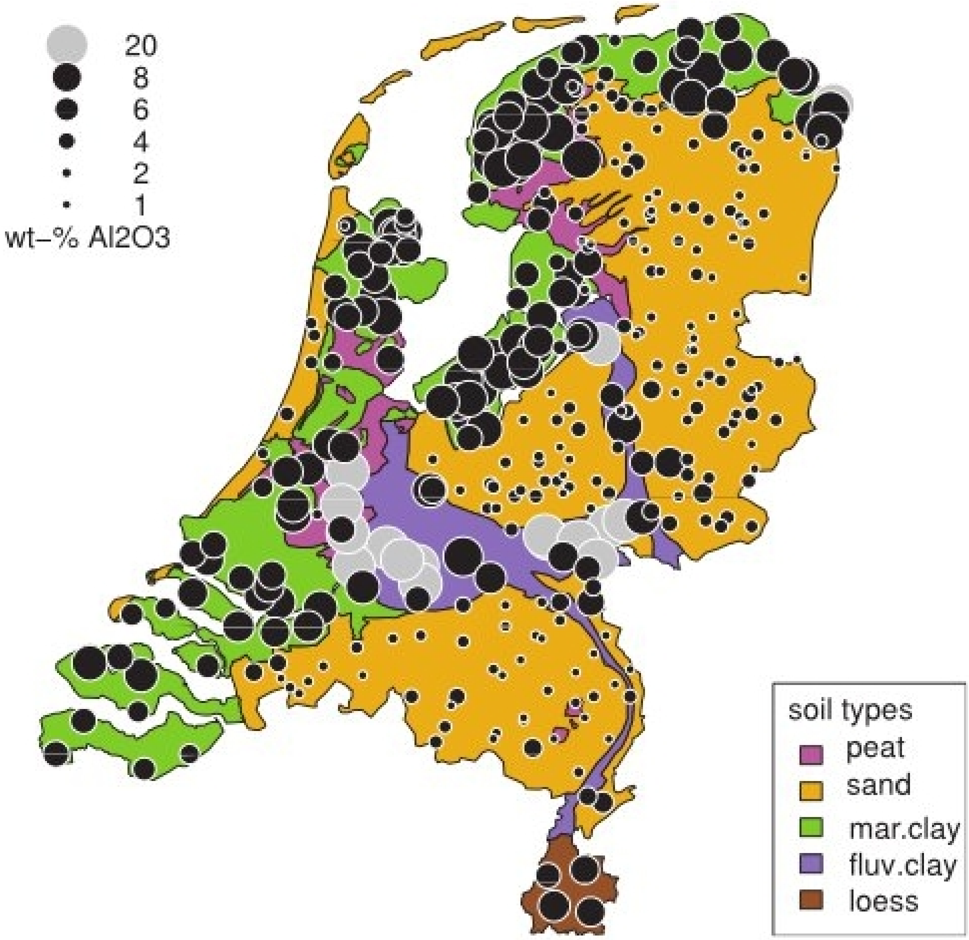


Figure 4.1.1.2: Map showing the spatial distribution of Al_2O_3 *in the Netherlands in relation to the four major soil lithologies and loess.*

4.2 Anthropogenic enrichment and reactivity

Using these baseline models, the estimated concentrations can be compared with the actual measured concentrations; this gives the enrichment of elements compared to the baseline. Based on the ratio between estimated baseline concentrations and enrichment, the elements Cd, Pb, Sb, Zn and Cu are in general considered as enriched.

Figure 4.2.1 gives four examples of the baseline models: for Cd, Cu, Pb and Zn (Spijker et al., 2011). On the left-hand side of the figure it can be seen that the topsoil concentrations (black circles) are enriched in comparison with the subsoil concentrations (green crosses). Considering that the baseline model gives the natural background concentration as needed by the added risk approach, the enrichment then defines the added fraction (the risk level, see Section 5.2.1). An assumption in the added risk approach is that this added fraction, the enrichment, is fully reactive while the background is inert. On the right-hand side of Figure 4.2.1 the relation between reactivity (i.e. potential availability) and enrichment is depicted. The 1:1 line is shown for comparison. From the figure it is apparent that the reactivity of these four metals is indeed comparable with the enrichment, considering the scatter around the 1:1 line. This agrees with the assumption behind the added risk approach, although for Zn the reactivity is somewhat overestimated.

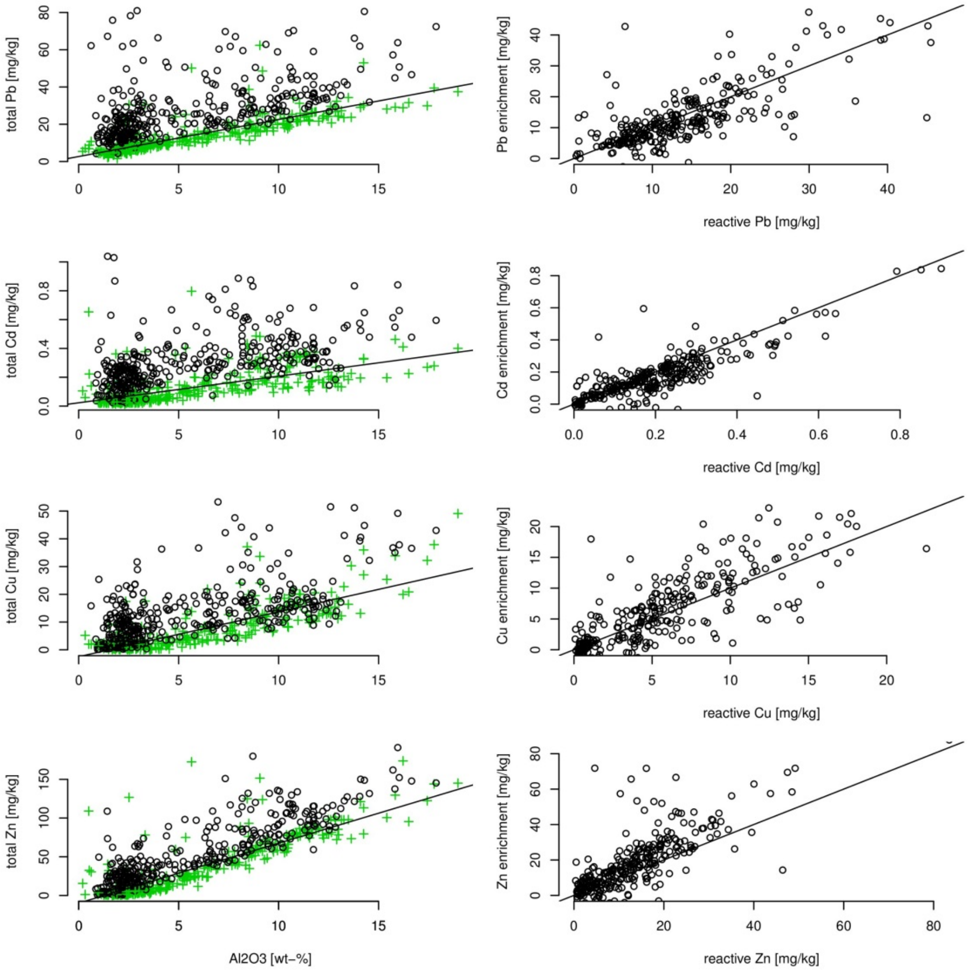


Figure 4.2.1: (Left) Scatter plots depicting the way in which metal enrichments in the topsoil are estimated by a geochemical baseline model; green crosses, subsoil sample metal concentrations; lines, Al_2O_3 baseline models; black circles, topsoil sample metal concentrations. (Right) Linear relationships between reactive metal concentrations (0.43 M HNO_3 extractable metal concentrations) and enrichments (topsoil concentrations mines baseline-estimate concentrations). The line depicts the 1:1 relation.

4.3 Reactivity of background concentrations in soil

In the previous section we explained how we can obtain an estimate of the reactivity of enriched soil. In such soil, the reactivity can be explained by the enriched concentrations. But for non-enriched soils, i.e. soils with concentrations at the level of the natural background, another estimation is needed. For most elements, both total and reactive concentrations are available from the Dutch Geochemical Atlas. Subsoil samples from this atlas indicate no enrichment and are used for the natural baseline concentrations. We used the ratio between the total and reactive subsoil concentrations as a partition coefficient to estimate the reactivity of non-enriched soils, according to:

P = measured reactive concentration / total concentration

*estimated reactive concentration = total concentration * P*

For each element and for each soil layer (top- and subsoil), we divided the reactive concentrations in each sample by the total concentration of the same sample. This resulted in a range of ratios which are depicted in Figure 4.3.1. From this range we took the median value as partition coefficient. These partition coefficients are listed in Table 4.3.1.

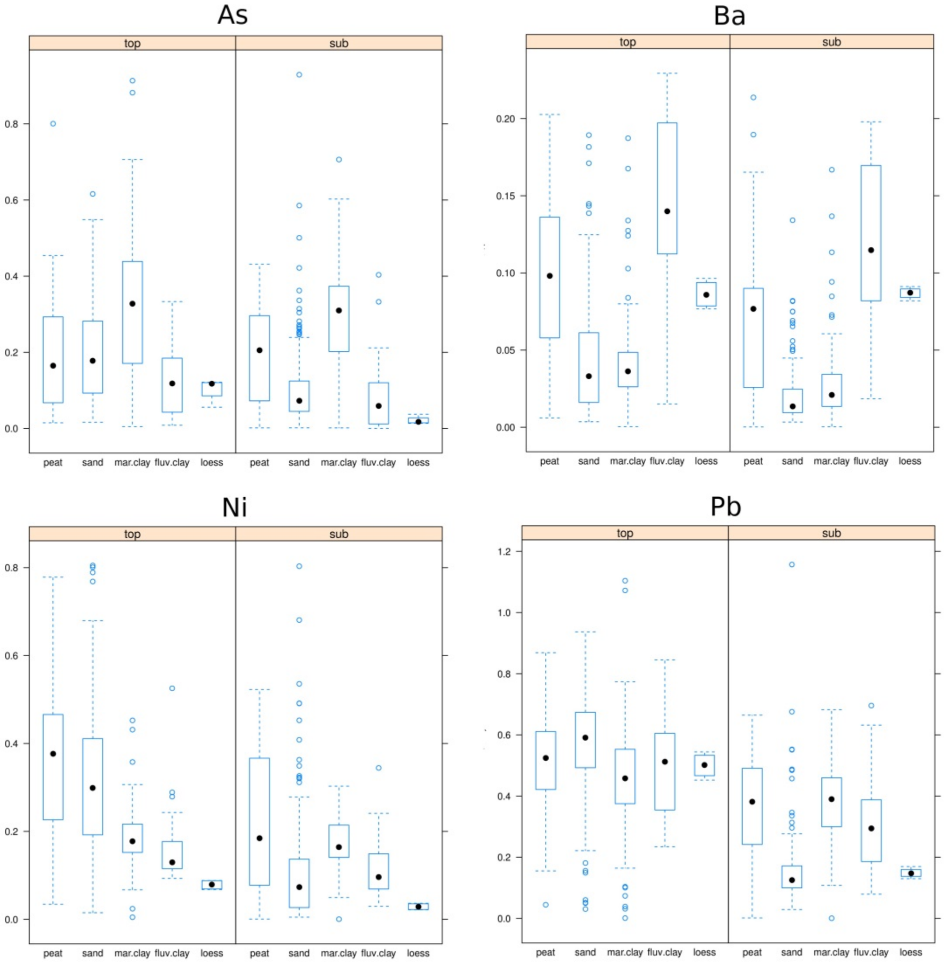


Figure 4.3.1: Example figures showing box-and-whisker plots of reactive/total concentration ratios

Table 4.3.1: Ratios of reactive/total concentrations in the four soil types

Layer	Soil type	As	Ba	Cd	Cr	Cu	Ni	Pb	Sb	Sn	V	Zn
top	fluv. clay	12	22	69	2	44	13	51	4	0.3	9	20
	loess	12	9	73	1	53	8	50	4	0.4	13	29
	mar. clay	33	4	68	2	41	18	46	4	0.4	11	17
	peat	16	13	77	3	31	38	53	4	0.8	22	41
	sand	18	3	77	3	56	32	59	6	1.1	20	52
sub	fluv. clay	6	24	50	2	35	10	29	2	0.2	7	12
	loess	2	9	19	1	14	3	15	1	0.2	3	6
	mar. clay	31	2	46	2	37	17	39	3	0.3	9	14
	peat	21	8	62	2	23	31	38	2	2.0	16	33
	sand	7	1	18	1	28	8	13	3	1.3	3	15

4.4 Actual concentrations in shallow groundwater

In this study the emission from soil into groundwater is estimated. To put this emission into perspective, a criterion is needed to assess the resulting groundwater concentrations. In earlier studies, using the principle of the added risk approach, the Maximum Permissible Addition (MPA) was used as the criterion (see Section 5.2.1). However, this MPA is not related to actual groundwater concentrations. Where the MPA was a minor fraction of the actual groundwater concentration, exceedance of the MPA suggested an unacceptable situation while in reality this exceedance was irrelevant compared with the variability of actual groundwater concentrations.

For this study we wanted to compare the leached concentrations with actual concentrations in shallow groundwater from the same area. Therefore, we aimed to establish a criterion, a concentration limit, for groundwater. This criterion should be based on the variance of concentrations as observed in the different shallow groundwater types and be independent of situations influenced by local or sub-regional pollution. Therefore, the aim of this analysis was to derive a robust upper limit of shallow groundwater concentrations for each groundwater type. These groundwater types are often based on arbitrary criteria based on the chemical composition of major elements. In line with Frapporti et al. (1993) we chose to base the groundwater types on the covariance of both major and minor elements, preventing the need for arbitrary criteria.

4.4.1 Materials and method

For this analysis, the groundwater data from the National Minerals Policy Monitoring Network was used, in which concentrations were measured in the first metre of groundwater under agricultural plots using a piezometer or measured in groundwater from drains which discharge the water infiltrating the plot . The locations of these measurements are shown in Figure 4.4.1.1. Each year, several measurements were taken from the location and measurements were averaged over each year. From the years 1994–2009, all samples were added to the dataset. If a sample was not complete, because not all the required elements were measured, the record was deleted. The final database contained 2,233 samples from 612 locations.

To group the groundwater data a fuzzy c-means (FCM) clustering was applied to the dataset, according to Frapporti et al. (1996). The components As, Ca, Cl, Cu, Fe, Mg, Mn, K, Na, NH4, Ni, NO_3, total P, SO_4 and Sr, together with pH and DOC, were used to create the FCM model. After the clustering the elements Cd, Cr, Pb and Zn were added to the dataset so that their variability in concentration could be assigned to one of the resulting clusters.

To obtain a criterion based on the variance of ambient concentrations, it was chosen to set it at the upper limit of the actual measured concentrations. This upper limit was defined by the 95th percentile. However, in the presence of outliers, for example as the result of local pollution, the uncertainty in the 95th percentile can be large. To create a more robust 95th percentile, the median and the median absolute deviation (MAD) were used. The MAD is defined as:

$$MAD = median(|Xi - median(X)|)$$

Where X is a normal distributed dataset (X1,X2,X3,…,Xn) and Xi is the i^{th} element of this set. The MAD is equal to the standard deviation σ according to:

$$\hat{\sigma} = \frac{1}{\phi^{-1}(3/4)}$$

In which φ^{-1} is the inverse of the cumulative distribution. Then for a normal distribution Z, with $\sigma = 1$, it is true that:

$$\hat{\sigma} \approx \frac{1}{0.67} \approx 1.4925$$

Also for Z it is true that the $median = 0$ and the $MAD \cdot 1.4826 \approx \sigma$. And for Z the 95th percentile $p95 \approx 1.64$. So $p95 \approx 1.64\sigma \approx 1.64 \cdot 1.49 \cdot MAD \approx 2.43 \cdot MAD$.

In conclusion, when the data are normally distributed, the 95th percentile is equivalent to the median plus $2.43 \cdot MAD$. This criterion is called the MAD criterion or MC in this report. Assuming that logarithmically transformed trace element concentrations follow a normal distribution with an ‘enriched’ distribution of diffuse contamination superimposed on it, the MC is robust towards the added variability of the superimposed distribution.

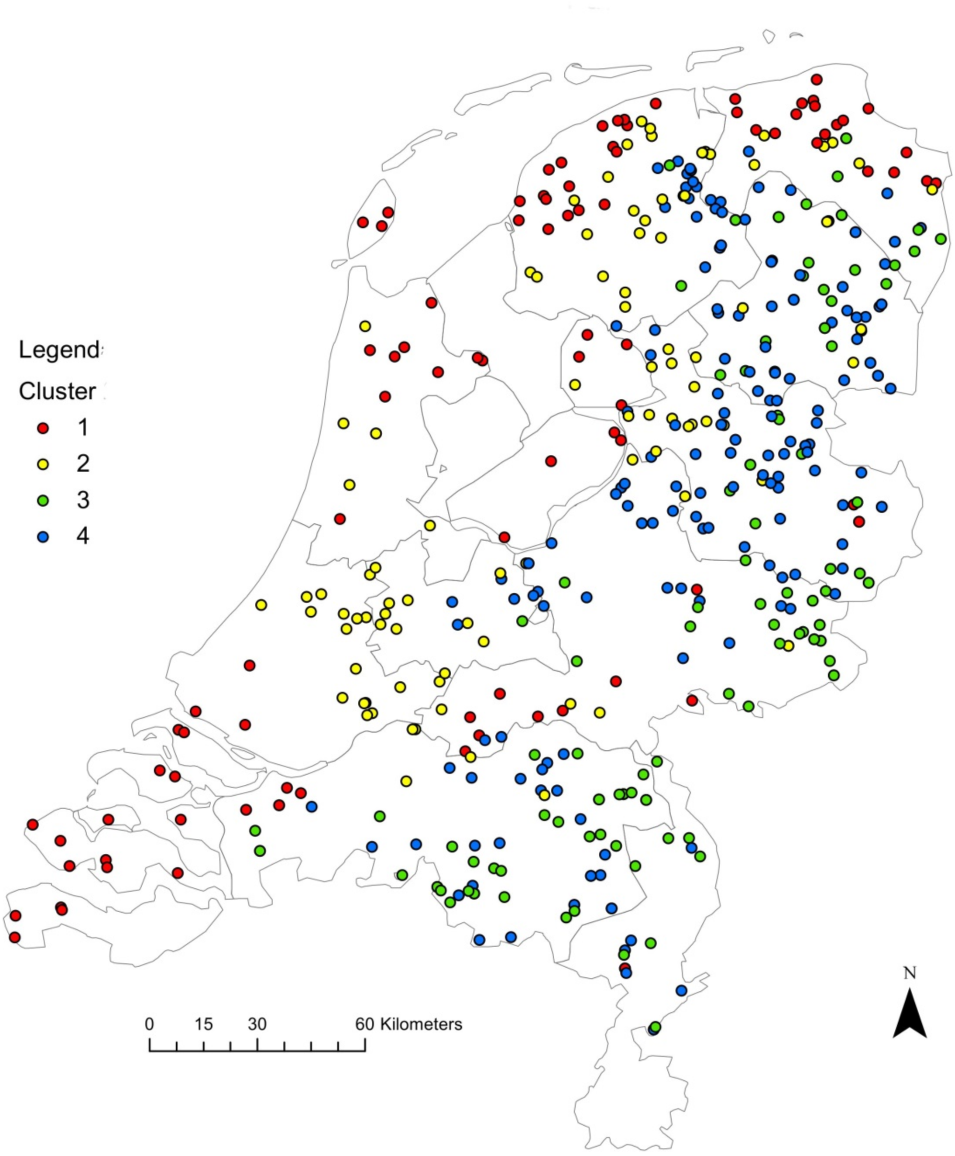


Figure 4.4.1.1: Sample locations of the National Minerals Policy Monitoring Network used for assessing the background concentrations in groundwater. Colours indicate fuzzy cluster membership.

4.4.2 *Results: Characteristics of groundwater clusters*

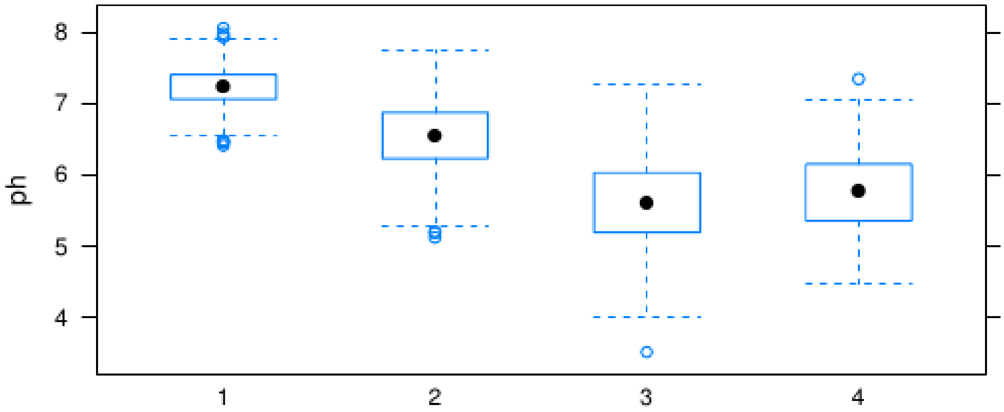
After studying several FCM models, a model with four clusters and a *q* of 1.5 was chosen (see Vriend et al., 1988 for further explanation). This model represented an optimum between separation of the data and interpretability. Modelling was performed using the *cmeans* function from the *e1071* package of the R Statistical Software (R Core Team, 2013).

The results of the statistical analyses were graphically studied in detail and in this report we show a selection of these results. In Figure 4.4.2.1 two contrasting box plots are given: of pH and Fe. In the pH box plot of

Figure 4.4.2.1, the highest pH is seen in cluster 1, followed by cluster 2, the lowest in clusters 3 and 4. High pH values are common in carbonate-rich groundwater, usually related to a marine environment. Seawater and marine sediments contain high calcite concentrations due to shell and diatom detritus. The locations of the first cluster are close to the coast, confirming the marine influence on groundwater.

The box plot of Fe in Figure 4.4.2.1 shows the dissolved Fe concentration. This concentration is highest in anaerobic groundwater (measurements of Fe^{2+} were not available). In more aerobic groundwater Fe^{3+} precipitates as Fe-oxide and is thus removed from the dissolved phase. The second cluster has the highest Fe concentration, and relatively high pH values. On the map this cluster is associated with the peaty areas in the Netherlands. Soils in these areas are a result of the Holocene marine environment, hence the high pH, but due to oxidising organic matter the local groundwater is reduced, confirming the high dissolved Fe concentrations.

Clusters 3 and 4 show similar pH values but differ in Fe concentrations. On the map these clusters are situated in the Pleistocene area of the Netherlands, which generally has a sandy lithology. Clusters 3 and 4 also differ in NH_4^+ concentration: cluster 3 has a lower NH_4^+ concentration than cluster 4. We consider that cluster 4 indicates a groundwater type which is more influenced by fertilisation than cluster 3. This fertilisation results in higher NO_3^- input, which is reduced to NH_4^+ under anoxic conditions.



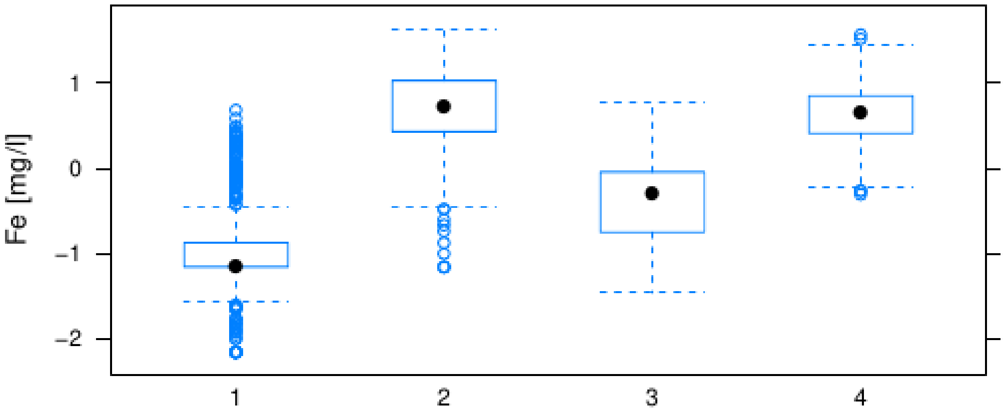


Figure 4.4.2.1: Box-and-whisker plots of pH (top) and dissolved Fe (bottom). Cluster numbers are plotted on the x-axes For Fe logarithmic (^{10}log) concentrations are plotted on the y-axis.

For each cluster the MC of the concentrations of trace elements was calculated, if possible, together with an overall MC of the unclustered data. Many elements appeared to be censored due to detection limits; for these elements no MC could be derived. Table 4.4.2.1 gives the resulting MC values.

Table 4.4.2.1: Percentiles for the concentrations in the groundwater dataset: the 5th (p05), 50th (p50) and 95th (p95) percentiles are given. The MAD is the Median Absolute Deviation of the log-transformed data. The MC is the MAD criterion, the MPA is the Maximum Permissible Addition. Additionally the values for the former Threshold Value Groundwater (GW) and the Threshold Value for Drinking Water (DW) are given. Concentrations are given for the total dataset (clusters 1–4) and for each of the clusters separately.

Element	**Cluster**	**p05**	**p50**	**p95**	**MAD**	**MC**	**MPA**	**GW**	**DW**
As	1-4	0.56	2.60	15.47	2.83	14.36	24.00	10.00	10.00
µg / l	1	0.47	2.66	16.44	4.02	26.07			
	2	1.10	3.65	12.00	1.94	10.79			
	3	0.40	1.15	5.30	2.09	3.85			
	4	1.10	3.54	22.14	2.37	14.60			
Ba	1-4	4.67	74.75	162.20	1.84	203.64	29.00	50.00	
µg / l	1	3.00	11.00	104.60	3.57	88.48			
	2	5.90	71.50	206.10	2.41	302.63			
	3	44.50	83.75	163.47	1.47	157.18			
	4	43.65	91.50	165.35	1.50	178.58			
Cd	1-4	0.03	0.11	0.63	3.58	0.89	0.34	0.40	5.00
µg / l	1	0.03	0.04	0.12	1.68	0.10			
	2	0.03	0.04	0.13	1.39	0.06			
	3	0.10	0.28	0.91	1.94	0.82			
	4	0.04	0.15	0.70	2.24	0.58			
Cr	1-4	0.70	1.10	3.85	1.95	3.30	8.70	1.00	50.00
µg / l	1	0.43	0.70	0.83	1.00	0.70			
	2	0.70	0.85	3.80	1.33	1.36			
	3	0.70	1.50	3.75	2.13	5.19			
	4	0.70	1.85	4.21	2.05	5.99			
Cu	1-4	0.70	5.00	19.79	3.01	30.50	1.10	15.00	2000.00
µg / l	1	1.10	2.30	5.20	1.60	4.97			
	2	0.42	1.32	6.58	2.82	7.26			
	3	3.27	9.57	26.74	1.93	28.22			
	4	1.63	7.24	19.62	2.05	23.56			
Ni	1-4	1.85	7.45	35.47	2.52	33.86	1.90	15.00	20.00
µg / l	1	1.85	4.06	9.05	1.65	9.19			
	2	0.85	4.78	21.27	2.67	23.83			
	3	2.90	10.97	61.19	2.14	38.17			
	4	2.53	10.45	41.14	2.26	39.67			
Pb	1-4	0.14	0.45	2.95	4.82	5.94	11.00	15.00	10.00
µg / l	1	0.14	0.14	0.30	1.00	0.14			
	2	0.14	0.22	2.32	1.95	0.66			
	3	0.14	1.00	3.45	2.43	4.28			

Element	Cluster	p05	p50	p95	MAD	MC	MPA	GW	DW
	4	0.15	0.78	3.12	2.38	3.23			
Zn	1-4	2.80	20.00	106.20	3.89	185.61	7.30	65.00	
µg / l	1	2.80	2.80	14.04	1.00	2.82			
	2	2.0	10.50	54.90	2.41	44.41			
	3	8.53	42.00	144.86	2.26	159.85			
	4	8.76	31.50	116.04	2.29	122.81			

The calculated MC values (see Table 4.4.2.1) are in general much lower in clayey and peaty soils. This is partly due to the lesser extent of leaching of contaminants from overlying soils than in sandy soils. However, a bias towards lower concentrations in the data of clayey and peaty areas cannot be excluded. It is known from field observations when sampling the drains in these clayey and peaty areas that a brownish deposition is visible in the drain opening. Assuming that this brown deposition consists of iron oxides, these oxides can sequester the dissolved metals transported through the drain. This might result in a bias towards lower MC levels for these areas.

5 Materials and methods: Description of the model

In this chapter we explain the construction and principles of the geochemical model used for this study. First we explain the conceptual model and basic principles of the modelling. Then we continue with an explanation of how hydrology and soil data are used in the model. This is followed by a detailed geochemical description of the model. At the end of this chapter the modelling endpoints and criteria used to assess the impact of the results are described.

5.1 Conceptual model set-up and model scales

The conceptual model in this study is the same as in previous studies (Verschoor et al., 2006; Spijker et al., 2009) – a single soil profile divided into three parts (or layers):

1. top layer: this is the diffusely contaminated soil layer up to the level of the Maximum Value.
2. sub layer: this is a clean soil layer with concentrations at the level of the natural background.
3. groundwater: this is a clean soil layer with concentrations at the level of the natural background; the water phases in this layer have negligible concentrations of metals/metalloids.

All soil layers are saturated and transport is linear, i.e. a constant downward water flux. For the first layer a reactive concentration is assumed according to the Maximum Values (MV, in Dutch: "Maximale Waarden"). This reactive concentration reacts chemically with components and surfaces in the solid phase and dissolved phase. Components in the dissolved phase are transported downwards.

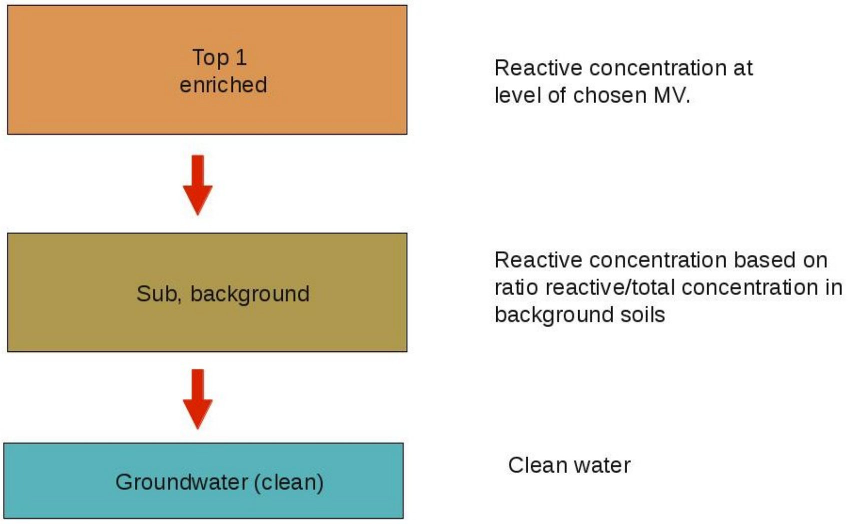


Figure 5.1.1: Conceptual model showing soil layers (boxes) and water transport (arrows)

The conceptual model (see Figure 5.1.1) describes a single case in the modelling of the transport through a single soil profile. Such a single soil profile can be studied in detail and insight can be obtained into the geochemical processes of contaminant transport. A single soil profile can be regarded as a single point in geographical space. The representativeness of a single point for the total area, such as the area of the Netherlands, can be regarded as limited. Verschoor et al. (2006) and Spijker et al. (2009) studied the results of the modelling of a single soil profile but it was subsequently decided that better insight was needed into the variability between soil profiles. However, modelling and interpreting a soil profile takes considerable time. Therefore, it was chosen in this study to look at different scales with for each scale an increasing amount of modelled soil profiles but using less detailed, i.e. aggregated, results. These scales are shown in Figure 5.1.2. The soil profiles are discussed in detail in Section 5.4.

The first scale is that of the single soil profile. We used the three 'standard' profiles as defined in Verschoor et al. (2006). These three profiles are representative of the Dutch sandy, clayey and peaty lithologies. Each soil profile is studied in detail.

The next scale uses the soil profiles with the largest area within each major soil type in the Netherlands. The model results of these profiles are studied at an aggregated level, in this case as variability, shown in box-and-whisker plots.

The third scale is all the soil profiles together. Since the soil profiles can be related to a spatial location, it is possible to create a map of the modelling results. This level is studied at the scale of these maps which shows results binned in four groups, including a 'no data' group for locations were no results were available.

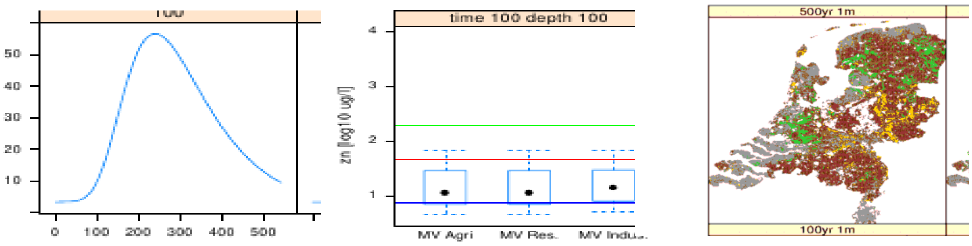


Figure 5.1.2: Illustration of model scales and associated detail, these figures are parts taken from the figures in the result section. The single profile case shows a breakthrough curve in which the concentration is given for each time step. The 20 profiles scale show box-and-whisker plots with summarised data of many profiles. The 'all profiles' scale shows a spatial overview of binned results.

5.2 Model scenarios

The aim of the model is to predict future changes in groundwater concentration below a diffusely contaminated soil. This contamination is the maximum allowed mixture of contaminants according to the Dutch Soil Quality Decree. In this decree legislative maximum values are given for three types of soil use, with increasing threshold concentrations: agricultural use, residential use and industrial use. The legislative values are called Maximum Values (MV) (Dutch: Maximale Waarden). The MV Agricultural is based on a normalised 95th percentile concentration from a survey sampling in the Netherlands (n=100) (see Brus et al., 2009 for details). The MV Residential and Industrial are based on the MV Agricultural plus an added concentration based on exposure modelling, with the ecosystem and human health as endpoints.

The modelling scenarios assume a soil with element concentrations at the level of one of the MVs. Data from such soils, if they exist at all, is not available. Therefore, it is necessary to estimate the soil composition which is needed as input for the model.

The input concentrations for the model are so-called reactive concentrations. These are concentrations which can be measured by a cold 0.43 M nitric acid extraction. Dijkstra et al. (2009) has shown that the reactive concentrations so obtained reflect the reactivity of elements in soils. To estimate the reactive concentration, the principle of the added risk approach is used.

5.2.1 *Added risk approach*

The added risk approach distinguishes between natural and anthropogenically enriched levels (Struijs et al., 1997). In the added risk approach only risks resulting from anthropogenic addition are considered; the natural concentration does not, by definition, add to the perceived risks to ecosystems, groundwater or surface water. The local ecosystem is considered to be adapted to local circumstances.

The added risk approach follows the model of Struijs et al. (1997). In Figure 5.2.1.1 the simplified model is given. In this model the natural background concentrations are considered inert, i.e. not reactive, and the anthropogenic addition is considered fully available, i.e. reactive. These simplifications can be regarded as a worst case approach towards the availability of the anthropogenic addition.

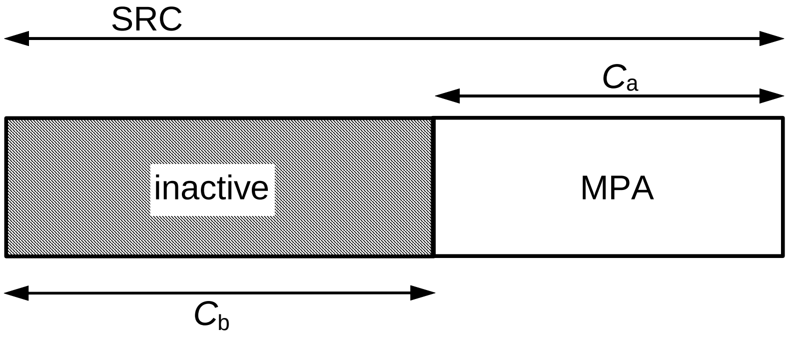


Figure 5.2.1.1: Illustration of differences in presumed availability used in the added risk approach (from Struijs et al., 1997)

Considering that the added part (C_a) is reactive we can use this part as input for the model after estimating for each MV which part is natural and which part is added.

5.2.2 *Estimation of reactive concentrations from Maximum Values*

As shown in Chapter 4, using the geochemical baselines natural background concentrations can be estimated. Considering a soil with concentrations up to an MV Agricultural, Residential or Industrial, the difference of the concentration with the natural background concentration determines the reactivity. This is in line with the results as shown in Figure 4.2.2. However, it is assumed that at higher concentrations, like the MV Industrial, the estimated reactivity is overestimated.

To obtain the reactive concentration the soil-type-specific MV for the soil profile was calculated using the organic matter and clay (grain size <2 um) content, according to the Soil Type Correction procedure in the Soil Quality Decree. This soil-type-specific MV was subtracted from the natural baseline concentration (see Appendix A). When no baseline was available or when the MV was below the natural concentration, representative values were chosen based on data from the Geochemical Atlas.

5.3 Hydrology

The basic principle of the modelling of hydrological transport is that the breakthrough time of the concentration front is of less importance than the breakthrough concentration itself. This means that the maximum concentration reached is more important than the time after which this maximum concentration is reached. The modelling of downward transport can therefore be kept simple. Processes like evaporation, dispersion, diffusion and preferential flow can be omitted from the model.

In the Netherlands the average precipitation surplus is 300 mm/a. This surplus is used as influx in the soil and it is assumed that this 300 mm/a is also the groundwater recharge. This assumption is a simplification when considering the real groundwater recharge, which varies between a few mm per year to more than 300 mm/a. Since the time of breakthrough or transport is not important and considering other uncertainties due to our assumptions, such as linear transport, this assumption is justifiable.

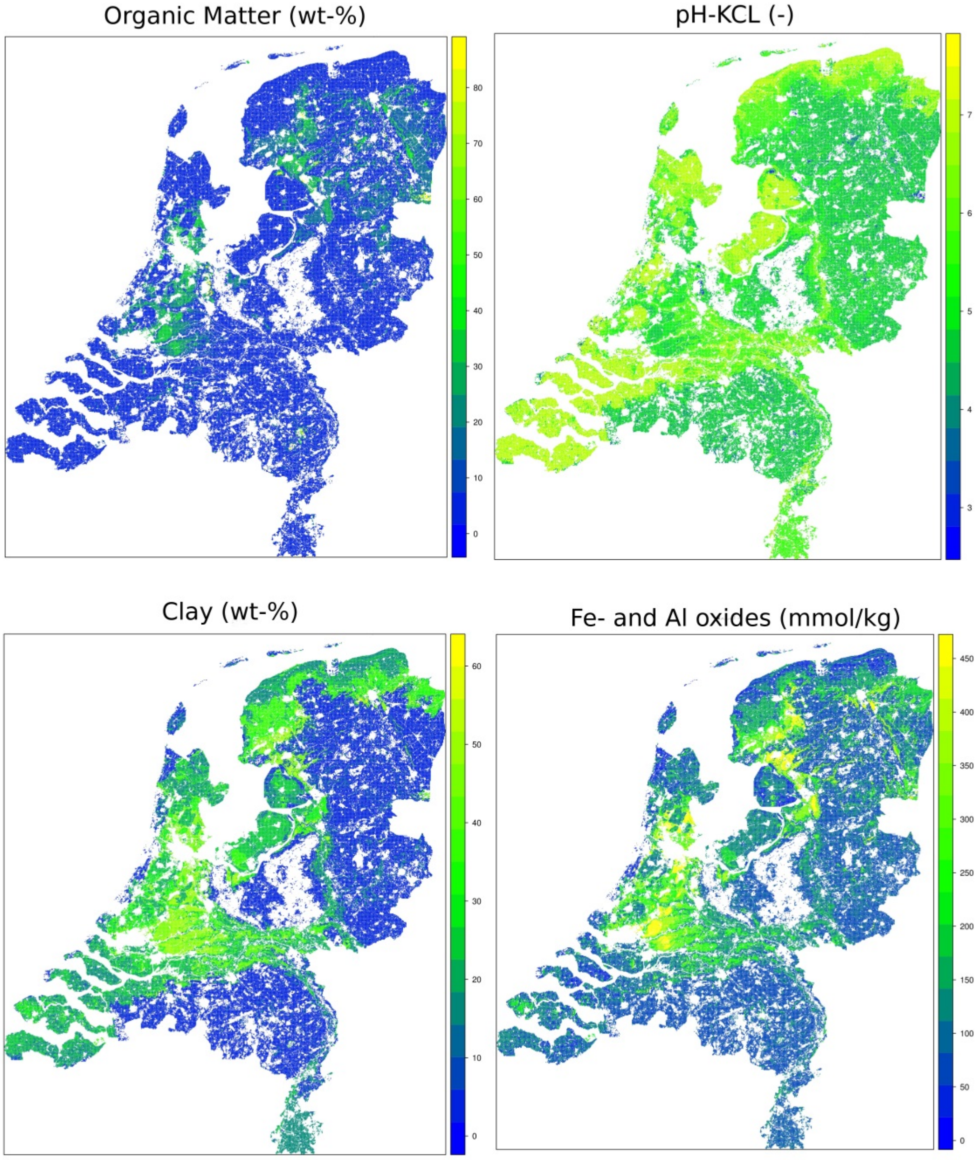
A simple hydrological model is assumed. Linear transport over a one-dimensional soil profile, with cells (defined as numerical nodes) about 10–15 cm deep, is simulated. There is a constant downward water flux of 300 mm/a, in agreement with the average evaporation rate in the Netherlands of 300 mm/a. Dispersion is only determined by numerical dispersion over the soil profile. It is considered that dispersion of strong adsorbing substances is of minor importance.

5.4 Soil data

Soil data for the soil profiles were taken from the STONE schematisation of soils of the Netherlands. This schematisation is a combination of hydrology, land use and soil composition. The soil composition consists of organic matter, clay content (lutum), pH, and concentrations of iron and aluminium oxides. In Figure 5.4.1 the spatial distributions of these parameters are shown.

This schematisation consists of 6,405 plots, 250 x 250 m grid cells of the agricultural area of the Netherlands. In this study only the soil profiles of the STONE database were used, resulting in 456 soil profiles. These soil profiles were divided into 21 major soil types (so-called PAWN types). These 21 soil types were then divided over four general soil types: sand, peat, clays and loess. On account of the small area of loess and a lack of data, however, this soil type was not taken further into account for the modelling.

The values of clay and organic matter content, pH, Fe-(hydro-)oxides, and Al-(hydro-)oxides, in the three main soil types are shown Figure 4.5.2.



Organic Matter (wt-%)

pH-KCL (-)

Clay (wt-%)

Fe- and Al oxides (mmol/kg)

Figure 5.4.1: Maps of the distribution of STONE plots and the associated values for clay content (particles < 2um), organic matter, sum of Fe- and Al (hydro-)oxides and pH (KCl)

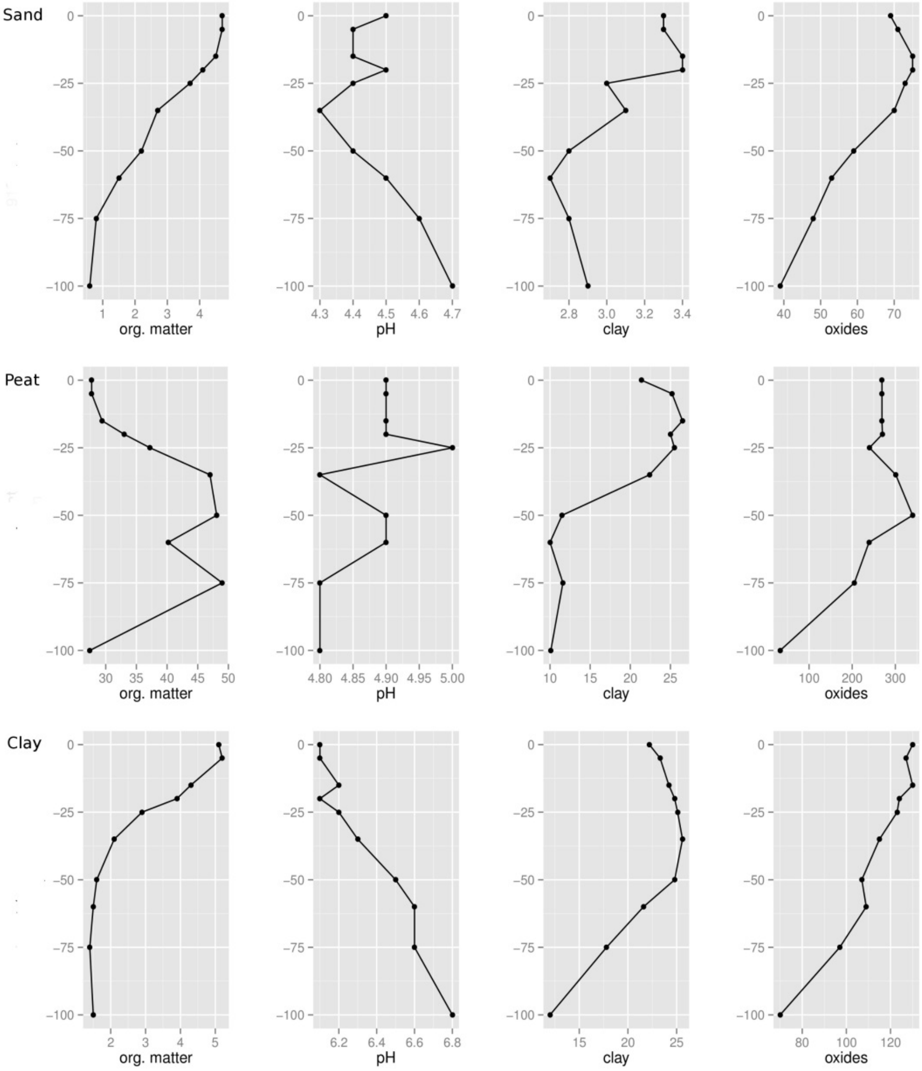


Figure 5.4.2: Soil profiles of the three main soil types (rows). Clay content and organic matter are given in wt-%, the sum of Fe- and Al-hydroxides (oxides) is given in mmol/kg. The y-axis indicates the depth in cm.

5.5 Mechanistic Multi-surface Modelling

For the modelling of mineral saturation, solution speciation, sorption processes, and transport the ORCHESTRA modelling framework was used (Meeussen, 2003) In this framework a model was set up equal to the model used in earlier studies of Verschoor et al. (2006) and Spijker et al. (2009) and based on the model of Dijkstra et al. (2009). The model consists of submodels for the adsorption to surfaces, speciation models for the dissolved fraction, and a hydrological transport model.

5.5.1 Adsorption surfaces

The major reactive surfaces in soil are (dissolved) organic matter, iron and aluminium oxides, and clay. For each surface an adsorption model was chosen for which thermodynamic parameters were available for the elements in this report.

For organic matter, both solid and dissolved, the NICA-Donnan model was used (Kinniburg et al., 1999). This model describes the specific and non-specific binding of components to solid and dissolved organic matter. The model uses the generic binding parameters and constants.

The adsorption to Fe- and Al-(hydro)-oxides was modelled using the model of Dzombak and Morel (1990). This model describes the specific binding of metal cations and (oxy)anions to hydrous ferric oxide (HFO). Binding to amorphous Al-hydroxides was modelled as binding to HFO, assuming 1 mole HFO equals 1 mole Al-hydroxides.

Non-specific adsorption of elements to permanently charged clay surfaces was modelled using a simple Donnan model, according to Dijkstra et al. (2004). A CEC of 25 eq/kg was assumed, in agreement with the average CEC of illite. The Donnan volume was fixed at 1 l/kg.

5.5.2 *Description of major elements*

Major elements like Fe^{3+}, Al^{3+}, Ca^{2+} and PO^{4+} are competing with other elements, like the heavy metals, in the modelled soil. These other elements have concentration levels at the MV for the respective soil types.

The most important competitors for binding to organic matter are Fe^{3+}, Al^{3+} and Ca^{2+}. For Fe^{3+} and Al^{3+} the dissolved and adsorbed concentrations are regulated by the presence of ferrihydrite ($Fe(OH)_3$) and gibbsite ($Al(OH)_3$), which dissolve or precipitate as result of pH and organic matter. The concentration of Ca^{2+} in soils with a pH below 7 is usually not determined by the precipitation of minerals due to instability under these conditions. Therefore, the initial background concentration of Ca^{2+} was set at $2*10^{-3}$ M. To counterbalance the Ca^{2+} charge, the SO_4^{2-} concentration was also set at $2*10^{-3}$M, according to the data of Dijkstra et al. (2004). Concentrations of Na^+ and Cl^- were set at 10^{-3} M, also according to the data of Dijkstra et al. (2004). During the calculations this concentration changed due to the presence of other cations like the metals leached from the enriched soils.

Other assumptions and model constraints are:

- Adsorption of anions is allowed. The influence of competition with phosphate (dissolving of hydroxyapatite $Ca_5(PO_4)_3OH$) was negligible; therefore, to simplify the model, P was not incorporated.
- Other major elements, like Mg^{2+} or Sr^{2+}, were not part of the model. Dijkstra et al. (2004) showed that even with this simplification the concentrations of heavy metals can still be satisfactorily predicted.
- To account for the higher CO_2 pressure in soils, a CO_2 pressure of $10^{-2.5}$ atm was assumed. This is ten times the atmospheric CO_2 pressure, according to the assumptions in Dijkstra et al. (2004).

Considering the concentrations of Ca^{2+} and SO_4^{2-}, Groenenberg (pers. comm.) showed during this study that field concentrations can be ten times lower than the concentrations used in this study. For comparability with the study of Spijker et al. (2009) the concentrations of $2*10^{-3}$ M were maintained.

5.5.3 *Precipitation of minerals*

A selection of minerals whose solubility can be satisfactorily modelled was made on the basis of the expectation of precipitation. Table 5.5.3.1 gives the mineral phases which are allowed to precipitate. Considering the oxic conditions of the model (see below), adsorption is the most important process, making precipitation less important. Precipitation of sulfide minerals, as result of anoxic conditions, is excluded.

Table 5.5.3.1: Selected mineral phases which are allowed to dissolve or precipitate in the speciation model

- Barite ($BaSO_4(s)$)
- $Ca_2V_2O_7$
- $Ca_3[VO_4]_2$
- $CaMoO_4[c]$
- $CaSb[OH]_6[s]2$
- $CaSeO_3{:}_2H_2O$
- Ca_Vanadate
- Calcite ($CaCO_3(s)$)
- $Cd[OH]_2[c]$
- Cerrusite ($PbCO_3(s)$)
- $Cr[OH]3[c]$
- $Cu[OH]_2[s]$
- Ferrihydrite ($Fe(OH)_3(s)$
- Fluorite ($CaF_2(s)$)
- Gibbsite[c] ($Al(OH)_3(s)$)
- Gypsum ($CaSO_4(s)$)
- $HgCO_3$
- Malachite ($CuCO_3(s)$)
- Montroydite ($Hg(OH)_2(s)$)
- $NiCO_3[s]$
- $Ni[OH]_2[s]$
- Otavite ($CdCO_3(s)$)
- $Pb_2V_2O_7$
- $Pb_3[VO_4]2$
- $Pb[OH]_2[C$
- Witherite ($BaCO_3(s)$)
- Zincite ($ZnO(s)$)

5.5.4 *pH and Redox*

pH varies over depth according to the data from the soil profiles used. The model assumes mildly oxic conditions. The pe value is determined by the equation pH+pe=15. This simplification was used since the possibility of modelling a dynamic redox environment is currently limited.

5.5.5 *Dissolved organic matter (DOC)*

The DOC concentrations are constant over depth and time in the model, based on the data from the soil profiles used. Hence, DOC is not transported. However, the fraction of element concentrations adsorbed to DOC is transported over depth. This approach simulates the equilibrium of adsorption and degradation of DOC in soil profiles.

5.6 Model endpoints

One of the aims of this report is to assess the impact of the MVs for soil managed under the SQD on groundwater. For such an impact assessment it is necessary to establish criteria that determine whether acceptable conditions are met. It is not within the scope of this report to discuss what are acceptable conditions or not. Therefore, we give several options, or indicators, each describing a type of impact. These indicators are ratios of an estimated groundwater concentration divided by a reference concentration. Table 5.6.1 lists these indicators.

The endpoint of groundwater concentration is defined as the maximum average concentration over 1 metre soil (or groundwater) profile. This means that for each time step in the model the groundwater concentration of a specific element is averaged over 1 metre (i.e. 10 cells); then the maximum concentration is taken over the full time range (i.e. 100 or 500 years). This concentration is the modelling endpoint. Maximum average concentrations are given after 1, 100 and 500 years, and at 100 cm depth (depth interval 100–200 cm in the soil profile) or 500 cm depth (depth interval 500–600 cm). The one-year time range is the situation where one pore-volume of soil profile is leached and this is used as the reference for the 100- and 500-year time ranges. The 100-year time range is equal to the time range which was used for deriving the emission criteria for construction products (Verschoor et al. 2006). According to Verschoor et al. (2006) this time range was too short for some elements because they did not reach a maximum concentration in the groundwater within that time period. However, since constructed works are temporary, 100 years was considered sufficient. In this study the 500-year range was added so that it was also possible to estimate the maximum concentration of these elements with a higher retardation. Also in Verschoor et al. (2006) the estimated concentrations in groundwater were assessed at 100 cm depth. However, in many areas the actual groundwater level is below this depth, especially in the Pleistocene areas. Therefore the 500 cm depth was added.

Endpoints were calculated for each element for which an MV exists in the Soil Quality Decree. These elements are: As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Sn, V and Zn.

Table 5.6.1: Indicators and their meaning for the impact assessment of leaching from soil to groundwater

Indicator	**meaning**
Max. avg. conc. / MC	The estimated maximum average concentration is compared with the upper limit (95th percentile) of the actual concentrations in groundwater. This indicates whether leaching under the conditions of the selected scenario concentrations will exceed current groundwater concentrations.
Max. avg. conc. / MPA	The estimated maximum average concentration is compared with the Maximum Permissible Addition risk level. This indicates whether leaching under the conditions of the specific scenario will exceed an acceptable risk level. However, this risk level is conservative and does not account for bioavailability or speciation. The MPA is the standard limit in preventive soil and groundwater policy.
Max. avg. conc. / Max. avg. conc. agriculture	The estimated maximum average concentration of a specific scenario (residential area or industrial area) is compared with the maximum average concentration for agricultural areas. According the definitions in the Soil Quality Decree, the Maximum Values for agricultural areas are representative of clean soil, despite the fact that these soils have been diffusely contaminated by human activities over several centuries. This comparison is a reference for curative soil policy. If one assumes that the leaching of these clean, but altered, soils results in an increase in concentration in groundwater in the future, then this can be compared with the increase in soils under other soil usage scenarios to which the Maximum Values for residential and industrial areas have been applied.

6 Model validation/evaluation

To gain insight into the accuracy of the reactive transport model, the model was evaluated stepwise, starting with an evaluation of the geochemical model using laboratory experiments, followed by an evaluation of the reactive transport model using laboratory column leaching experiments and finally a field-scale evaluation of the transport model. A full description of the results can be found in the published journal papers; here we summarise the main results relevant to this study.

6.1 Evaluation of the geochemical model

The geochemical model was evaluated on its predictions of measured solution concentrations in pH static experiments (Dijkstra et al., 2009), solution extracts from archived soil samples and soil solution obtained from field samples (Groenenberg et al., 2012). The model was tested for most of the elements included in the Soil Quality Decree, i.e. As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V and Zn.

The comparison of model predictions with measurements using data from pH-static leaching experiments performed with eight diffusive to industrially contaminated soils over a wide pH range (pH 0.4-12) provides a thorough evaluation of the model performance. Figure 6.1.1 shows the model performance for the elements As (an oxyanion), Cu (metal cation with a high affinity for binding to organic matter) and Zn (metal cation with a moderate affinity for binding to organic matter). Figures for all elements can be found in Dijkstra et al. (2009). In addition, the model evaluation of solution extracts and soil solution from a large number of soil samples (>100 from the Netherlands and 15 from Portugal), including the major soil types from the Netherlands, provides information on the model performance over a wide range of soil properties and element concentrations. Results are presented for the elements As, Cu and Zn in Figure 6.1.1. Figures showing results for the other elements are given in Groenenberg et al. (2012). The results of the pH-static experiments show that the model is able to predict the change in concentrations with pH for all elements except Sb over a wide pH range, though predictions are somewhat poorer at the low and high ends of the pH range.

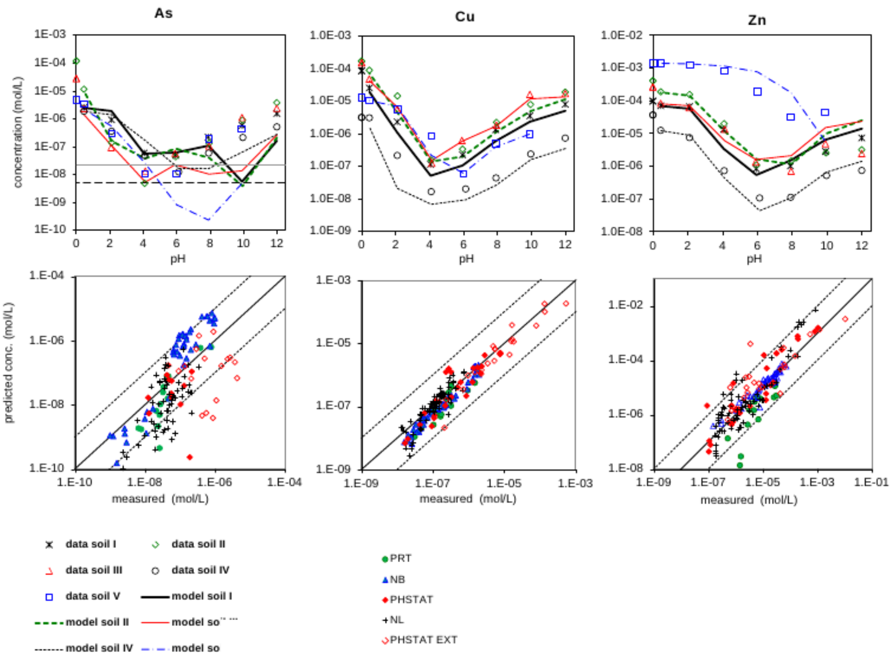


Figure 6.1.1 Comparison of model predictions with measurements of the pH-static experiments (Dijkstra et al., 2009) and with solution extracts and soil solution from an extensive set of soils (Groenenberg et al., 2012). PRT = portrugese soils, NB = Noorderbos (field samples), PHSTAT = pH-static experiments, PHSTATEXT (pH<4 or pH>8), NL = Dutch soils. For more information on soils see Dijkstra et al., 2009; Groenenberg et al., 2011, 2012.

A statistical measure of model performance is the Root Mean Square Error (RMSE). Here we use the log RMSE, which is defined as:

$$\mathrm{RMSE}_{\log} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\theta-\hat{\theta}\right)^{2}}$$

With n = number of data points, θ = model prediction, measured value. The log RMSE was calculated for all data (pH-static data and soil solution/solution extracts) in the pH range 3–8, this being the relevant range for natural soils.

Figure 6.1.2 shows that for the metal cations with moderate and strong affinity for binding with organic matter the RSME is <0.5 except for Pb. For the oxyanions and metal cations with lower affinity the RMSE is higher, with values up to 1. Generally, the error is due to both over- and underestimation; however, the model systematically overestimates concentrations of Pb and Sb. The prediction for V can be improved when only the (reduced) vanadyl (VO^{2+}) ion is considered (Dijkstra et al., 2009)

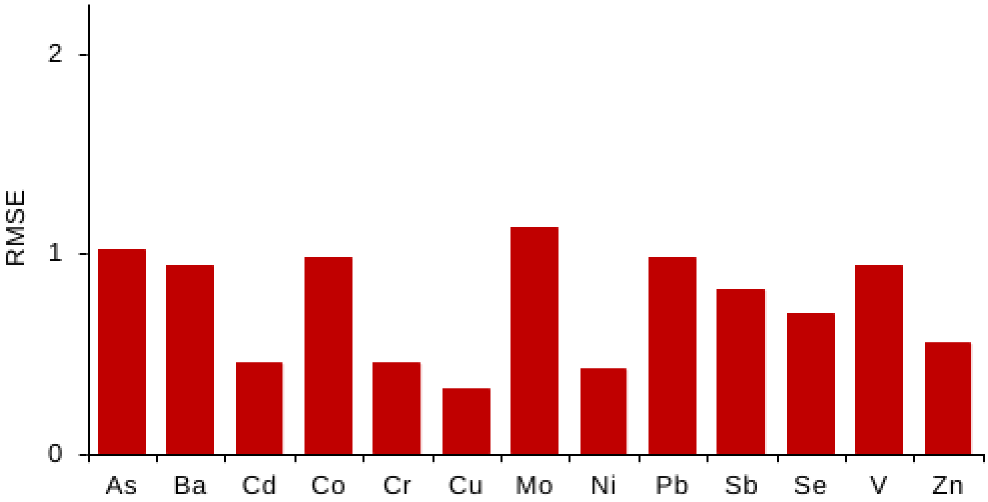


Figure 6.1.2 Root Mean Square Error (RMSE) for the predictions of the pH-static experiment and for the soil solution and solution extracts in the pH range 3–8 (Groenenberg et al., 2012)

6.2 Evaluation of the reactive transport model on column leaching tests

Testing the performance of the geochemical model has so far been limited to batch experiments. Although data from such experiments have demonstrated an adequate performance of models under conditions close to equilibrium as a function of pH and soil characteristics (Dijkstra et al., 2004; 2009; previous section; Groenenberg et al., 2012), the physical and chemical conditions in transport systems are quite different from those under batch conditions. It is therefore not certain that similarly adequate model performances will be found under transport conditions:

- Most importantly, the liquid-to-solid ratio (L/S, in L/kg dry matter) of a soil percolated with water is much lower than in a typical batch experiment. Assuming an average dry bulk density of 1,500 kg/m^3 and a volumetric pore fraction of 0.3 (v/v), the L/S ratio of a fully saturated soil in a column experiment (such as ISO/TS21268-3) is 0.2 L/kg, which is a factor of 10 to 50 more ‘concentrated’ than in a typical batch experiment performed at L/S = 2 or 10 L/kg (such as ISO/TS21268-1, ISO/TS21268-2 or ISO/TS21268-4). Therefore, in column experiments a very different chemical equilibrium condition will develop than in batch experiments due to the concentration effects of salts, dissolved ligands including DOC and other reactive surfaces, changed competitive sorption interactions, and precipitation reactions.
- Chemical conditions in the column are also different because dissolved elements and ligands are carried away due to the flow of water, which does not occur in batch systems.
- Contact times in column experiments (residence times) are usually shorter (~15 hours during the flow period in ISO/TS21268-3) than in batch experiments (48 hours, ISO/TS21268-4), which may more easily lead to non-equilibrium conditions.
- Reactive transport model predictions are much more sensitive to seemingly small deviations between model and data (as would be inferred from batch systems), because of chromatography effects.

For the reasons given above the performance of the Dijkstra et al. (2009) model approach is tested in combination with one-dimensional transport, using data from column tests for a broad range of inorganic elements including metals, metalloids and oxyanions (Dijkstra et al., submitted). The relatively simple one-dimensional transport scheme is chosen because it reflects how such models are presently used in generic risk assessments that underlie policy decisions in the Netherlands. The main results are presented and discussed below. The full results and discussion are presented in Dijkstra et al. (2013).

The column experiments were performed largely according to ISO/TS 21268-3 (ISO/TC190, 2007)on four soil samples, consisting of mixed samples of topsoils (0–50 cm) from different locations in the Netherlands. The Noorderbos sample was taken from a wastewater infiltration field that had been used for about 50 years, during which time the soil had become loaded with various metals, but most prominently with Cr, originating from industrial (including tannery) waste and domestic wastewater from the city of Tilburg. The sample was also used to evaluate the reactive transport model at a field scale (next paragraph). The other three soil samples were agricultural soils with an unknown anthropogenic contamination history. The Kekerdom sample is a riverside clay sediment (Millingerwaard, NL); Woold is a sandy soil taken from the vicinity of Winterswijk (NL), and Zegveld is a peat soil sample (vicinity of Nieuwkoop, NL).

6.2.1 *Chemical part of the model*

The chemical part of the model and its parameterisation is similar to those described by Dijkstra et al. (2009), to which readers are referred for details. In comparing the performance of the model with the results of the reference studies, the same assumptions were made with respect to the reactivity of particulate and dissolved organic matter (for details see Dijkstra et al., 2009). In short, the amount of reactive particulate organic matter is taken to be the sum of the extracted humic and fulvic organic matter fractions, and the amount of reactive dissolved organic matter estimated by assuming a reactivity of 50% of the total dissolved organic carbon (DOC) and assuming that organic matter consists of 50% carbon. All reactive organic matter was represented by 'humic acid' in the model (for details see Dijkstra et al., 2009).

6.2.2 *Modelling the column test eluates*

The model was used in two different 'modes' to predict the column test eluates, indicated as 'batch model' and 'reactive transport model', as explained below.

Batch model. First, the batch model of Dijkstra et al. (2009) was applied to predict the total dissolved concentrations of metals and oxyanions in the column eluate fractions directly, without considering the transport of water. This calculation needs as input the pH, the total dissolved concentrations of DOM and major elements (Ca, Mg, Fe, Al, PO_4, CO_3,..) in each eluate fraction, which are all 'fixed' to their measured value, as if the eluate fractions were separate batch experiments. Furthermore, the calculation needs the L/S ratio in the column (generally ~0.2 L/kg when porosity is 0.3 and bulk density 1,500 kg/m^3), the amounts of reactive surfaces in the column (POM, Fe/Al-hydroxides, clay) and the available amounts of contaminants as determined by 0.43 M HNO_3 extraction. The advantage of this approach is that it takes into account variations in a number of important parameters during the column experiment (e.g. pH and DOC), which are generally less well understood and poorly predictable with a 'forward' transport model. The batch model output can therefore be regarded as a benchmark of the model performance that could be achieved with the 'forward' reactive transport model of the next step, when all variations in important parameters would be 100% predictable. The batch approach applied here to a column experiment is only sensible when the mass of sorbate removed is negligible compared with the locally available amounts (i.e. at the outlet of the column).

Reactive transport model. In this model set-up, the batch-model of Dijkstra et al. (2009) is coupled with a simple one-dimensional transport scheme. The transport set-up is similar to the model used for deriving limit values in the Dutch soil quality decree (Verschoor et al., 2006). In the model, the columns (of 20 cm length) are represented by five equally sized layers; predicted concentrations in the eluate are punched out in the fifth layer. The (numerical) dispersion length generated by this transport scheme is 1/10th of the column length (~2 cm). Diffusion is not taken into account.

As the processes that control pH and DOM solubility in soils are still poorly understood (see, for example, Figure 6.1.1) and hence (semi-) mechanistic models for, in particular, DOM solubility are still lacking, pH and DOM are in the model fixed to their average value as measured in each column experiment (see discussion below). Similar complications for major elements have been discussed elsewhere and therefore the total dissolved concentrations of Ca, PO_4, SO_4 and CO_3^{2-} are also fixed at the average values measured in each column experiment. Total dissolved Fe and Al concentrations in the model are regulated by dissolution of ferrihydrite and gibbsite. Na and Cl are added to the model system in the concentrations as measured in the first eluate fraction of the column experiment, and are allowed to be washed out of the column. No other major elements are taken into account in the reactive transport model. Furthermore, the L/S in the column is needed (~0.2 L/kg), as well as the amounts of reactive surfaces and the available amounts of contaminants whose concentrations in the eluates are to be predicted.

The effect of 'fixing' DOM concentrations in solution in the transport set-up is that metals sorbing to DOM are allowed to be transported downwards and out of the column, but the amount of DOM in the column remains invariant (i.e. as if the production and removal of DOC were equal). As will be discussed below, similar simplifications with respect to pH, DOC and major elements are generally also made in cases where the transport model is used for long-term predictions (several years, decades, centuries); in those cases, the value of these parameters is often based on monitoring data (e.g. average soil pore water or groundwater data). Therefore, the comparison between the 'benchmark' batch model and the reactive transport model is of great importance.

6.2.3 *Predicted concentrations of elements in 'batch-mode' model calculations*

Figure 6.2.3.1 shows the measured and modelled concentrations of metals and oxyanions in the column eluates. With a few exceptions, elements show a relatively constant (albeit variable) or increasing concentration level as a function of eluated pore volumes, which generally indicates that there is no depletion of the available amount in the column. On the other hand, decreasing concentration patterns (e.g. Ba, Woold) do not automatically imply depletion, as other factors may influence concentrations in solution (e.g. pH, DOC).

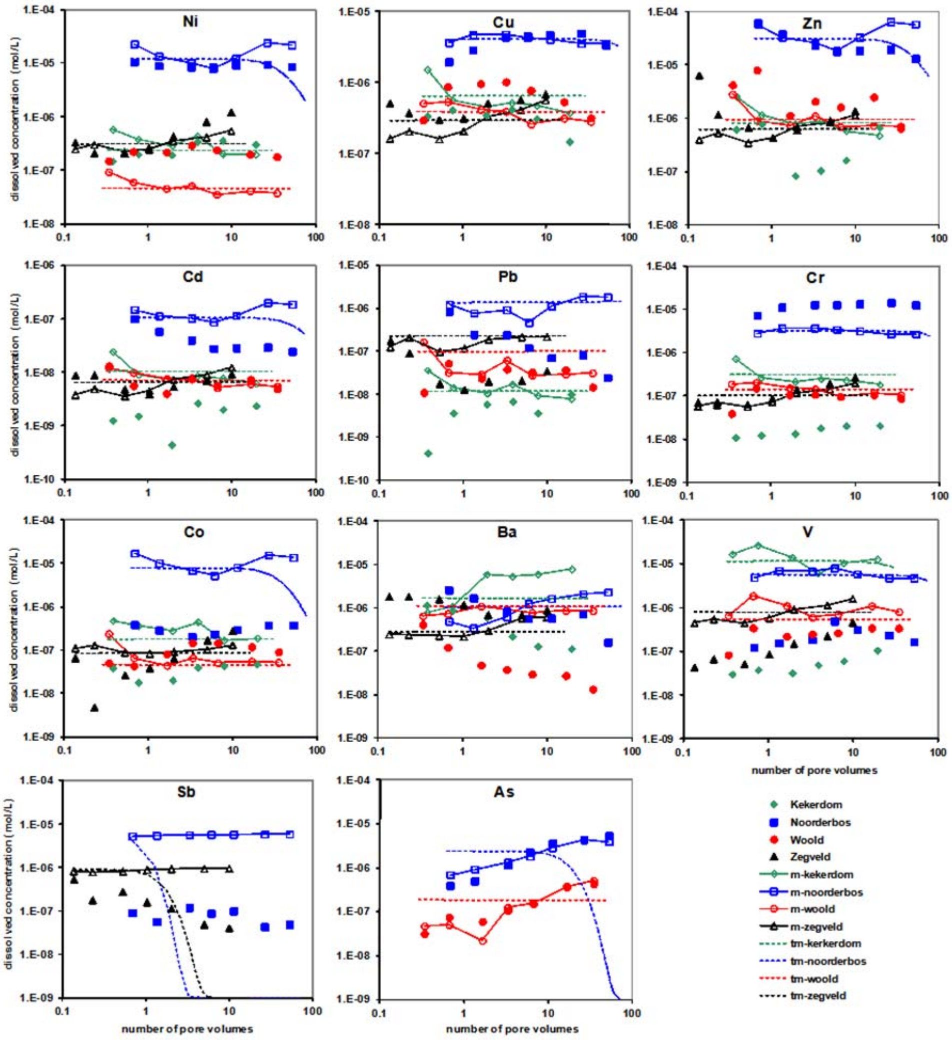


Figure 6.2.3.1: Measured dissolved concentrations in the column eluates of the four soils versus the cumulative number of pore volumes. For clarity and comparability between the soils, a double log scale is used. Model predictions are shown for the 'batch' and 'reactive transport' mode (see text for explanation); batch mode predictions are indicated by 'm-', transport mode predictions by 'tm-'.

First, we interpret the batch model predictions. These model predictions vary per element, and per soil. Generally, the elements can be classified in different groups:

1. metals that bind strongly to organic matter; this group includes Cu, Cr, and V (as vanadyl; see Dijkstra et al., 2009);
2. metals that bind relatively weakly to organic matter; this group consists of Ni, Cd, Zn, Co and Ba;

. oxyanions that bind only to (hydr)oxide surfaces in the model; this group consists of Sb and As. Lead (Pb) is somewhat exceptional as it binds strongly to both organic matter and (hydr)oxide surfaces (Dijkstra et al., 2004; 2009).

Representatives of the first group binding strongly to organic matter, Cu and Cr, are predicted within an order of magnitude or better (in particular, Cu is well predicted in all soils). Model predictions for this group are mainly dependent on an adequate estimate of the availability and the ratio of dissolved and particulate organic matter to which these metals bind almost 100% (e.g. see Dijkstra et al., 2004; 2009). Judging from Cu and Cr, of which adequate predictions are also found in batch systems (Dijkstra et al., 2009), the ratio dissolved/particulate organic matter in the soils is estimated adequately (an important finding; see discussion on group 2 metals below). Vanadium (V) is systematically underestimated; this has previously been found in batch systems as well (Dijkstra et al., 2009). Vanadium follows the increasing trend of DOC in the Zegveld peat soil (compare Figures 6.1.1 and 6.2.3.1) but is underestimated; an explanation for this observation could be that its availability is underestimated (reasoning from the model’s construction).

Group 2 representatives Ni and Zn are overall predicted within an order of magnitude; but concentrations of Zn, Cd, Co and Ba tend to be systematically overestimated. These elements bind (relative to the first group) only weakly to organic matter; and because the first group is predicted well (see discussion above), the deviations between model and data for these metals (mostly overestimates) must be sought either in an inadequate description of their binding to other surfaces (Fe/Al (hydr)oxides) or in an inadequate estimate of their availability. In this respect, it must be noted that the predictions for the Woold and the Zegveld samples are generally adequate for Ni, Cd, Co and Zn (not for Ba); in these soils, the ratio of extracted (hydr)oxides versus particulate organic matter is much lower than in the other two soils. This means that in Woold and Zegveld, organic matter is a much more important sorbing surface than (hydr)oxides; and model performance therefore mainly depends on how well the interactions of these metals with organic matter are described by the model (i.e. the NICA-Donnan approach). The adequate description for Ni, Co, Cd and Zn may therefore be attributed to the good performance of the NICA-Donnan model parameters for these metals (probably less well for Ba); the weak performance of the model for the other soils may be due to inadequate description of sorption to (hydr)oxide surfaces (i.e. to effects that are not taken into account in the current ‘additive’ multi-surface approach such as ternary complexes and mutual electrostatic influences.

Arsenic (for which reliable data are available only for the Kekerdom and Woold soils) is predicted very well, while antimony is generally strongly overestimated (consistent with batch experiments and model application; see Dijkstra et al., 2009). Predictions for lead vary and are best in the Woold sample; but overestimated in the Zegveld sample. Model predictions for lead are usually inadequate in soils (Groenenberg et al. ,2012)

6.2.4 *Predicted concentrations of elements in reactive transport set-ups*

The transport model predictions differ in two main respects from the batch mode predictions discussed in the previous paragraph: (1) due to the transport of water, dissolved metals are carried away and therefore their ‘availability’ is not constant, but decreases with increasing eluted pore volume; (2) the model predictions are based on the averaged values of pH, DOM and major element concentrations. The two features listed above result in model curves that are virtually constant or in curves that sharply decrease (Figure 6.2.3.1.).

With a few exceptions, transport model predictions result in a virtually flat curve. This is the result of the important parameters that are fixed to an average value in the model, most notably pH and DOC, but also major competitive elements such as Ca and PO_4. It is therefore not expected that the transport model set-up will result in very different concentration levels from the batch set-up. The curves are flat when the amount of contaminant that is washed out of the column is smaller than the available amount; in this respect it must be noted that the result of the column test itself, as well as the model predictions, mainly represents the final section of the column where the eluate leaves the column. Only in cases where significant depletion of the locally available amount is predicted will the curves bend downwards, indicating that depletion from the final column section is complete.

The model predictions for Sb are examples of an element that is predicted to be washed out of (depleted from) the column in a virtually conservative way. The predicted interactions of Sb with the soil matrix are evidently too weak to explain the observations under batch and both column conditions (Dijkstra et al., 2009).

In general, in those cases where availability is underestimated (e.g. due to sample heterogeneity), underpredicted concentrations can be expected in both the batch mode and in the transport mode of the model. Overall, the estimated availability is much larger than the mass eluted from the column, except for Noorderbos, where the estimated availability is smaller than the mass eluted from the column for As (by a factor of 5) and Cr (by a factor of 2). These observations indicate the possible inadequacy of estimating availability for some of the samples; sample heterogeneity is the most likely explanation.

6.2.5 *Discussion*

Overall, the observed deviations between (transport) model and data are considered acceptable. This is encouraging given the large differences between batch and column tests and the consistency in model performance under both test conditions. The deviations between model and data seem to be caused by inadequate estimates of important parameters (e.g. availability) rather than failure of the underlying model components (NICA-Donnan, GTLM, Donnan models) due to the highly different loadings under transport conditions as a result of different L/S ratios. Furthermore, transport-related physical features, such as the influence of non-equilibrium, do not seem to be a major source of deviations between model and data, as the sensitivity of the model curves to important chemical parameters is demonstrated to be very important.

It should also be noted that a percolation test should not be (over-)interpreted as a quick simulation of leaching behaviour in practice on longer time scales. The washout of salts and major elements and the dynamic behaviour of DOC are effects typically observed in a column experiment, but are for a number of obvious reasons unlikely to be seen in the same magnitude in practice, where these parameters can be assumed to remain fairly constant over long time scales.

6.3 Evaluation of the reactive transport model at field scale

Evaluation of reactive transport models for field conditions is hampered by the availability of suitable field data. Because metal transport is a very slow process with typical travel velocities between 0.01 and 1 cm per year due to strong retardation, only long-term transport events of tens to hundreds of years will give meaningful information for model evaluation. A possible way to overcome this problem is retrospective or hindcast modelling of long-term historical pollution events in which present contaminant profiles are predicted by starting from an uncontaminated site using (estimated) historical inputs (Groenenberg et al., in prep). In this study we evaluate the overall performance of the model for its ability to simulate transport of metals in a field soil. For this study we selected a site that had been used as a wastewater infiltration field for about 50 years, during which time the soil had become loaded with various metals, but most severely with Cr, originating from industrial (including tannery) waste and domestic wastewater from the city of Tilburg. The selected plot is very useful for the evaluation of the long-term effects of metal transport and for modelling because of the large amounts of wastewater, equalling about four times the normal precipitation surplus, that have infiltrated the field. The total amount of water that has infiltrated these fields since the start of wastewater infiltration is equal to the infiltration of about 280 years by precipitation only.

Data were used from a monitoring study established in 2000 for a risk assessment of accumulated metals. To study the effect of the transformation of pasture into afforested land on the availability and mobility of metals, part of the field plots were acidified by applying elemental sulphur to the soil in 2003. Two soil profiles (composite samples from ten subsamples), one untreated and one acidified, were sampled in 2009 in layers of 10 cm thickness to a depth of 150 cm. Reactive soil concentrations (0.43 M HNO_3) and solution concentrations in pore water obtained by centrifugation or in 0.002 M CaCl2 extracts were determined, as well as the contents of the reactive surfaces, i.e. humic substances (HS), in soil organic matter (SOM) and dissolved organic matter (DOM), Al/Fe-(hydr)oxides and clay.

The hindcast simulation was run for a period of 80 years divided into three or four periods: (1) wastewater infiltration (50 years); (2) meadow (20 years); (3) forest (10 years). For the acidified plot the last period was split to include (4) the period after acidification (7 years). For the simulations we used measured pH values. The total added load of metals to the soil was derived from the present reactive metal concentration in the soil minus a background level.

Figure 6.3.1 shows the comparison of predicted concentrations of Cr in solution with measurements for solution obtained by both centrifugation and extraction with $CaCl_2$ in the undisturbed and acidified profiles. Results of the predictions for other metals also match favourably with measurements, except for Pb, for which the model predicted higher solution concentrations. Concentrations in centrifuged samples were systematically higher than those of the $CaCl_2$ extracts due to the much higher DOC concentrations in the centrifuged samples. The model was well able to predict the effect of DOC on metal concentrations in solution.

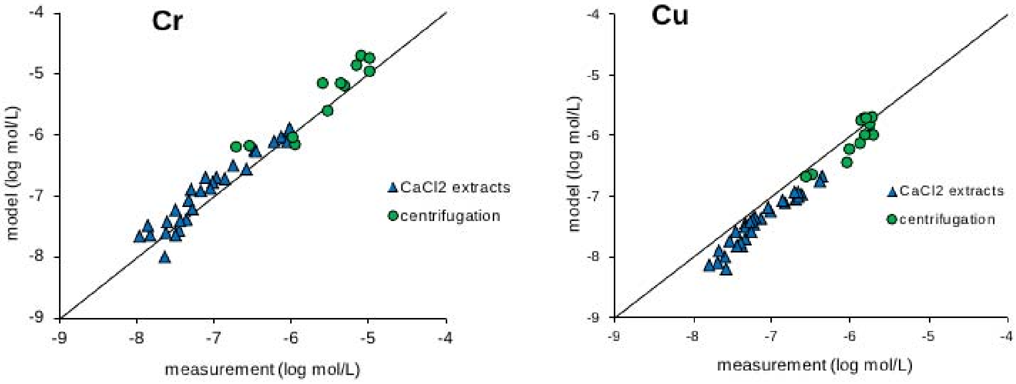


Figure 6.3.1: Predicted and measured concentrations of Cr and Cu in solution obtained by centrifugation (circles) and $CaCl_2$ extraction (triangles) (Groenenberg et al., 2011).

Figure 6.3.2 shows the results of the simulated Cr and Cu profiles for the untreated soil. Similarly good results were obtained for the other metals, except again for Pb, for which the predicted concentrations in the topsoil were too high whereas concentrations deeper in the profile were too low. This cannot be explained by the overprediction of solution concentrations by the geochemical model. It is possible that other mechanisms, such as colloidal transport, play an important role for Pb. We tested the sensitivity of the model to changes in model inputs by varying the water infiltration flux (fluxmin and fluxplus) and the concentration of DOC (docmin and docplus). When we used DOC concentrations as determined in the $CaCl_2$ extracts instead of those from centrifuged samples, simulated transport was far too low, resulting in predicted concentrations being too high in the topsoil and too low in the subsoil. This clearly shows the need to use realistic DOC concentrations in transport modelling.

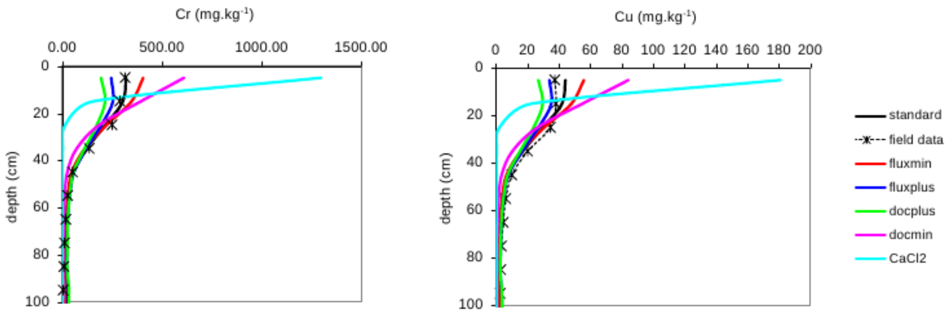


Figure 6.3.2: Predicted and measured concentration profiles of Cr and Cu in the undisturbed field plot (Groenenberg et al., 2011). The black line represents the standard run. Other lines give the sensitivity of the model to changed model inputs for water infiltration rate and DOC (see text for further explanation).

The model was able to predict the increased transport of metals induced by acidification as shown in Figure 6.3.2. Predictions were especially good for metals for which solubility strongly depends on pH, such as Cd (Figure 6.3.3) and Ni and Zn (data not shown).

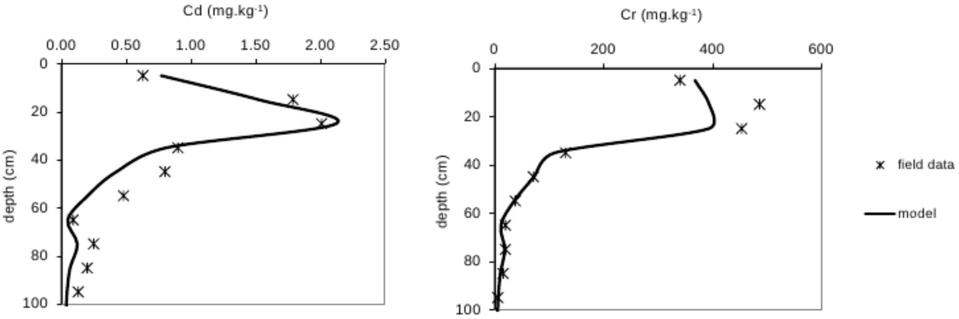


Figure 6.3.3: Predicted concentrations of Cd and Cr in the acidified soil plot (Groenenberg et al., 2011)

7 Results

7.1 Introduction

The large amount of data generated by the model makes it necessary to show only selected results here. In this chapter an overview of these results is given for the three model scales (see section 5.1):

1. Showing detailed leaching behaviour in the three standard sand, peat and clay profiles for the scenarios with the MV Agricultural;
2. Aggregated data of selected STONE soil types with the largest spatial areas for the scenarios with the MV Agricultural, Residential, and Industrial;
3. A spatial overview of all STONE scenarios at the level of the MV Agricultural.

Note that in the above scales, the soil profiles under 1 are not a subset of the profiles of point 2.

Sections 7.2–7.15 in this chapter each discuss the results for a single element. The sections start with the actual soil concentrations from the Dutch Geochemical Atlas and compare these values with the input parameters. Then the results of the modelling are discussed.

For the first scale, results are shown using breakthrough curves and soil profiles. The breakthrough curves show the change in concentrations over time at a certain depth. The soil profiles show the change with depth at a specific moment in time. The results for the three standard soil profiles are given in a table. The breakthrough curves and soil profiles are shown in Appendix B.

Second, the aggregated data, based on the 20 soil profiles, are given as box-and-whisker plots for each scenario and soil type. These results give an indication of the ranges of predicted concentrations compared with actual ambient groundwater concentrations (MC values) and the MPA.

Finally, spatial overviews of all the soil profiles are given as maps in which the ratios of the predicted concentrations to the soil type-specific MCs are shown. These maps do not cover the whole research area since the model cannot predict leaching for each separate soil profile in the STONE dataset. These soil profiles are shown as missing values. The empty areas in the STONE database are also shown as missing values.

For each scale, predicted groundwater concentrations are given for 100- and 500-year time frames and at 100 and 500 cm depths. Exact concentrations in e.g. breakthrough curves are given at the soil layers at this depth, while average peak concentrations are given over a 1 m range, i.e. 100–200 cm and 500–600 cm.

At the end of this chapter is a discussion of all the elements together and their relation to each other.

7.1.1 Model runs

The geochemical speciation and reactive surface model tries to dynamically solve a large amount of chemical equilibrium equations. However, there is a possibility that the model algorithm will not find (i.e. will not converge to) a satisfying solution. Scenarios where the model could not find a solution were disregarded from the results. Although the parameterisation of the model in these cases can be adjusted to obtain a proper solution, on account of time constraints such an effort was not undertaken.

Table 7.1.1.1 lists the model scales, the number of scenarios set up for calculation for each scale and the final number of scenarios used in these results. Most scenarios which did not converge to a solution were located on (marine) clayey soils with pH values in the range of 6–8. Leaching of most metals in these soils is expected to be limited.

Table 7.1.1.1: Number of scenarios used as input for each model scale and number of scenarios used in the data analyses

Model scale	**Number of input scenarios**	**Number of scenarios used in results**
Standard scenarios	3	3
Major soil type scenarios	20	15
All available STONE profiles	456	356

7.2 Arsenic (As)

7.2.1 Input parameters

The input parameters for As are given in Table 7.2.1.1. The MV differs between all soil profiles as a result of the Soil Type Correction, which for As is dependent on grain size and organic matter. Ambient total concentrations (95th percentile) of As range from 0.4 mg/kg for sand to 2.9 mg/kg for fluvial clays. Reactive ambient concentrations (95th percentile) range from 0.3 mg/kg for sand to 2.41 mg/kg for peat.

Table 7.2.1.1: Input concentrations for As for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	3.2	12.6	9.3
	peat	8.4	24.4	16.0
	clay	8.3	18.0	9.8
residential	*sand*	3.2	16.9	13.7
	peat	8.4	33.0	24.5
	clay	8.3	24.4	16.1
industrial	*sand*	3.2	47.7	44.5
	peat	8.4	92.8	84.3
	clay	8.3	68.6	60.3

7.2.2 Concentration ranges

Figure 7.2.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. All the concentrations are far below the levels of the MC and MPA.

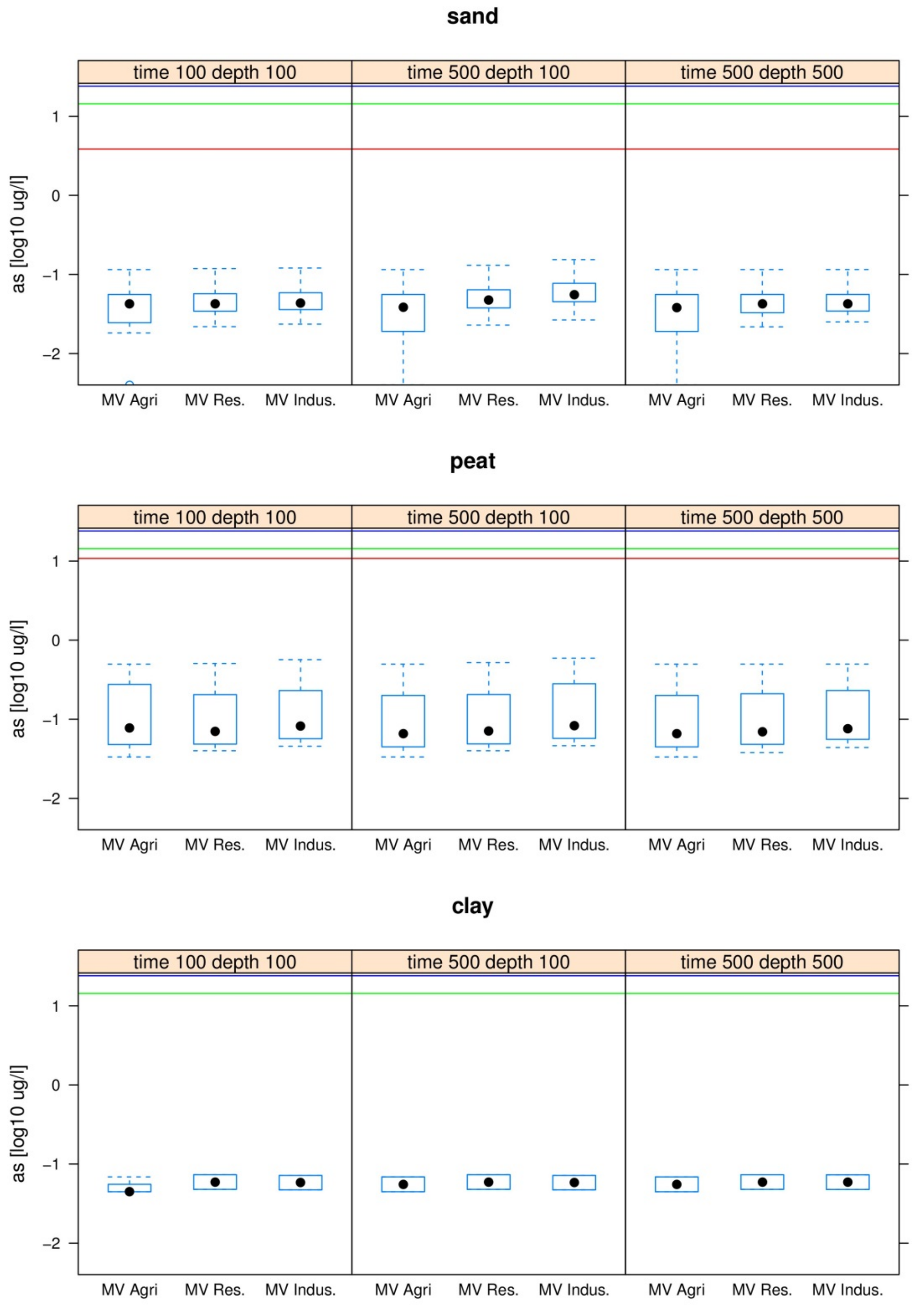


Figure 7.2.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC. For clay the MC is 26.1 ug/l, which is 1.42 ug/l on a log scale (not shown .

7.2.3 *Map*

Figure 7.2.3.1 shows the map with the estimated exceedance of the soil type-specific MC of groundwater concentrations for several scenarios. Only in some small areas in the northeast of the country is the ratio between predicted concentration and MC larger than 1 (brown colours); for most of the areas no exceedance is predicted.

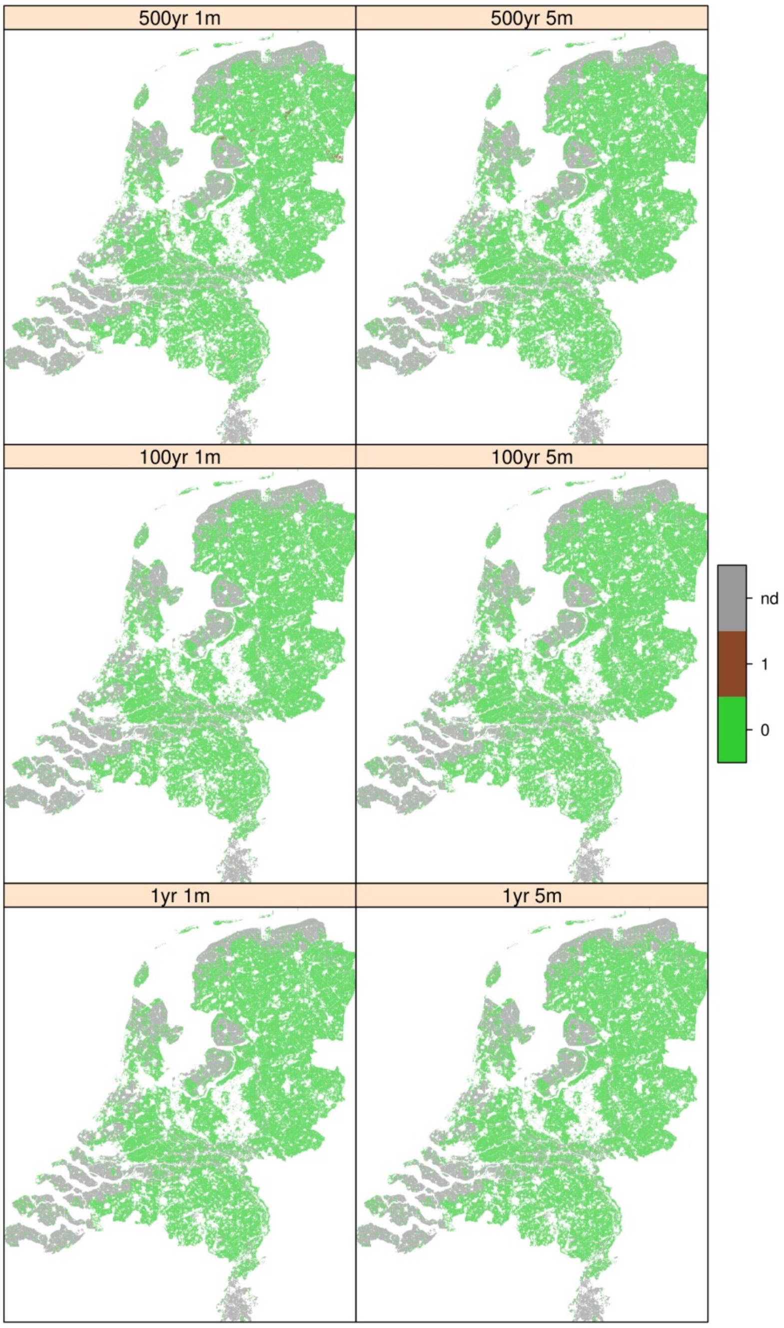


Figure 7.2.3.1: Maps of As showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.2.4 *Interpretation*

Arsenic is an element whose behaviour is highly susceptible to changes in oxidation levels of the environment. In general, As is mobile in reducing environments and immobile in oxidising environments. The model assumes a mild oxidising environment and this is a possible reason why no leaching of As is predicted. For the upper layers in sandy soils this is a valid assumption. For clayey and peaty soils the assumption of an oxidising environment can be challenged. In these soils, located in the low-lying areas of the west, As is often found in relatively high concentrations due to mobilisation of natural As as a result of a changing redox environment, although some of this naturally occurring As is transported and enriched as a result of human interference with groundwater levels.

In the model the estimated speciation of As is also limited by the assumptions for the concentrations of PO^{4+}. Using more realistic concentrations of PO^{4+} can improve the prediction of As.

The modelled sand and peat profiles show some higher soluble concentrations of As in the upper layer, which sharply decreases in the subsequent layer (see Appendix B). For peat this variability of As over depth in the solid phase is related to the Fe-ox content of the standard soil profile. These Fe-ox values are high in the upper part of the profile (around 200 mg/kg) but decrease to values of 13 mg/kg in the lower part (>100 cm depth). Also, the reactive concentration used as input is relatively high compared with ambient concentrations.

Specific soil processes which can influence As, such as As mobilisation from pyrite due to (nitrate) acidification, are specific to certain areas and therefore not incorporated in this (generic) model assessment.

7.3 Barium (Ba)

7.3.1 *Input parameters*

The input parameters for Ba are given in Table 7.3.1.1. The MVs differ between all soil profiles as a result of the Soil Type Correction, which for Ba is dependent on grain size only. Ambient total concentrations (95th percentile) of Ba range from 259 mg/kg for sand to 641 mg/kg for peat. Reactive ambient concentrations (95th percentile) range from 25 mg/kg for sand to 218 mg/kg for peat.

The MVs in Table 7.3.1.1 are below the actual background concentrations from the Geochemical Atlas. This is a result of using different analytical techniques to obtain these concentrations. For the MVs an extraction with aqua-regia was used, while for the Geochemical Atlas total concentrations were obtained using X-Ray Fluorescence. When a reactive concentration is estimated using the methodology of Section 4.2, this will result in negative concentrations in the case of Ba. In cases where the MV is below the Cb, the reactive Ba concentrations are calculated by multiplying the Cb value by the partition coefficient of Section 4.3 (See Appendix A for detailed methodology).

Table 7.3.1.1: Input concentrations for Ba for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	263.9	57.0	8.7
	peat	449.7	179.6	59.3
	clay	444.6	176.2	16.1
residential	*sand*	263.9	165.0	8.7
	peat	449.7	519.8	70.1
	clay	444.6	510.1	65.5
industrial	*sand*	263.9	276.0	12.1
	peat	449.7	869.5	419.8
	clay	444.6	853.2	408.6

7.3.2 Concentration ranges

Figure 7.3.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. The predicted concentrations are far lower than the MC and MPA values. Also, the variability for each scenario is small (small compressed boxes in the box-and-whisker plot).

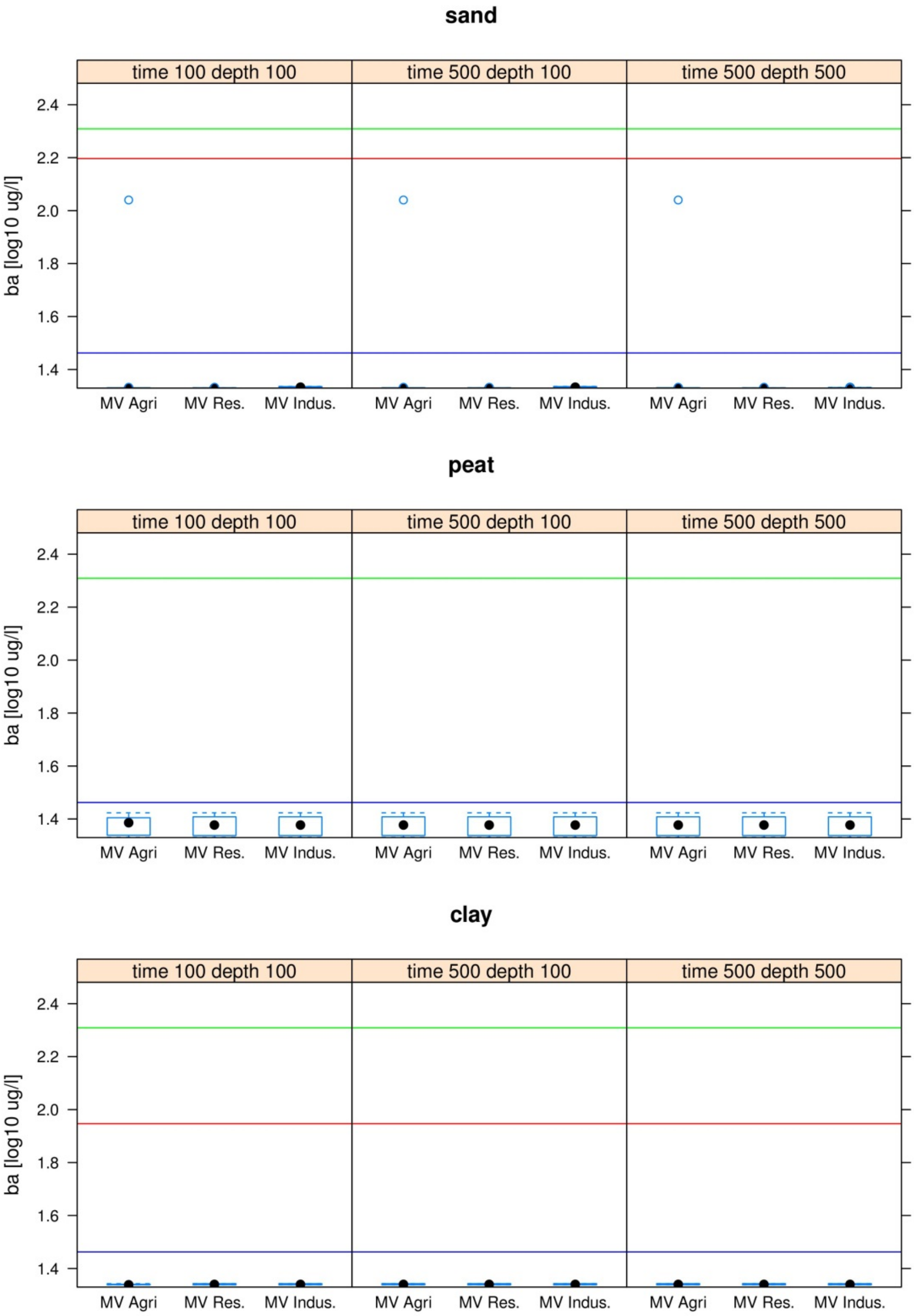


Figure 7.3.2.1: Box-and-whisker plots of groundwater concentrations (logarithmic scale) in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.3.3 *Map*

The results of the spatial prediction showed no exceedance of the MC in any of the soil profiles. Therefore, no map is shown.

7.3.4 *Interpretation*

Barium is known to be rather insoluble in soils. Due to the abundant presence and high affinity with SO_4, any dissolved Ba quickly precipitates as $BaSO_4$. In Figure 7.3.2.1 there is variability in concentrations between the different MVs. This shows that all Ba for each scenario is immediately precipitated and not transported through the soil profile. In Appendix C the results of scenario calculations for the MV Agricultural are presented with SO_4 input concentrations one order of magnitude lower than the above concentrations. From the results in Appendix C it is clear that a lower SO_4 concentration results in a higher predicted Ba concentration in the groundwater, showing that it is indeed the precipitation with SO_4 which determines the estimated Ba concentrations. Nevertheless, these higher concentrations are below the MC values.

7.4 Cadmium (Cd)

7.4.1 *Input parameters*

The input parameters for Cd are given in Table 7.4.1.1. The MVs differ between all soil profiles as a result of the Soil Type Correction, which for Cd is dependent on grain size and organic matter. Ambient total concentrations (95th percentile) of Cd range from 0.4 mg/kg for sand to 2.9 mg/kg for fluvial clays. Reactive ambient concentrations (95th percentile) range from 0.3 mg/kg for sand to 2.41 mg/kg for peat.

Table 7.4.1.1: Input concentrations for Cd for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		Cb	MV	Reactive
agricultural	sand	0.06	0.4	0.3
	peat	0.12	0.8	0.7
	clay	0.11	0.5	0.4
residential	sand	0.06	0.7	0.7
	peat	0.12	1.7	1.6
	clay	0.11	1.0	0.9
industrial	sand	0.06	2.7	2.6
	peat	0.12	6.0	5.9
	clay	0.11	3.7	3.6

7.4.2 *Concentration ranges*

Figure 7.4.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. MC and MPA criteria are for all three soil types exceeded in the 500-year, 100 cm depth scenarios. The MC value for clay and peat is eight times lower than for sand; for these soil types the MC is in general exceeded at 100 cm depth after 500 years. For sandy soils the range of predicted concentrations at 500 cm depth in the scenario with the MV Industrial is above the MPA and MC levels.

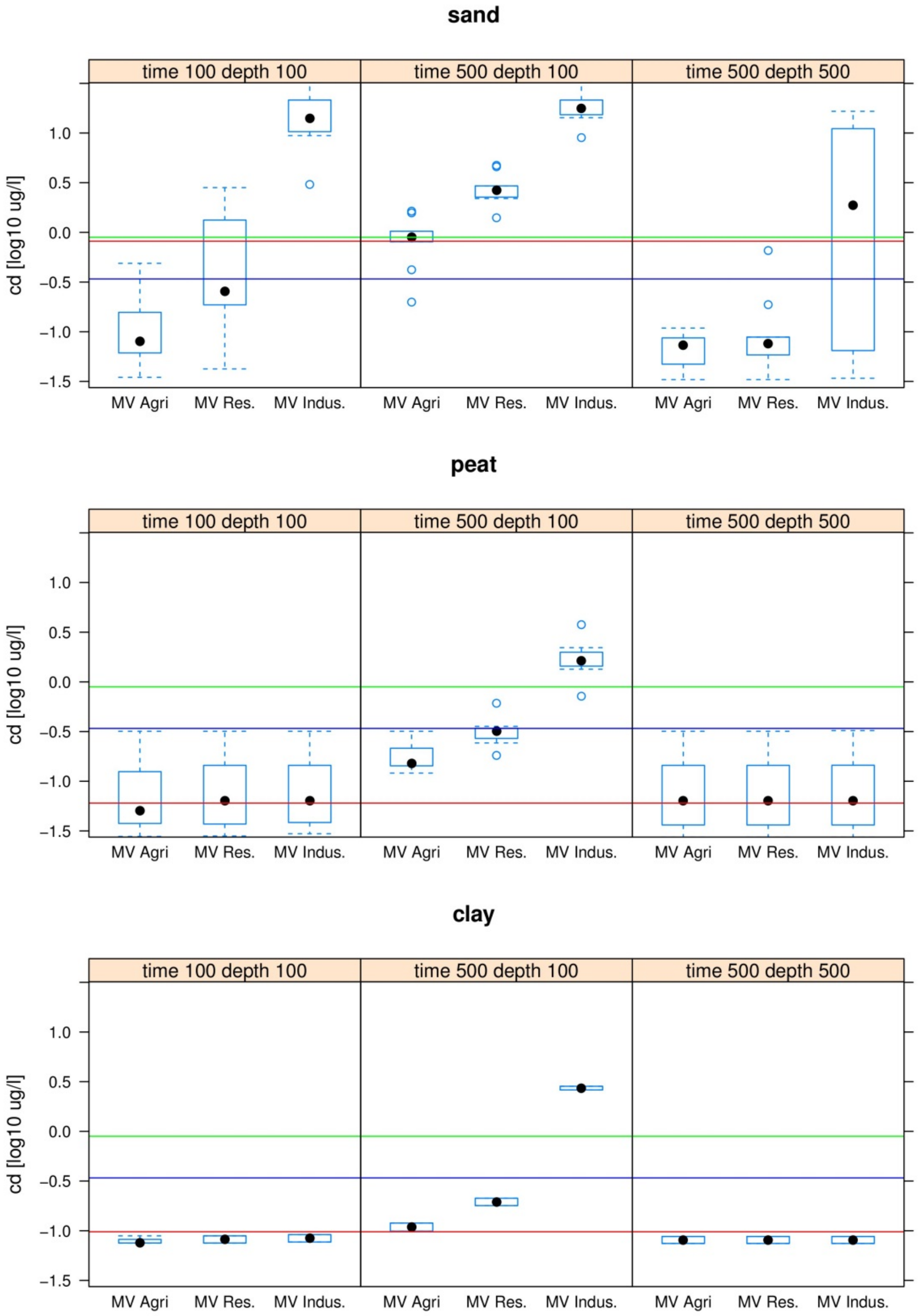


Figure 7.4.2.1: Box-and-whisker plots of groundwater concentrations (logarithmic scale) in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.4.3 Map

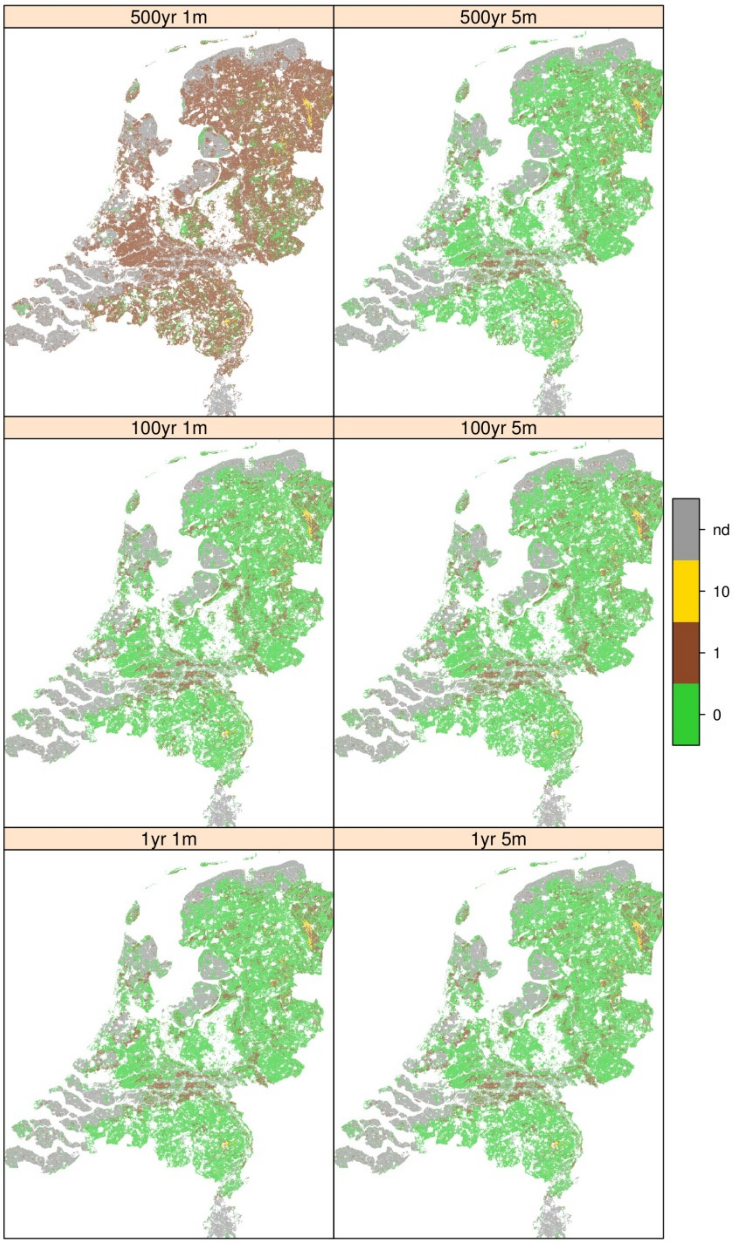


Figure 7.4.3.1: Maps of Cd showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

Figure 7.4.3.1 show the spatial distribution of the predicted Cd peak concentrations. The 5 m depth scenarios are more or less the same, except that after 500 years some small plots show a larger ratio of predicted concentration and MC (yellow areas). At 1 m depth the difference between the 100-year and 500-year scenarios is obvious: there is a significant increase in the concentration/MC ratio in areas with sandy and fluvial clay soils.

7.4.4 *Interpretation*

The model predicts pore water concentrations of Cd fairly well (see Chapter 6). The predicted concentrations at time t=0 and depth d=0 of 2.8 ug/l in the sand profile is in the range which is given in the Dutch Geochemical Atlas. The latter indicates concentrations in sand of 2.0 to 8.7 (median – 95th percentile range, based on 0.01 M $CaCl_2$ extracts). Therefore, we consider that the calculated ranges in pore water of the three standard scenarios are realistic.

Leaching of Cd is largest in the sandy profile. Based on the results of the 20 main scenarios, leaching can also be expected in sandy and peaty soils at shallow depths (1–2 m). However, this leaching is only visible in the 500-year scenarios. The ratio between predicted maximum peak concentrations and the soil type-specific MC is below 10.

The MV Industrial of Cd results in (predicted) groundwater concentrations 20-30 times above the MC at 100 cm depth. Also at 500 cm depth some scenarios result in predicted concentrations above The MC.

7.5 Cobalt (Co)

7.5.1 *Input parameters*

The input parameters for Co are given in Table 7.5.1.1. For Co no geochemical background values are known. Based on the results of the Dutch Soil Monitoring Network an arbitrary value of 5 mg/kg was chosen, which is an average value for the sampled soil type/land use categories.

The MV for sandy soils lies below this arbitrary value of 5 mg/kg and as a result (see calculations in Appendix A) the reactive concentration is set a 0.5 mg/kg.

Table 7.5.1.1: Input concentrations for Cr for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	5	4.9	0.5
	peat	5	14.2	9.2
	clay	5	14.0	9.0
residential	*sand*	5	11.4	6.4
	peat	5	33.1	28.1
	clay	5	32.6	27.6
industrial	*sand*	5	61.7	56.7
	peat	5	180.0	175.0
	clay	5	176.7	171.7

7.5.2 *Concentration ranges*

Figure 7.5.2.1 shows the concentration ranges based on the 20 soil profiles together with the MPA levels. No MC level is available for Co. The levels of the MPA are exceeded in the sandy and upper peaty soils. This exceedance goes up to 2–3 orders of magnitude.

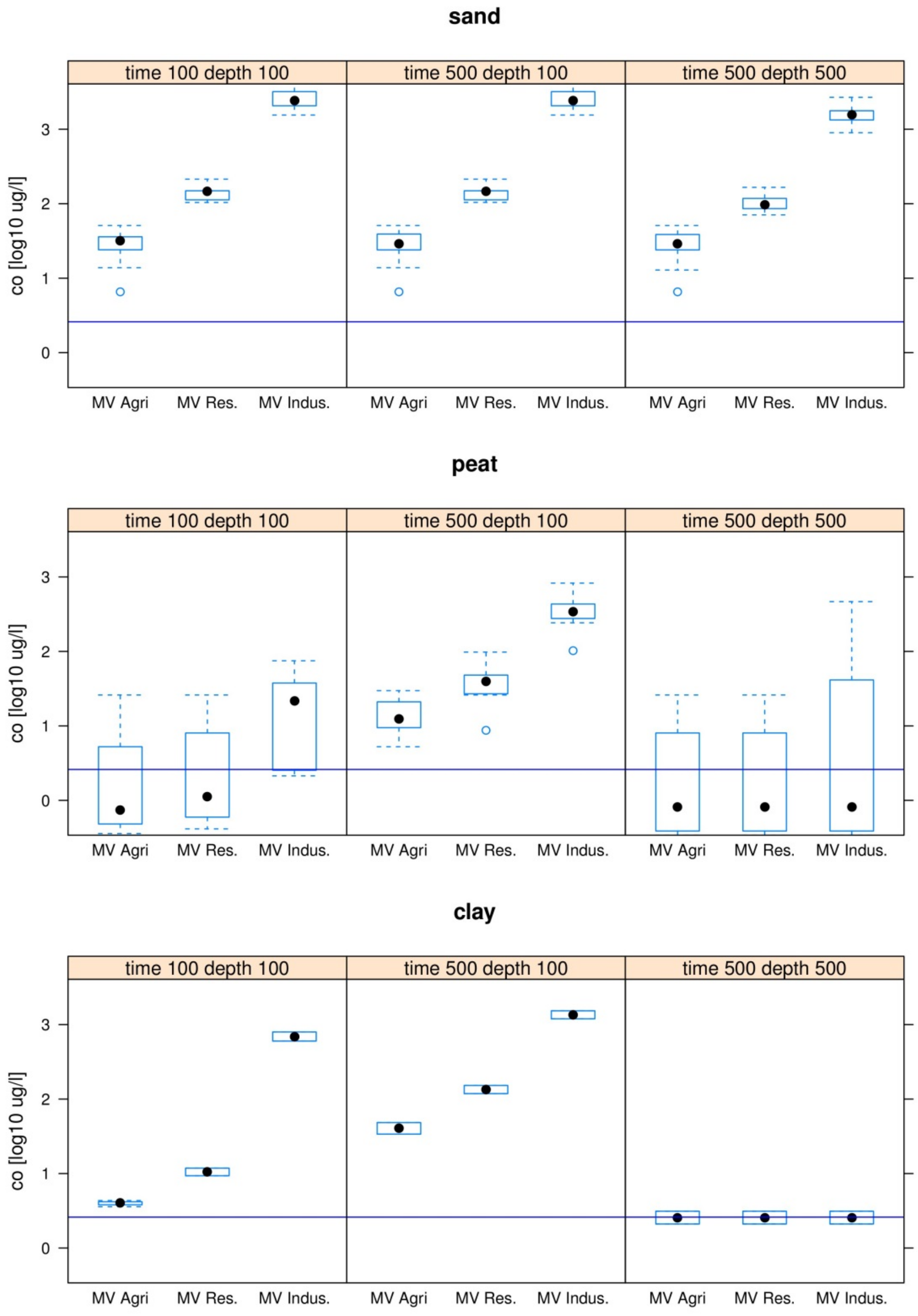


Figure 7.5.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.5.3 *Interpretation*

Since no detailed information about actual soil concentrations was available during the modelling stage of this research, the results should be treated with caution. The reactive input concentrations for the MV Agricultural range between

0.5 mg/kg and 9 mg/kg. Later on, data for Co became available which showed median and 95th-percentile values of 0.74 and 3.36 mg/kg, respectively, and this confirms the model input within a factor of 2 (Groenenberg, pers. comm.).

Fraters et al. (2001) Estimated 90th-percentile background concentrations of Co in surface groundwater at 8.5 to 39 µg/l, while our model estimates maximum average concentrations of between 0.4 µg /l for peat and 24.2 µg /l for sand at 100 cm depth and after 100 years, so within the same range as Fraters et al. (2001). From the evaluation it is known that the geochemical speciation modelling of Co is sufficiently good.

7.6 Chromium (Cr)

7.6.1 Input parameters

The input parameters for Cr are given in Table 7.6.1.1. The MVs differ between all soil profiles as a result of the Soil Type Correction, which for Cr is dependent only on grain size. Ambient total concentrations (95th percentile) of Cr range from 37 mg/kg for sand to 116 mg/kg for fluvial clays. Reactive ambient concentrations (95th percentile) range from 1.6 mg/kg for sand to 4.7 mg/kg for fluvial clays.

The natural background values for Cr in peat and clayey soils are above the MVs for agricultural and residential areas. This is possibly due to the difference in approach to deriving the background value. For this research natural background concentrations were based on the total concentrations derived from data in the Dutch Geochemical Atlas. For the MVs background concentrations are based on aqua-regia extracted soil samples, which give soil concentrations of about half of total concentrations. When the background value is higher than the MV, the reactive value is replaced in the model by the natural estimated background value times the partition coefficient form Section 4.3. In the case of Cr this results in the reactive concentration as given in Table 7.6.1.1, where the MVs for agricultural and residential areas are the same for peat and clay.

Table 7.6.1.1: Input concentrations for Cr for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	29.2	31.1	2.0
	peat	63.6	53.1	1.9
	clay	62.6	52.5	1.0
residential	*sand*	29.2	35.1	5.9
	peat	63.6	59.9	1.9
	clay	62.6	59.2	1.0
industrial	*sand*	29.2	101.9	72.7
	peat	63.6	173.9	110.3
	clay	62.6	171.9	109.3

7.6.2 Concentration ranges

Figure 7.6.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels.

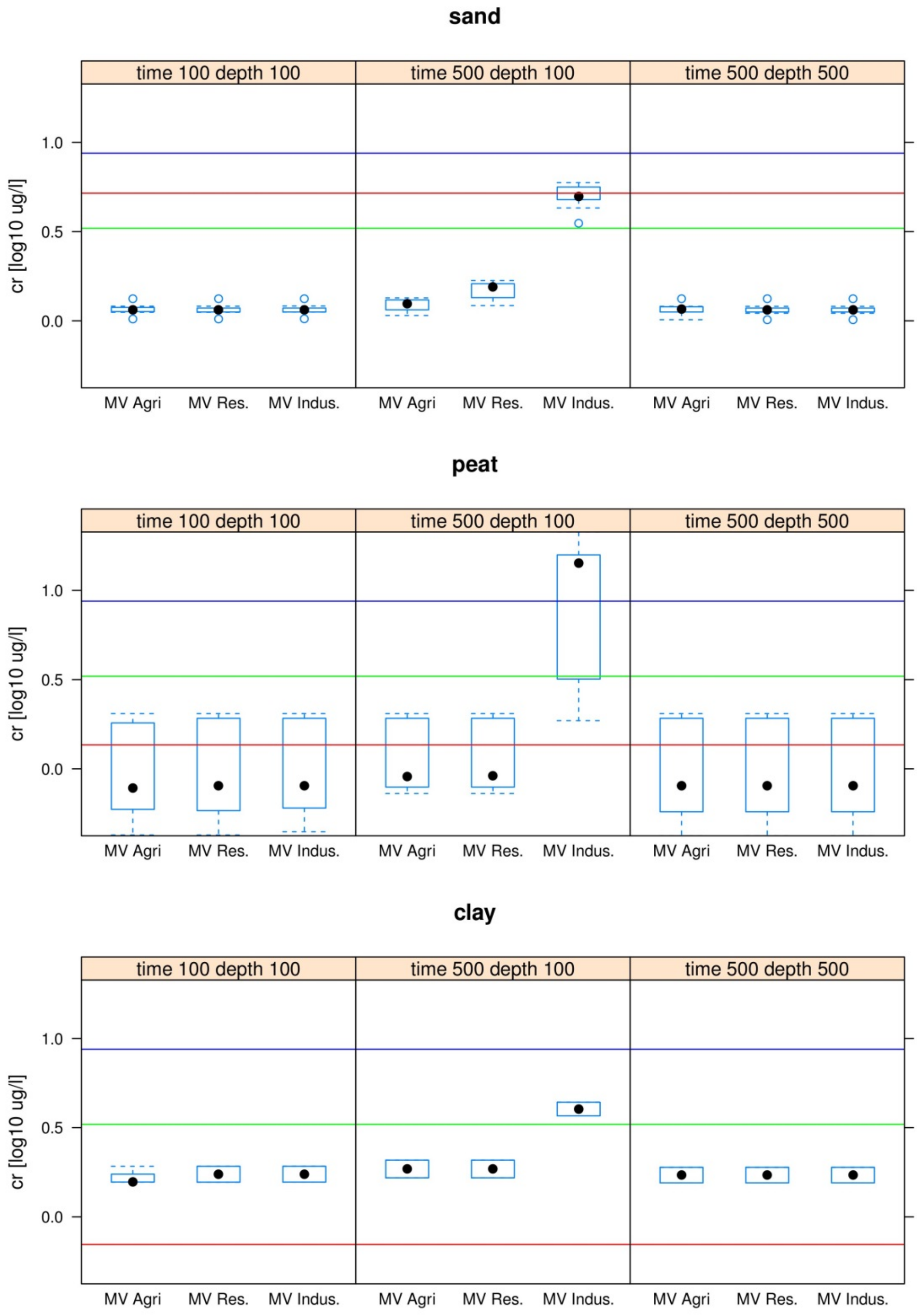


Figure 7.6.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.6.3 Map

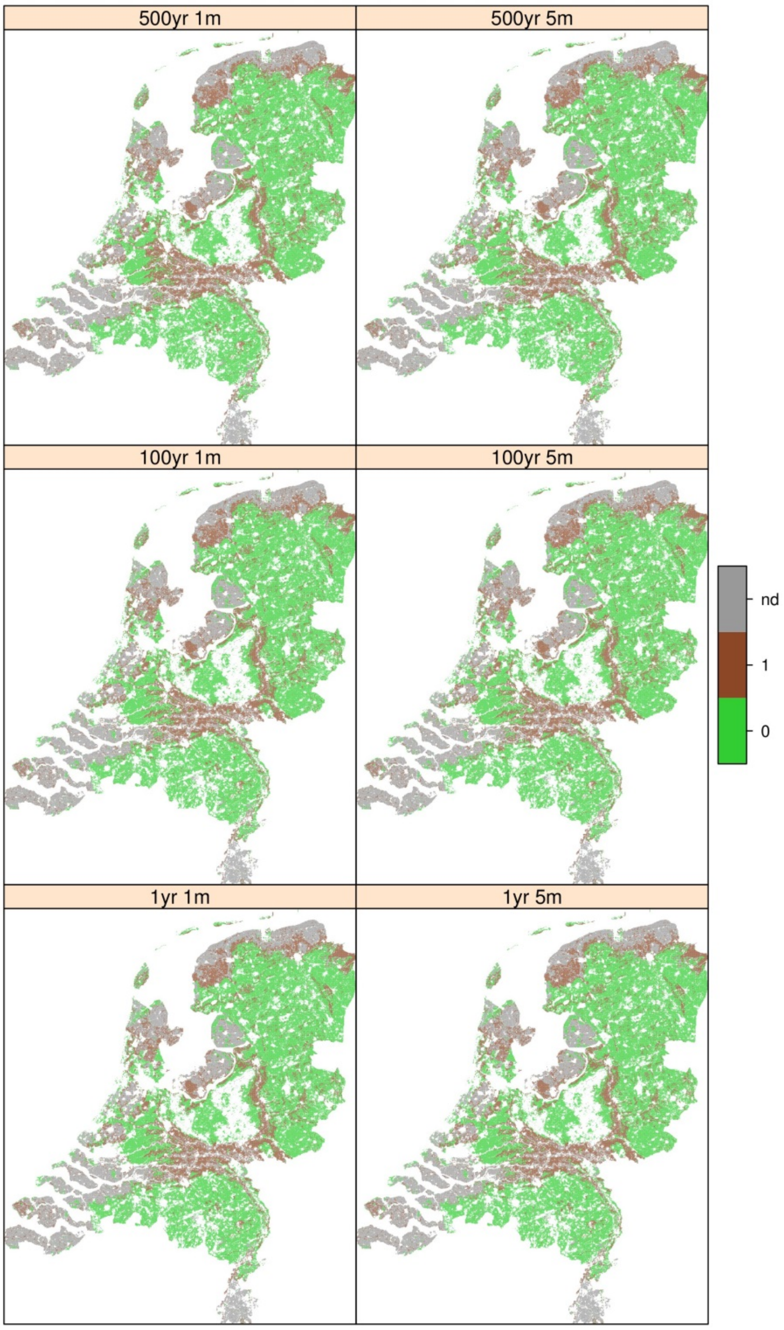


Figure 7.6.3.1: Maps of Cr showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.6.4 Interpretation

Despite the fact that the Cr concentrations for the MV Agricultural and the background values (Cb) are derived differently (aqua-regia extraction versus total concentrations), resulting in background values higher than the MVs, the pore water concentration of the MV Agricultural are in line with the pore water concentrations as measured in the field.

The predicted concentrations are below the MPA and the MC criteria. For clay, and to a lesser extent peat, all the concentrations are above the MC. This is due to relatively low MC values, which are 5.2 ug/l for sandy areas and 1.36 ug/l and 0.70 ug/l for peat and clay, respectively.

In general, the scenarios with the MV Industrial result in elevated groundwater concentrations at 100 cm depth and after 500 years. For the other scenarios no change in groundwater concentrations is predicted.

7.7 Copper (Cu)

7.7.1 Input parameters

The input parameters for Cu are given in Table 7.7.1.1. The MV differs between all soil profiles as a result of the Soil Type Correction, which for Cu is dependent on grain size and organic matter, and this results in relatively high MVs for peat. Ambient total concentrations (95th percentile) of Cu range from 20 mg/kg for sand to 65 mg/kg for fluvial clays. Reactive ambient concentrations (95th percentile) range from 12 mg/kg for sand to 32 mg/kg for peat.

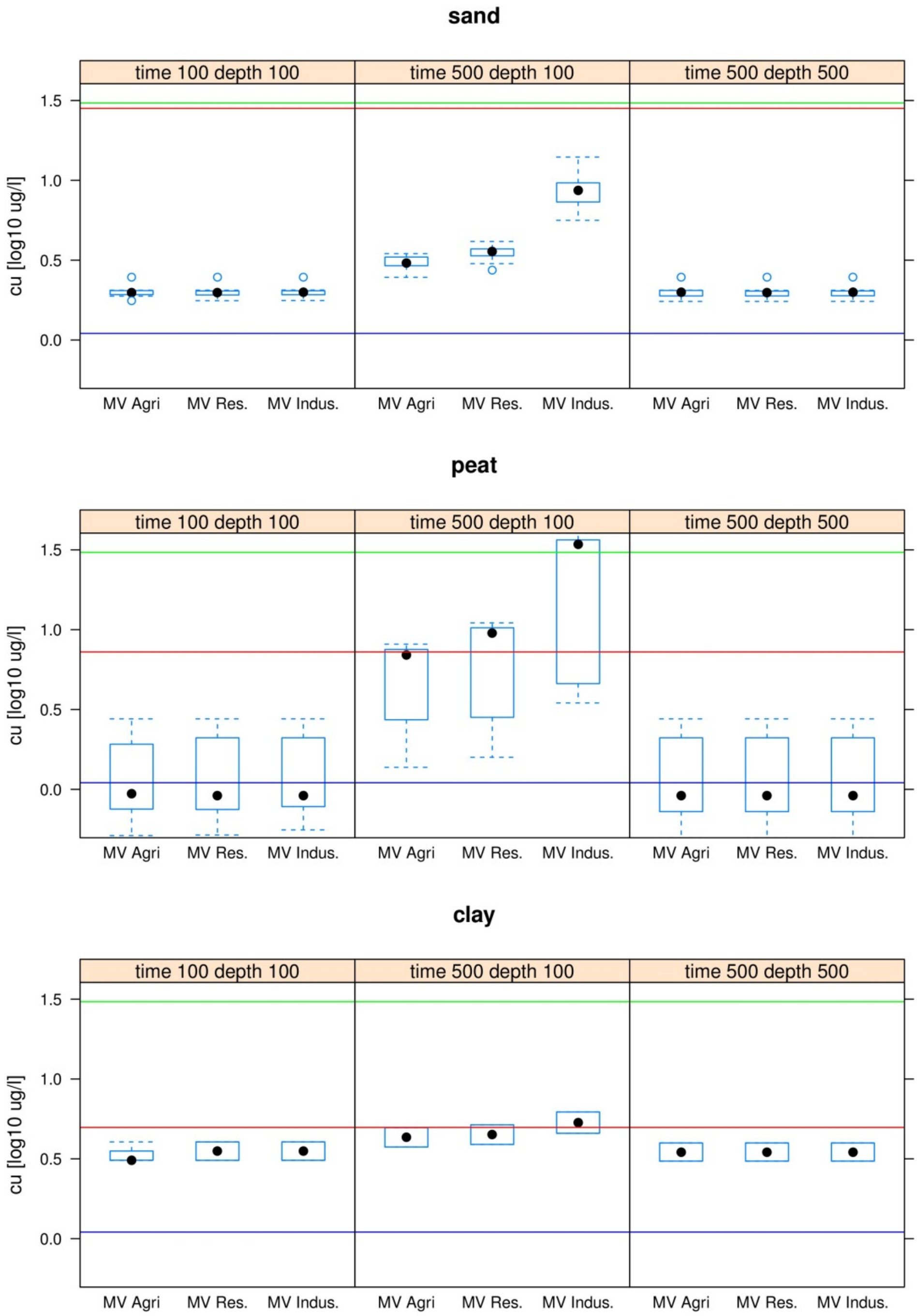
Table 7.7.1.1: Input concentrations for Cu for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	2.5	22.0	19.5
	peat	6.6	50.7	44.1
	clay	6.5	35.3	28.8
residential	*sand*	2.5	29.7	27.2
	peat	6.6	68.4	61.8
	clay	6.5	47.6	41.1
industrial	*sand*	2.5	104.5	102.0
	peat	6.6	240.7	234.1
	clay	6.5	167.5	161.0

7.7.2 Concentration ranges

Figure 7.7.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. In sandy soils no MC criteria are exceeded. This is because the MC values are based on diffusely contaminated groundwater, which has the highest concentration of Cu in sandy areas. The MPA, however, is exceeded in all cases in these sandy soils. For the peaty soils MC criteria are exceeded in the 500-year, 100 cm depth scenario, especially for the MV Industrial. For clayey soils the predicted peak concentrations are close to the soil type-specific MC, except for the 500-year, 100 cm depth scenario. In the latter scenario the peak concentrations are around, or just above, the soil type-specific MC. Also in the clayey scenarios, the MPA level is exceeded.

Figure 7.7.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the



plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.7.3 *Map*

The maps in Figure 7.7.3.1 show some areas with ratios between predicted peak concentrations and soil type-specific MC below 10. Note that the soil type-specific MC is about 4–6 times higher in sandy soils than in peaty and clayey soils. Also, in sandy soils the MC value is 15 times higher than the MPA.

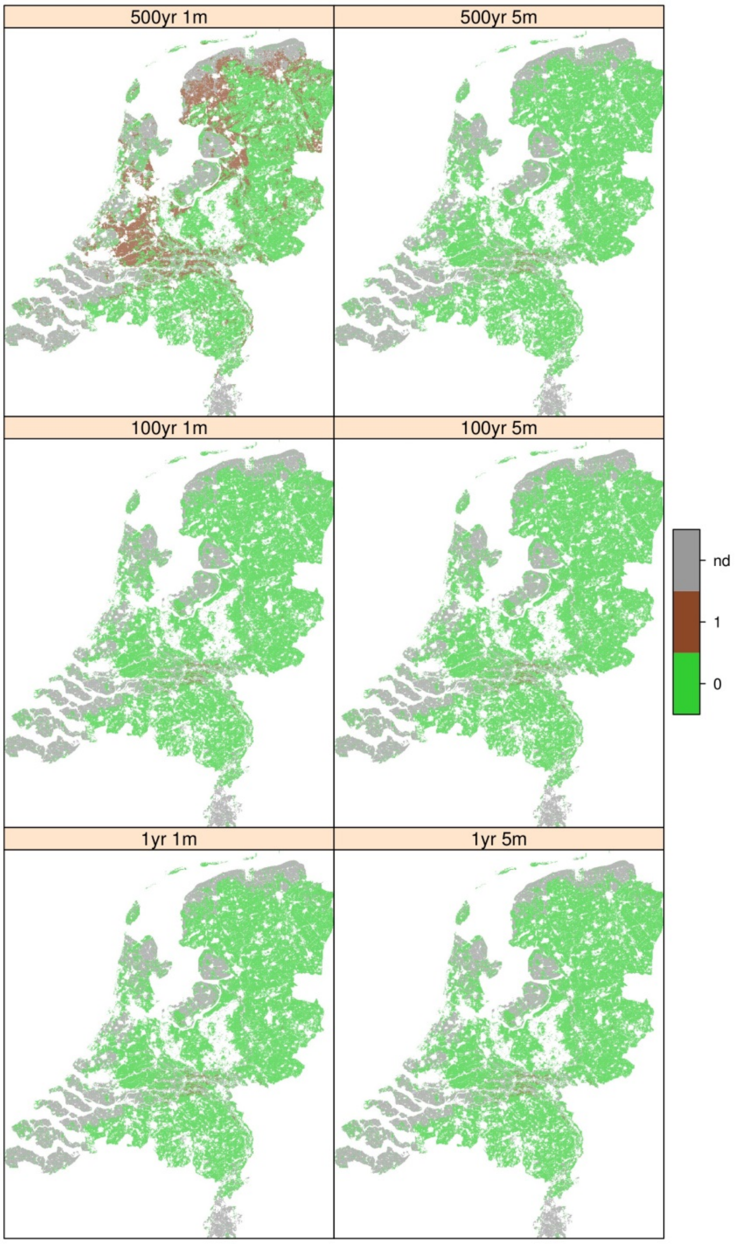


Figure 7.7.3.1: Maps of Cu showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.7.4 *Interpretation*

Ambient groundwater concentrations are highest in the sandy soils of the eastern Netherlands (see Chapter 4). The predicted peak concentrations of the MV Agricultural fall within these ambient, but diffusely polluted, concentrations. Higher MVs for residential and industrial areas show exceedance of soil type-specific MC for peat, as result of the high affinity of Cu for organic matter.

7.8 Mercury (Hg)

7.8.1 *Input parameters*

The input parameters for Hg are given in Table 7.8.1.1. Total concentrations for Hg vary between 0.12 mg/kg (95th percentile) for sand and 0.72 mg/kg for fluvial clays. No reactive concentrations for Hg are available from the Dutch Geochemical Atlas. The basic assumption in the model is that if no partition is available, a default partition of 0.1 is inferred, which means that 10% of the Cb concentration is considered reactive. In the case of Hg this results in the major part of the MV concentrations regarded as reactive. This is the result of the the relatively low Cb, which coincidentally reflects reality.

Table 7.8.1.1: Input concentrations for Hg for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	0.005	0.2	0.1
	peat	0.021	0.2	0.1
	clay	0.021	0.2	0.1
residential	*sand*	0.005	0.8	0.8
	peat	0.021	0.8	0.8
	clay	0.021	0.8	0.8
industrial	*sand*	0.005	4.8	4.8
	peat	0.021	4.8	4.8
	clay	0.021	4.8	4.8

7.8.2 *Concentration ranges*

Figure 7.8.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. Since no MC values could be derived for Hg, only the MPA level is shown. This MPA level is exceeded only for the MV Industrial at 100 cm depth after 500 years in the sand and peat profiles. This is also shown in Table 7.8.1.1, which shows the exact values.

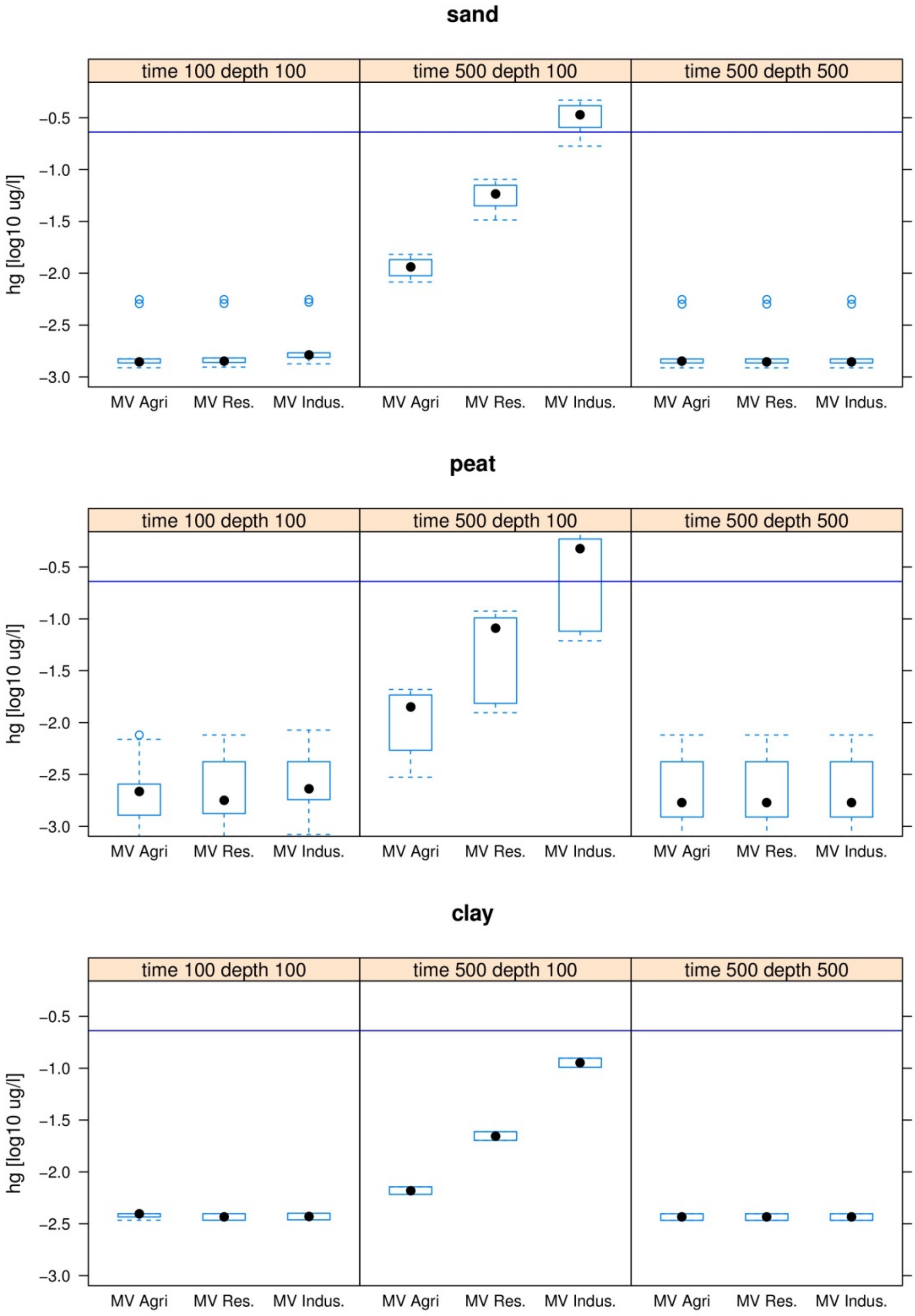


Figure 7.8.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The horizontal blue line denotes the MPA.

7.8.3 *Interpretation*

Since no MC value for Hg is available, the leaching of HG cannot be compared with ambient groundwater concentrations. However, the leaching of Hg is limited and generally does not exceed the MPA, except after 500 years at 100 cm depth in the scenarios with a MV Industrial on sand and peat.

7.9 Molybdenum (Mo)

7.9.1 Input parameters

The input parameters for Mo are given in Table 7.9.1.1. For Mo there are no soil type-specific correction factors, so the Soil Type Correction is not applied in deriving the MVs. Hence, the MV values are the same for each soil type. Total soil concentrations for Mo vary between 0.7 mg/kg (95th percentile) for sand and 3.4 mg/kg (95th percentile) for peat. Reactive concentrations vary between 32 ug/kg (95th percentile) for sand and 115 ug/kg (95th percentile) for peat.

According to the European Geochemical Atlas the variation of Mo is around 0.1 to 4 mg/kg. This is much lower than the 88 and 190 mg/kg for, respectively, the MV Residential and the MV Industrial. These MVs are concentrations levels where Mo precipitates with Pb to Wulfenite ($PbMoO_4$), a mineral associated with Pb ores. The precipitation of Wulfenite was turned off in the model to prevent Pb from being sequestrated by Mo.

Table 7.9.1.1: Input concentrations for Hg for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	0.1	1.5	1.4
	peat	0.3	1.5	1.2
	clay	0.3	1.5	1.2
residential	*sand*	0.1	88.0	87.9
	peat	0.3	88.0	87.7
	clay	0.3	88.0	87.7
industrial	*sand*	0.1	190.0	189.9
	peat	0.3	190.0	189.7
	clay	0.3	190.0	189.7

7.9.2 Concentration ranges

Figure 7.9.2.1 shows the concentration ranges based on the 20 soil profiles together with the MPA levels. For sand and peat soil types the MPA is exceeded for the MV Residential and the MV Industrial. For the clay soil types the MPA is exceeded in all scenarios. For Mo there is no MC value to compare the predicted concentrations with ambient groundwater concentrations.

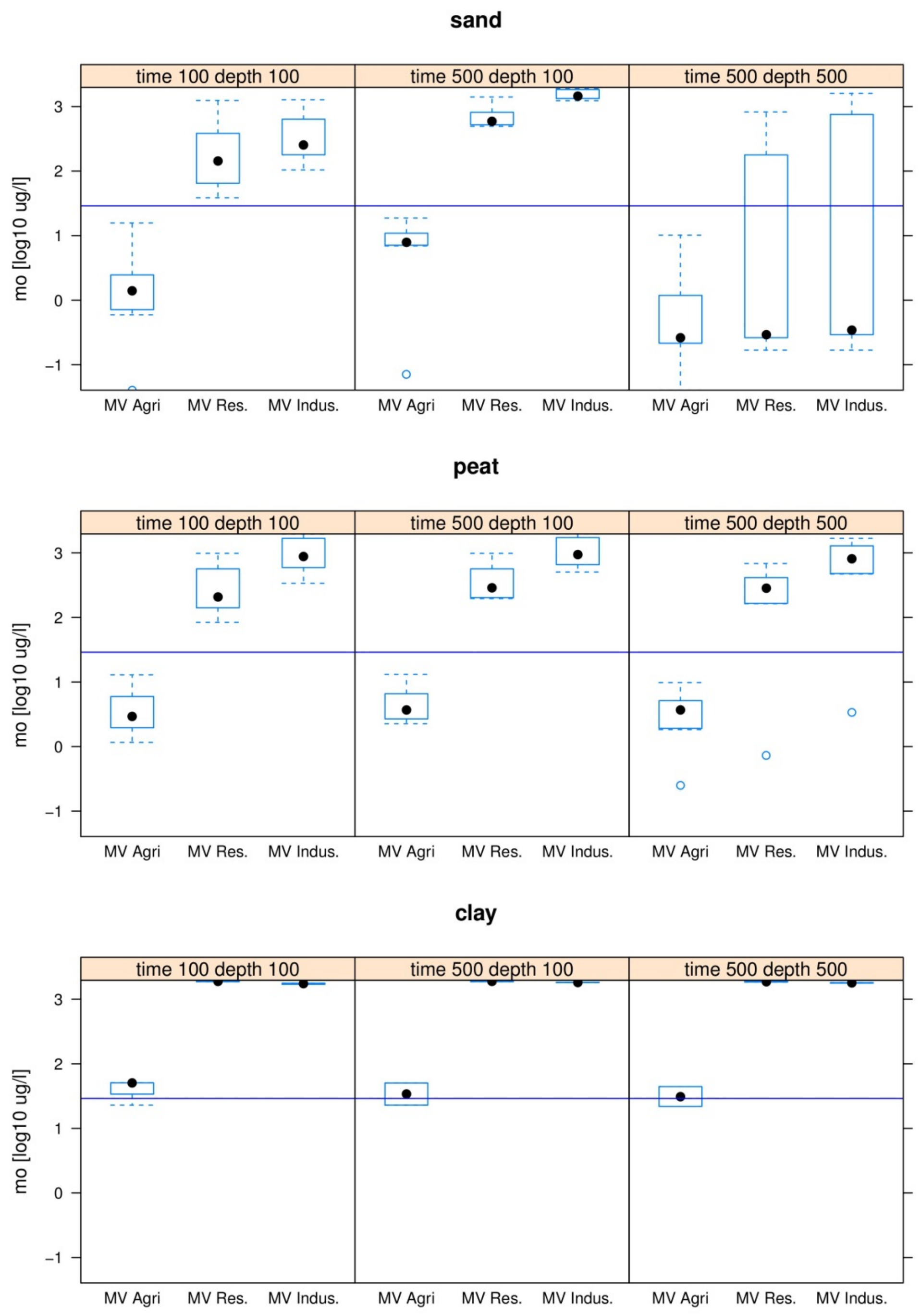


Figure 7.9.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The horizontal blue line denotes the MPA.

7.9.3 *Interpretation*

Molybdenum behaves as an oxyanion in the soil solution. Predictions for this type of anion are difficult. The very high values for the MV Residential and Industrial are unrealistic considering the natural variation of Mo. Therefore, due to these difficulties, no interpretation of Mo is given.

7.10 Nickel (Ni)

7.10.1 Input parameters

The input parameters for Ni are given in Table 7.10.1.1. The MV differs between sand and peaty/clayey soil profiles as a result of the Soil Type Correction, which for Ni is dependent on grain size only. Ambient total concentrations (95th percentile) of Ni range from 7.4 mg/kg for sand to 60 mg/kg for clays. Reactive ambient concentrations (95th percentile) range from 1.6 mg/kg for sand to 13 mg/kg for peat.

Table 7.10.1.1: Input concentrations for Ni for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	6.1	13.3	7.2
	peat	20.7	33.3	12.6
	clay	20.3	32.8	12.4
residential	*sand*	6.1	14.8	8.8
	peat	20.7	37.1	16.4
	clay	20.3	36.5	16.2
industrial	*sand*	6.1	38.0	31.9
	peat	20.7	95.1	74.4
	clay	20.3	93.6	73.3

7.10.2 Concentration ranges

Figure 7.10.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. For peat and clay soils the predicted Ni groundwater concentration is within the range of the MC. For the sand profile the predicted Ni concentrations are in some cases higher than the MC, but for the MV Industrial the MC is exceeded by two orders of magnitude.

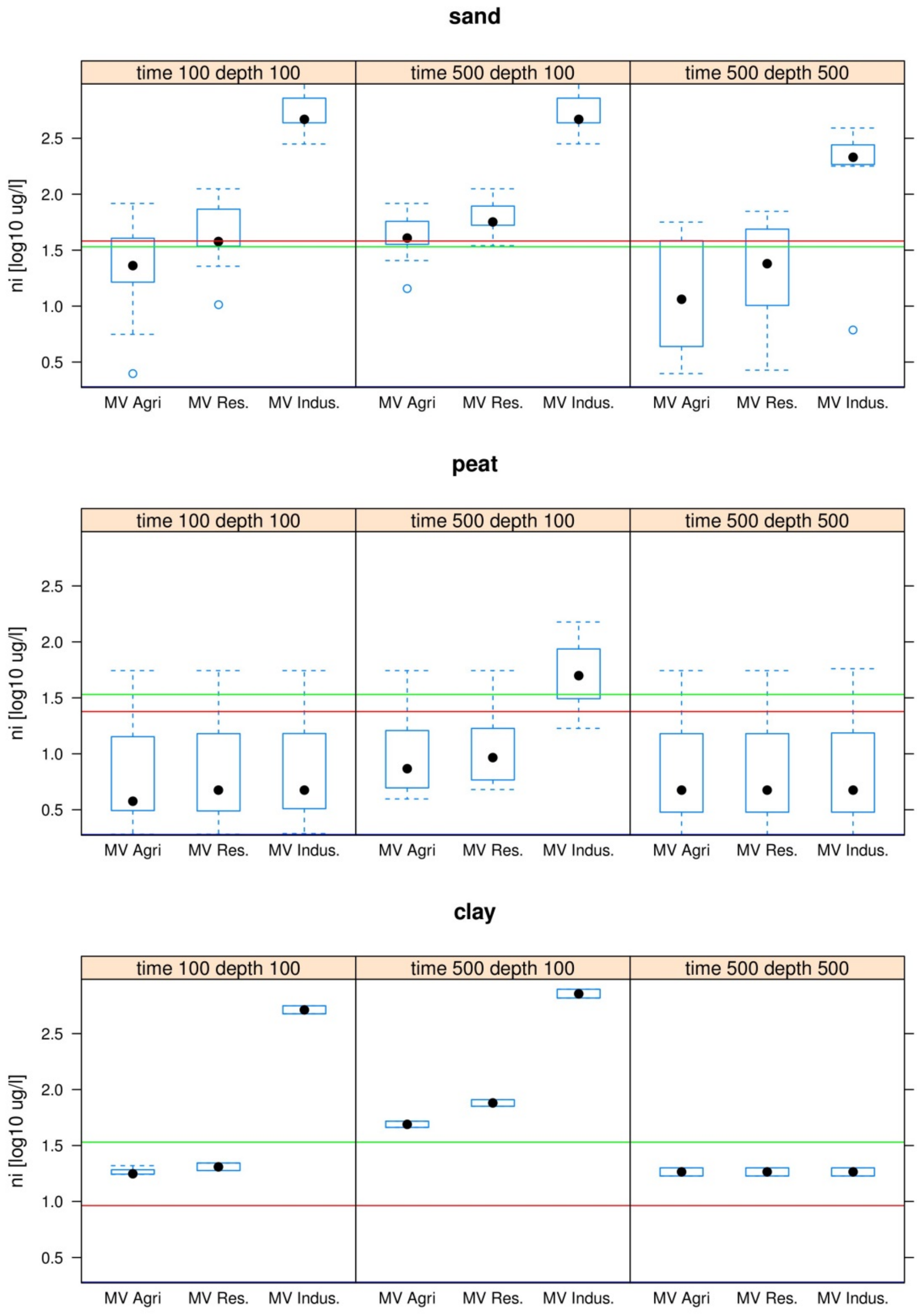


Figure 7.10.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.10.3 Map

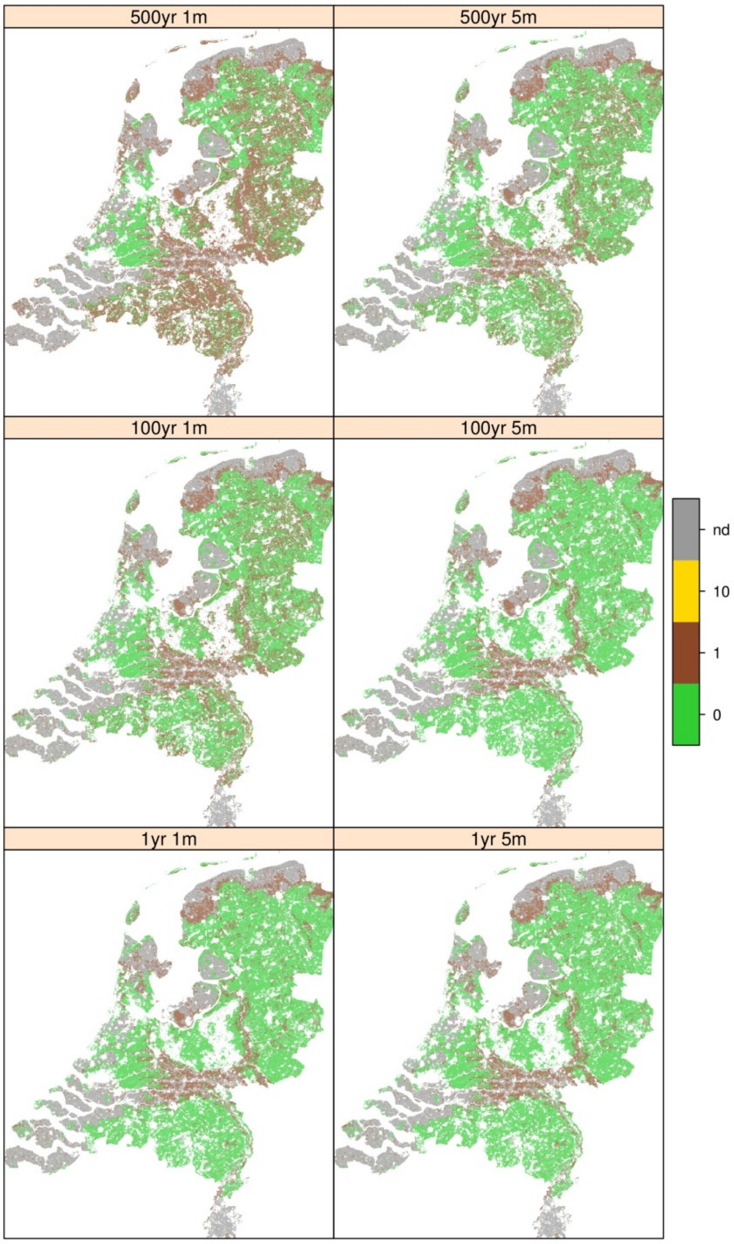


Figure 7.10.3.1: Maps of Ni showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.10.4 Interpretation

It is clear that the highest concentrations of Ni are predicted in the groundwater below sandy soils. From the groundwater characterisation (see Chapter 4) it has already been concluded that the highest ambient concentrations of Ni can be found below areas with a sandy soil cover.

The predicted groundwater concentrations in the upper part of the groundwater (depth range 100–200 cm) are in the range of 21–39 ug/l in sandy and clayey soils. For peat this value is 2 ug/l. This shows that the migration of Ni through organic-rich soil profiles is not to be expected. The predicted concentrations are in the same range as the ambient groundwater concentration, which for sand is in the range 41–61 ug/l, for peat 21 ug/l and for (marine) clay around 9 ug/l (see Chapter 4).

The spatial overview indicates minor exceedance of the MC; most of the area has an MC ratio below 1. Only in the scenario with the 500-year time frame and a 100 cm depth is there a clear exceedance of the MC value, in both sandy and clayey soils.

In the Dutch Geochemical Atlas nickel is categorised as a 'pristine' element, meaning that no anthropogenic enrichment has occurred during the last decades. The current MV for sandy soils in combination with the Soil Type Correction results in a soil type-specific MV which is roughly a factor of 2 higher than the ambient concentrations measured in the Atlas. This might explain the exceedance of the MC in the sandy areas. The exceedances in clays are caused by the relatively low MC value, approximately four times lower than sand.

7.11 Lead (Pb)

7.11.1 Input parameters

The input parameters for Pb are given in Table 7.11.1.1. The MV differs between all soil profiles as a result of the Soil Type Correction, which for Pb is dependent on grain size and organic matter. Ambient total Pb concentrations (95th percentile) range from 45 mg/kg for sand to 183 mg/kg for fluvial clays. Reactive ambient concentrations (95th percentile) range from 27 mg/kg for sand to 101 mg/kg for peat.

Table 7.11.1.1: Input concentrations for Pb for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	9.1	34.1	25.0
	peat	16.3	59.4	43.1
	clay	16.1	45.8	29.7
residential	*sand*	9.1	143.3	134.2
	peat	16.3	249.5	233.2
	clay	16.1	192.5	176.3
industrial	*sand*	9.1	361.6	352.5
	peat	16.3	629.8	613.4
	clay	16.1	485.7	469.6

7.11.2 Concentration ranges

Figure 7.11.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. The predicted concentrations in the sand profile are below the MC and MPA criteria. For the clayey and peaty profiles the predicted concentrations are above the soil type-specific MC. However, this MC is rather low: 0.14 ug/l for clay and 0.66 ug/l for peat, compared with the MPA

(11 ug/l). Except for the predicted concentrations in the peaty profile at shallow depth (100 cm) after 500 years, all predicted concentrations are below this MPA.

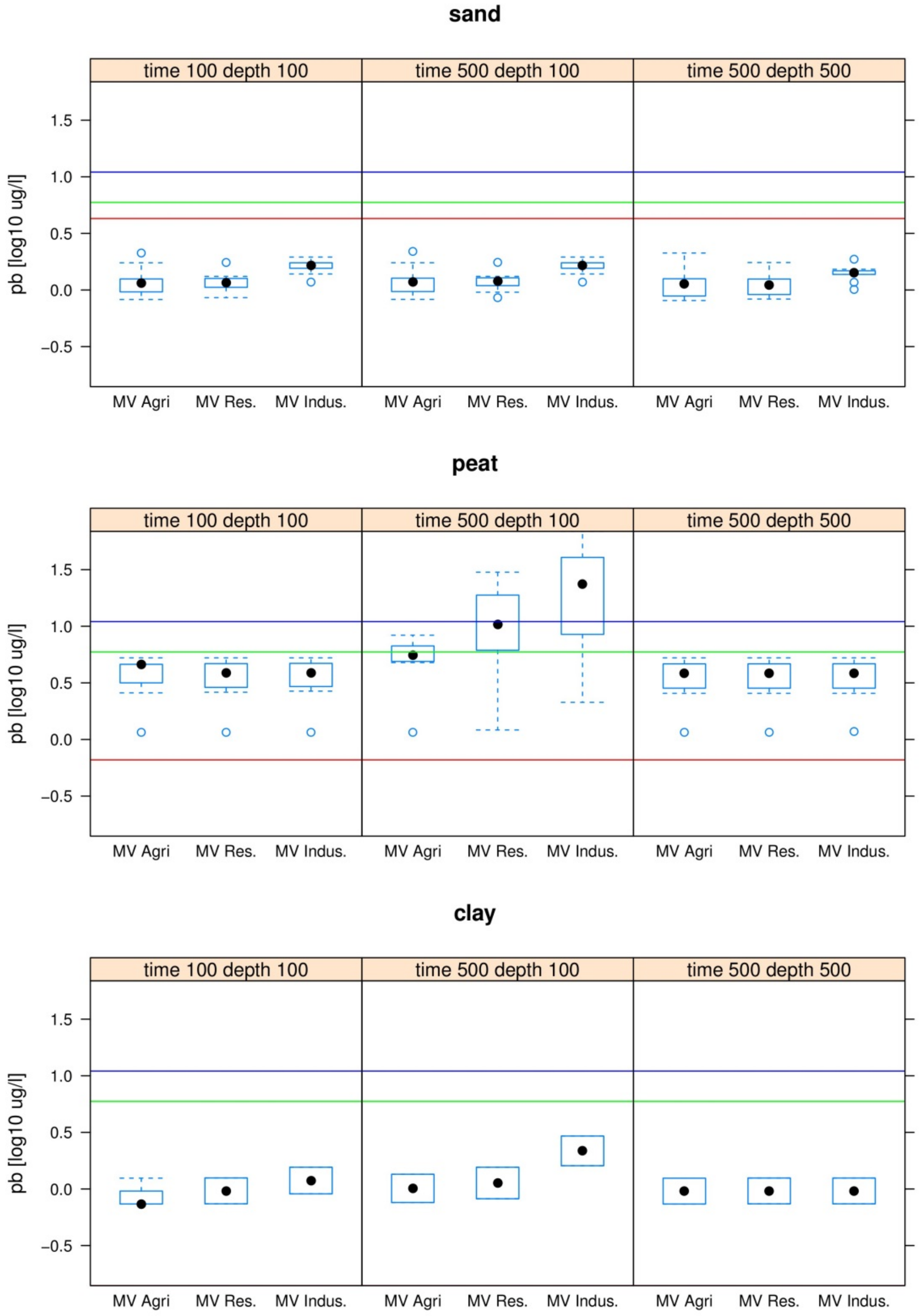


Figure 7.11.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC. For clayey soils the MC value is below the scale of the graph, at 10e-0.85 ug/l.

7.11.3 Map

On the maps the (organic-rich) fluvial and marine clays appear to be most vulnerable to leaching of Pb. Important to note is that the MC for these soil types is rather low, 0.14 ug/l, which results in these criteria being easily exceeded with small amounts of Pb in the pore water. From the soil profiles (Section 12.10.) it is clear that leaching of Pb is limited, and exceedance levels are low. For example, in the case of the 500-year, 1 m depth scenario the small increase in groundwater concentration results in an immediate minute exceedance of the cut-off levels of 1 (and 10), hence the colours on the map change. However, the absolute change is limited: from an MC ratio just below below 1 to a ratio just above 1.

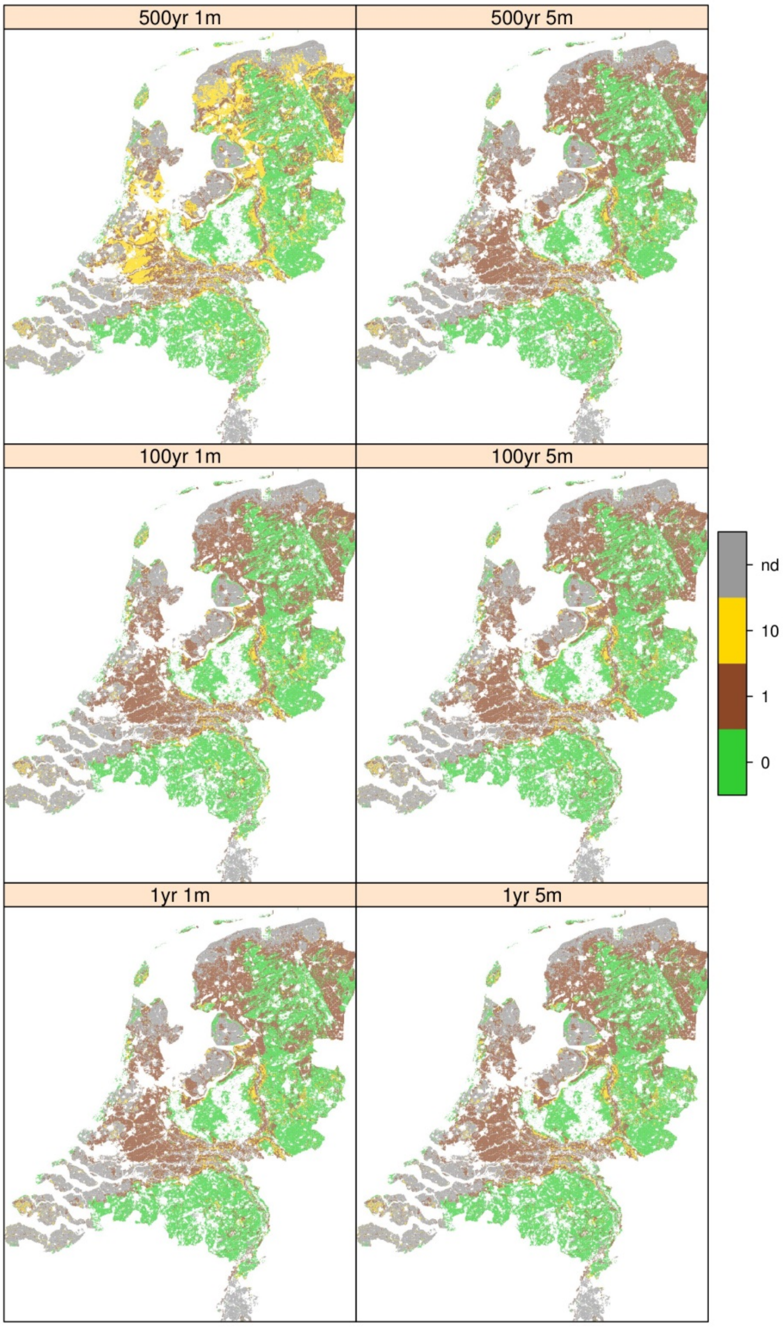


Figure 7.11.4.1: Maps of Pb showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.11.4 *Interpretation*

In general, Pb is known not to be mobile in soils. However, binding to DOC can facilitate the mobilisation of this element. Hence the higher predicted concentrations in peaty soils, although these are found only at shallow depth (100 cm) and after long time frames (500 years). Considering the nature of areas with peaty soils in the Netherlands, i.e. wet with a lot of surface run-off, it may be wondered whether these concentrations will be reached in reality. The relatively low MC values for clay and peat, compared with sand or the MPA, are in contrast with the relatively high ambient concentrations in these areas (Mol et al., 2012).

7.12 Antimony (Sb)

7.12.1 Input parameters

The input parameters for Sb are given in Table 7.12.1.1 The MV is independent of the soil type. Ambient total concentrations (95th percentile) of Sb range from 1.0 mg/kg for sand to 2.7 mg/kg for peat. Reactive ambient concentrations (95th percentile) range from 48 ug/kg for marine clays to 136 ug/kg for fluvial clays.

Table 7.12.1.1: Input concentrations for Sb for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	0.28	4.0	3.72
	peat	0.46	4.0	3.54
	clay	0.46	4.0	3.54
residential	*sand*	0.28	15.0	14.72
	peat	0.46	15.0	14.54
	clay	0.46	15.0	14.54
industrial	*sand*	0.28	22.0	21.72
	peat	0.46	22.0	21.54
	clay	0.46	22.0	21.54

7.12.2 Concentration ranges

Figure 7.12.2.1 shows the concentration ranges based on the 20 soil profiles together with the MPA levels. The predicted peak values are rather high, often above 1 g/l (10^3 ug/l). This greatly exceeds the MPA of 6.2 ug/l ($10^{0.8}$ ug/l).

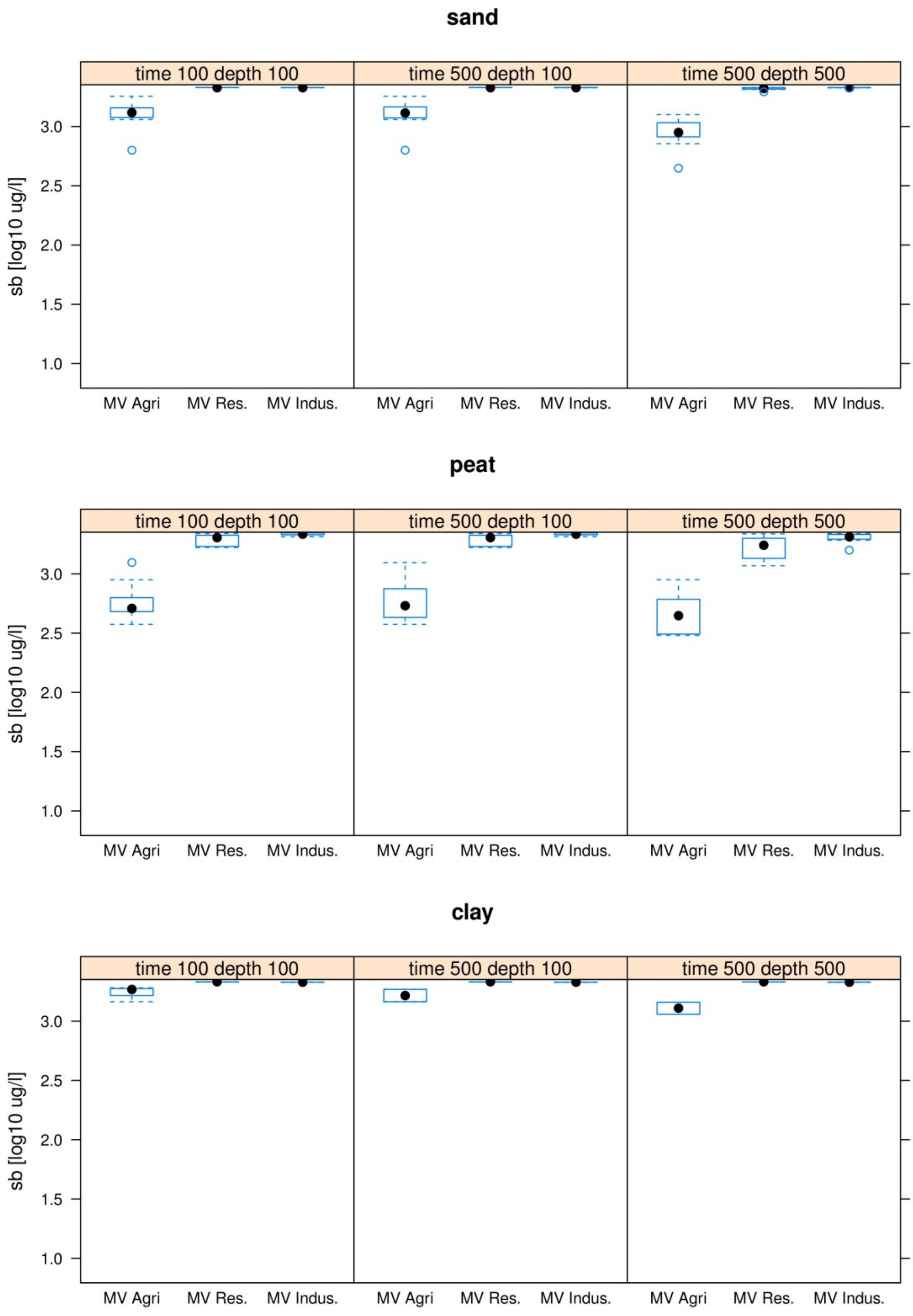


Figure 7.12.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC.

7.12.3 *Interpretation*

Prediction of Sb speciation based on thermodynamic equilibrium constants is uncertain due to the many unknowns about the behaviour of this element (Filella et al., 2009). In this study Sb does not show any retention, while it is known that Sb can be very immobile (Filella et al., 2009). Also, the input of the reactive concentrations of Sb are one to two orders of magnitude larger than the measured concentrations in actual soil samples according to the Dutch Geochemical Atlas. This results in high initial pore water concentrations.

Considering these two facts, uncertain modelling and high initial concentrations, the results should be treated with caution.

7.13 Tin (Sn)

7.13.1 Input parameters

The input parameters for Sn are given in Table 7.13.1.1. The MV for Sn is dependent only on particle size since no correction factors for organic matter exist for the Soil Type Correction. Total concentrations of Sn vary between 3.1 mg/kg (95th percentile) for sand and 12 mg/kg (95th percentile) for fluvial clays. Measured reactive concentrations are relatively low, from 47 ug/kg (95th percentile) for sand to 127 ug/kg (95th percentile) for fluvial clays. These reactive concentrations are an order of magnitude below the estimated reactive concentrations shown in Table 7.13.1.1.

Table 7.13.1.1: Input concentrations for Sn for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	0.7	2.0	1.3
	peat	1.7	6.2	4.4
	clay	1.7	6.0	4.3
residential	*sand*	0.7	56.7	55.9
	peat	1.7	170.3	168.6
	clay	1.7	167.2	165.5
industrial	*sand*	0.7	283.3	282.5
	peat	1.7	851.7	850.0
	clay	1.7	836.1	834.4

7.13.2 Concentration ranges

Figure 7.13.2.1 shows the concentration ranges based on the 20 soil profiles together with MPA levels. In general, the predicted concentrations are below the MPA. The scenarios with the MV Residential and Industrial exceed the MPA in peat soils at 100 cm depth and after 500 years. In this scenario ratios of predicted concentrations and MPA are up to about 100 for the MV Industrial.

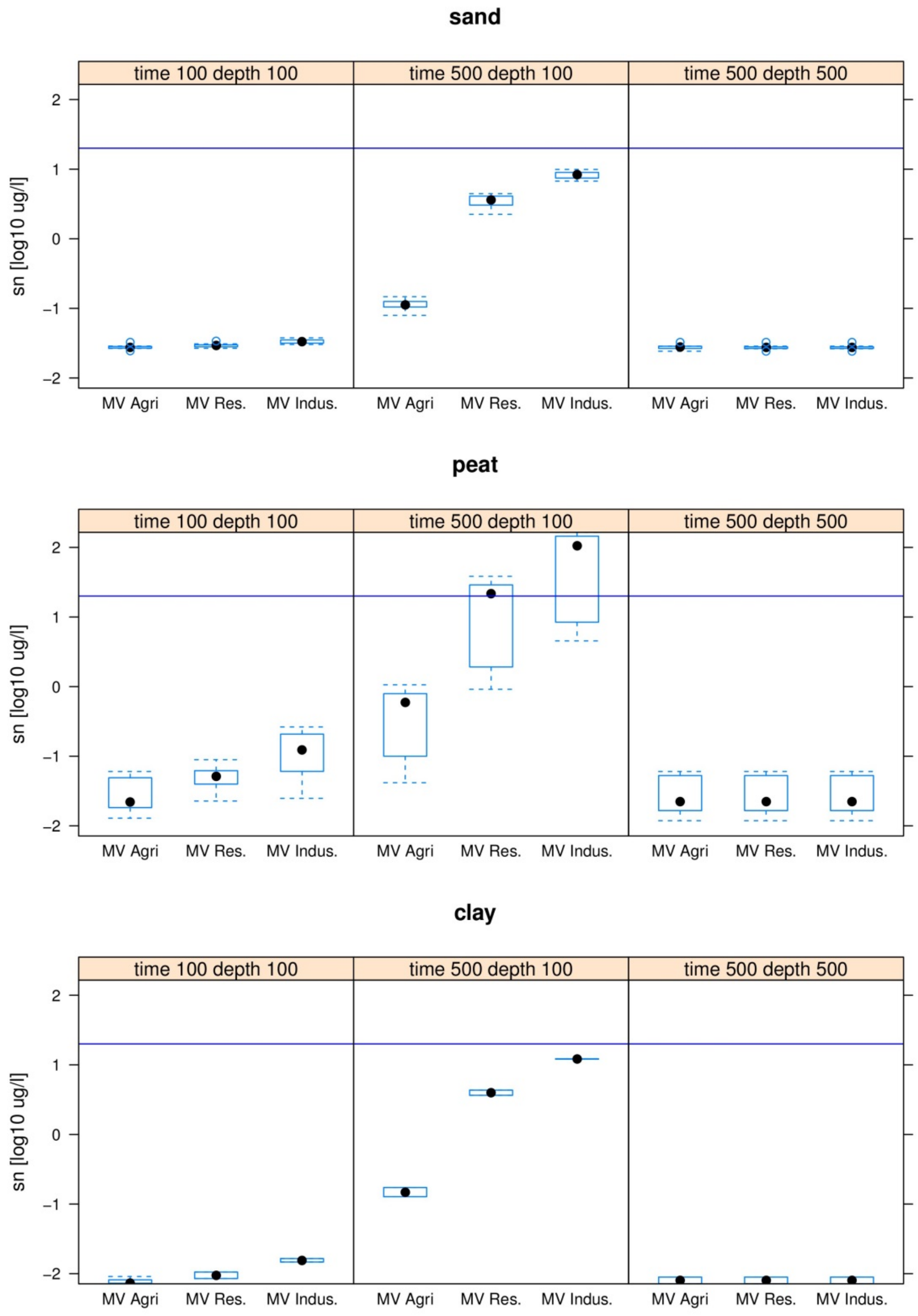


Figure 7.13.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The horizontal blue line denotes the MPA.

7.13.3 *Interpretation*

In soils rich in DOC, like peat, Sn is relatively mobile, which can result in exceedance of the MPA. Since no background concentration in groundwater is available, no MC values could be derived. It is important to note that the input values are an order of magnitude higher than the ambient soil concentrations.

7.14 Vanadium (V)

7.14.1 *Input parameters*

The input parameters for V are given in Table 7.14.1.1. The MV for V is dependent only on particle size since no correction factors for organic matter exist for the Soil Type Correction. Total concentrations of V vary between 43 mg/kg (95th percentile) for sand and 141 mg/kg (95th percentile) for peaty soils. Reactive concentrations vary between 13 mg/kg (95th percentile) for marine clays and 38 mg/kg (95th percentile) for peaty soils.

Table 7.14.1.1: Input concentrations for V for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	23.2	30.4	7.2
	peat	56.3	76.1	19.8
	clay	55.4	74.9	19.5
residential	*sand*	23.2	36.9	13.7
	peat	56.3	92.3	36.0
	clay	55.4	90.8	35.4
industrial	*sand*	23.2	95.0	71.8
	peat	56.3	237.9	181.5
	clay	55.4	233.9	178.5

7.14.2 *Concentration ranges*

Figure 7.14.2.1 shows the concentration ranges based on the 20 soil profiles together with the MPA levels. The predicted concentrations in this figure do not show much variation between the MVs for agricultural, residential and industrial areas; the concentration ranges appear to be independent of the MV. Only in peaty soil types does the upper part of the range of predicted concentrations exceed the MPA.

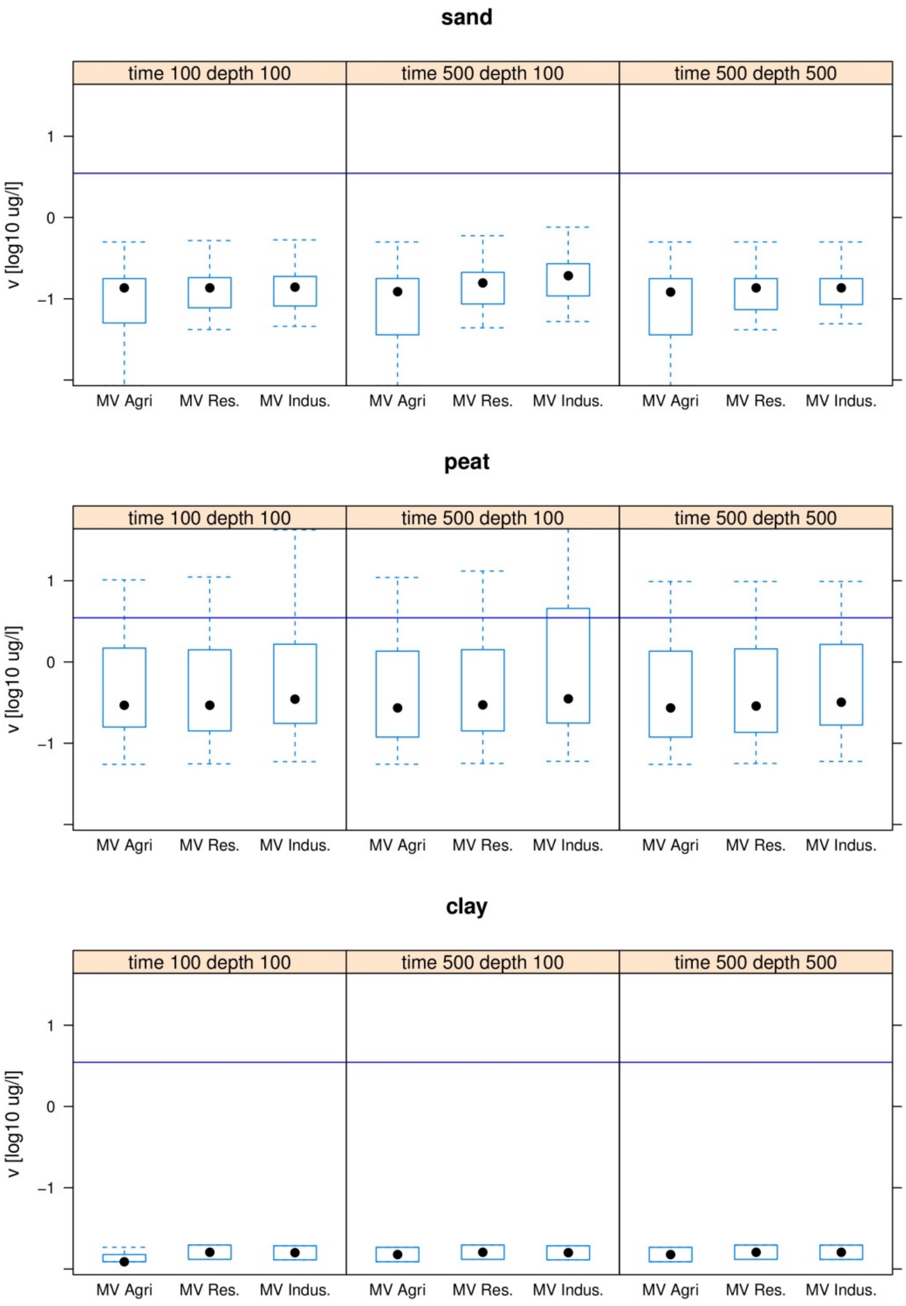


Figure 7.14.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The horizontal blue line denotes the MPA.

7.14.3 *Interpretation*

Dissolved V is closely related to organic matter content in the soil. When organic matter in the solid phase is high, the amount of V in the dissolved phase is rather low. In the peat profile this is clearly visible (see Appendix B): the first metre of the profile contains high organic matter (40–50 wt-%), deeper parts around 25 wt-% organic matter. The change in organic matter content is also clearly visible in the distribution of the V content between the solid and dissolved phases. This also explains the rather large variability in estimated groundwater concentrations shown in Figure 7.14.2.1.

In general the estimated groundwater concentrations for the 20 soil profiles are below the MPA; over time no relevant increases in groundwater concentrations are visible. So V can be regarded as immobile considering the result of these 20 profiles.

7.15 Zinc (Zn)

7.15.1 Input parameters

The input parameters for Zn are given in Table 7.15.1.1. The MV is strongly dependent on organic matter, and as a result of the use of the Soil Type Correction, the highest input concentrations can be found in the peat soil profile. Ambient total concentrations (95th percentile) of Zn range from 50 mg/kg for sand to 303 mg/kg for peat. Reactive ambient concentrations (95th percentile) range from 22 mg/kg for clay to 160 mg/kg for peat.

Table 7.15.1.1: Input concentrations for Zn for the upper layer (0–10cm) in the soil profile. For each scenario (agricultural area, residential area, industrial area) and each soil profile (sand, peat, clay) the maximum value (MV), the background value (Cb) and the estimated reactive concentration (Reactive) are given. All concentrations are in mg/kg.

Scenario		**Cb**	**MV**	**Reactive**
agricultural	*sand*	13.4	67.0	53.6
	peat	40.0	161.5	121.5
	clay	39.3	126.0	86.7
residential	*sand*	13.4	95.6	82.3
	peat	40.0	230.6	190.6
	clay	39.3	180.0	140.7
industrial	*sand*	13.4	344.3	330.9
	peat	40.0	830.3	790.3
	clay	39.3	647.9	608.6

7.15.2 Concentration ranges

Figure 7.15.2.1 shows the concentration ranges based on the 20 soil profiles together with the MC and MPA levels. In the sandy soil profiles the predicted groundwater concentrations are in general above the MPA and MC values, and ratios are orders of magnitudes above 1. In peaty soils the predicted concentrations are around the MPA value but below the MC value, except in the scenario at 100 cm depth and after 500 years. In the latter scenario an increase in exceedance is visible, with values above the MC.

For clayey soils the MC criterion is fairly low compared with sand and peaty areas. All predicted values are above this MC value.

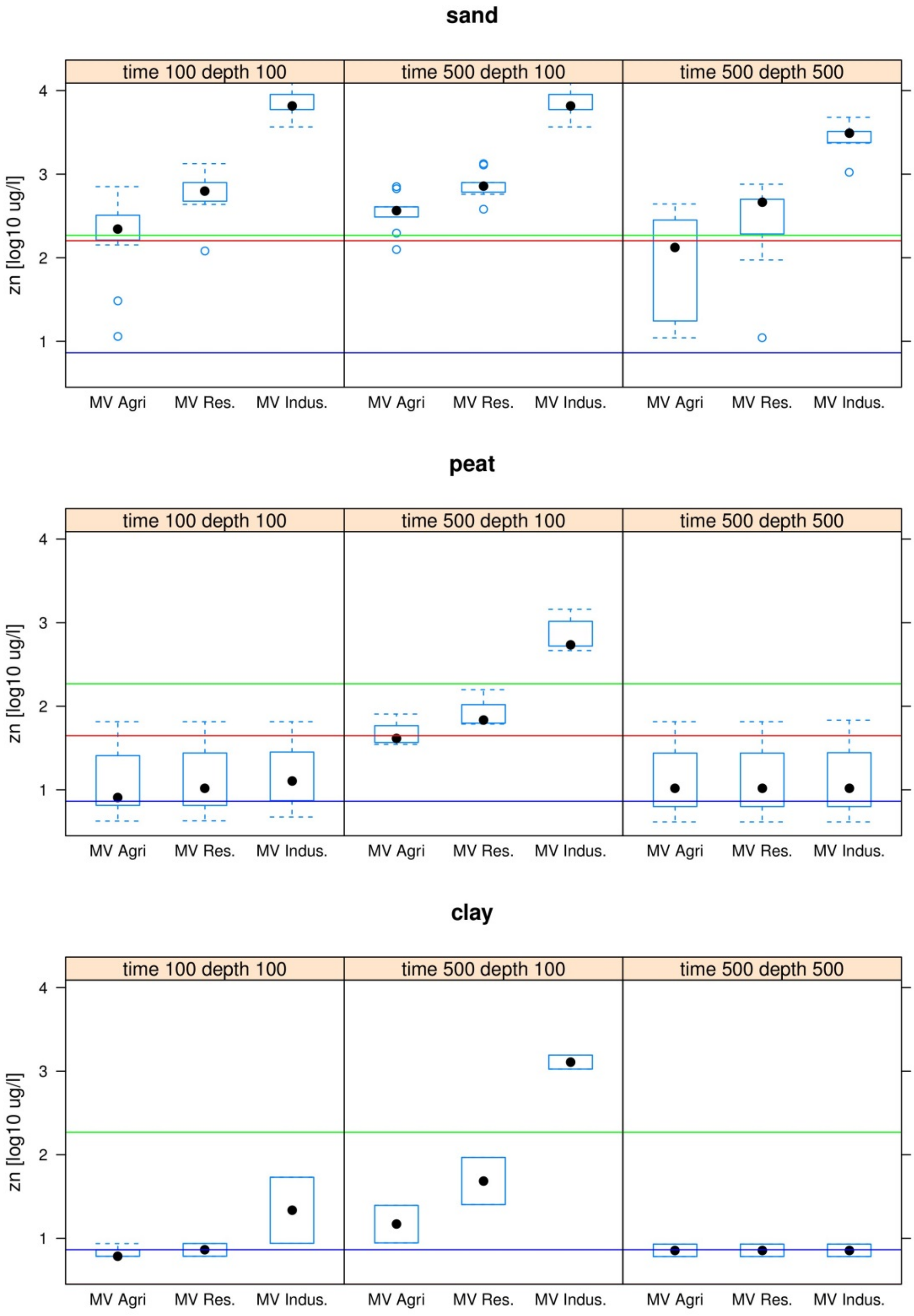


Figure 7.15.2.1: Box-and-whisker plots of groundwater concentrations in the selected soil profiles (n=20) related to the Maximum Values. The bars above the plot indicate time in years and depth in cm. The red horizontal line denotes the soil type-specific MC, the blue line the MPA and the green line the generic MC. The soil type-specific MC for clayey soils is around 10e0.45 and not depicted in the graph.

7.15.3 *Map*

The maps in Figure 7.15.3.1 show that there is great variability in exceedance of the MC. Sandy soils seem to be more sensitive to leaching. Also, at greater depths (5m) some small areas show exceedance ratios above 10.

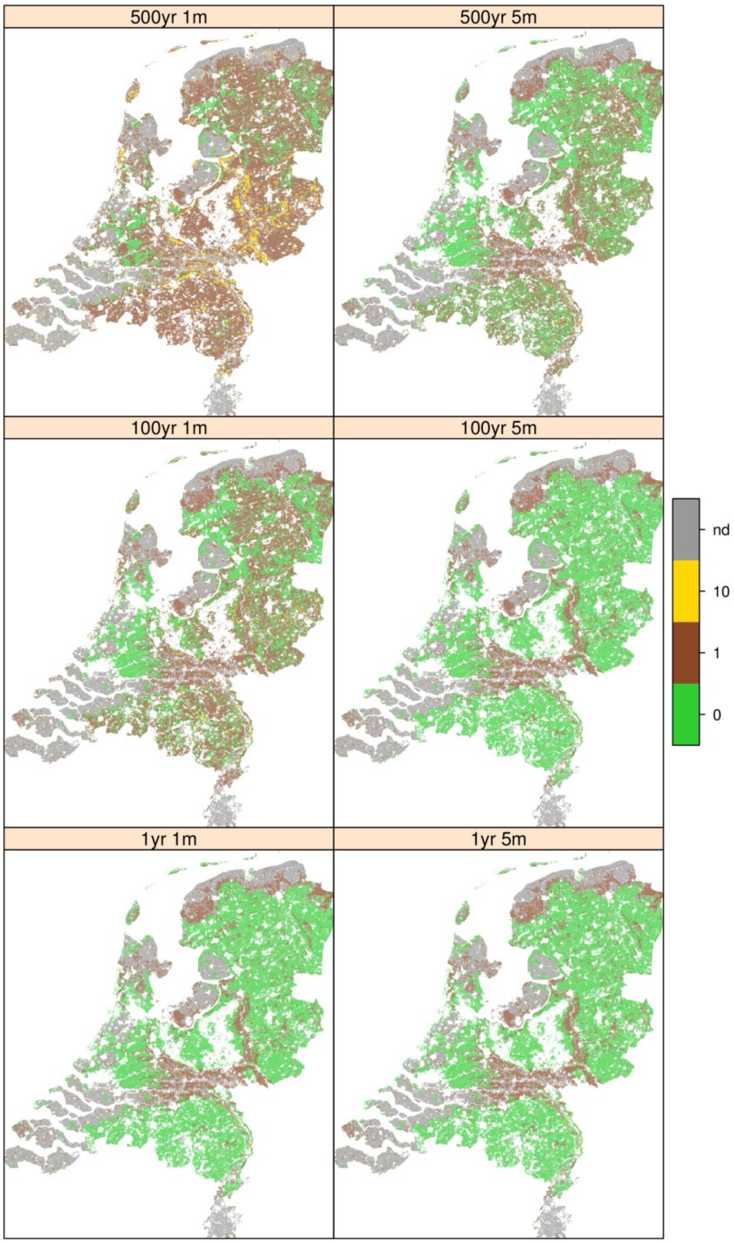


Figure 7.15.3.1: Maps of Zn showing how many times the MC value is exceeded for two depth ranges and two time frames. Three classes are defined: green is less than 1, brown is exceedance between 1 and 10 times and yellow is above 10 times exceedance. Grey areas are missing (discarded) values.

7.15.4 *Interpretation*

From the aforementioned results of the leaching of Zn it is clear that the highest concentrations of Zn are predicted in the groundwater below sandy soils. From the groundwater characterisation (see Chapter 4) it has already been concluded that the highest ambient concentrations of Zn can be found below areas with a sandy soil cover.

The predicted groundwater concentrations in the upper part of the groundwater (depth range 100–200 cm) are in the range of 200–300 ug/l. This is rather high compared with the ambient concentrations of 2–5 ug/l measured in groundwater. One reason is the high initial concentration of dissolved Zn calculated by the model: 167 ug/l for the upper layer (0–10 cm) in the sand profile enriched to the MV Agricultural. The soil type-specific MV Agricultural (125 mg/kg), resulting from applying the Soil Type Correction, lies above the MV measured in Dutch soils of 98.2 mg/kg (Mol et al., 2012). As a result, the estimated reactive concentration (87 mg/kg) is a factor of 3 above the actual measured value (95th percentile: 30 mg/kg). This might partly explain the high initial concentration, together with the (relatively small) overestimation of reactivity of Zn itself (see Section 4.2; Figure 4.2.2).

7.16 Overview of aggregated data

To obtain insight into how the different elements and scenarios compare with each other and to the calculated indicators shown in Table 5.6.1, the data are aggregated by combining the maximum average concentrations for each scenario. For the scenarios based on the MV Agricultural 356 scenarios were available, for the MV Residential and Industrial 20 scenarios were modelled and 16 scenarios resulted in a usable outcome.

7.16.1 *Agricultural*

Figure 7.16.1.1 shows the results of the 356 scenarios with concentrations in soils at the level of the MV Agricultural. In this figure the change over time of different groups of scenarios, given by soil type and depth, can be followed. From this figure we conclude the following:

- The increase in groundwater concentration over time is in general within one order of magnitude for each element in the depth range 100–200 cm (indicated as depth 100).
- The most mobile elements, i.e. elements with the largest increase in concentration between 1 and 500 years at 100 cm depth, are Cd (sand), Co (clay), Cu (peat), Mo, Ni (sand), Sb, Sn and Zn.
- The elements Cd, Co, Cu and Ni show mobility related to soil type.
- At 500 cm depth the most mobile elements are Sb, Cd (sand), Mo (clay), Ni (sand) and Zn (sand).

Figure 7.16.1.1: Results of the 356 scenarios with soil concentrations at the level of the MV Agricultural. On the x-axes the elements are given and for each element the individual scenarios are shown as points. These points are horizontally separated (i.e. jittered) for visibility. The maximum average concentrations are shown on the y-axes. These concentrations are given as ^{10}log transformed values. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 years. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

Figure 7.16.1.2 shows the ratio of the maximum average concentration to the MC values, for elements where an MC value is available. In the previous paragraphs for the maps two arbitrarily threshold levels were used: 1 times MC and 10 times MC. In Figure 7.16.2.1, which is on a log scale, these values are respectively 0 and 1. After one year (time 1) many scenarios already exceed the 1 time MC; in general, these are scenarios with clayey and peaty soils due to the low MC value compared with sandy soils. Based on this figure it is clear that Ni, and in sandy soils Cd and Zn, have increasing ratios with the MC over time.

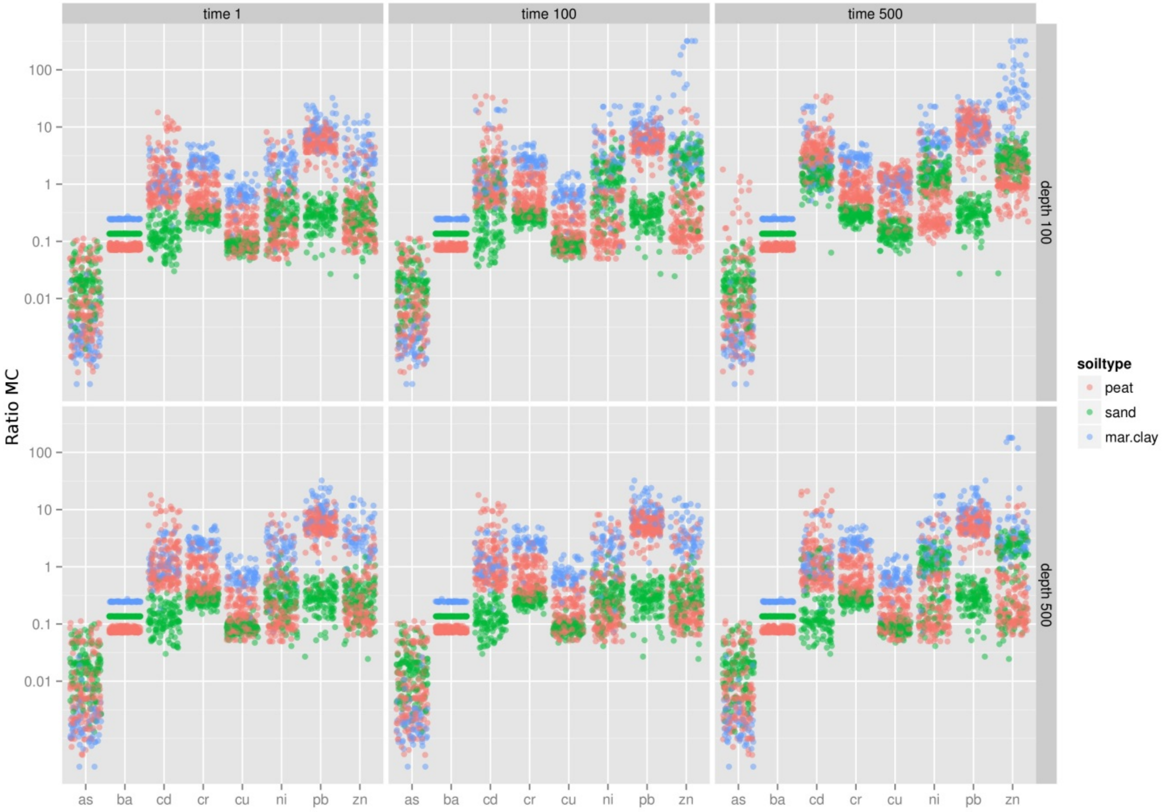


Figure 7.16.1.2: Results of the 356 scenarios with soil concentrations at the level of the MV Agricultural. On the x-axes the elements are given and for each element the individual scenarios are shown as points. These points are horizontally separated (i.e. jittered) for visibility. The ratios of the maximum average concentration divided by the MC are shown on the y-axes (see Table 5.6.1). These ratios are given as ^{10}log transformed values. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 years. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

Since it was not possible to estimate MC values for each element and to compare the maximum average concentration with current risk levels, the ratios of the maximum average concentrations to the MPA were calculated. These are shown in Figure 7.16.1.3, again using a ^{10}log ratio. Because the MPA is constant for each soil type, the results of Figure 7.16.1.3 are related to those of Figure 7.16.1.1 and the same observations apply. Considering the MPA, many elements (Sb, Cd, Co, Ni, V and Zn) already exceed the MPA after 1 year – Sb, Ni and Zn by up to two orders of magnitude. For Zn and Ni, MC values are available and these show that for sandy soils the range of predicted groundwater concentrations is within the range of the measured concentrations.

Figure 7.16.1.3: Results of the 356 scenarios with soil concentrations at the level of the MV Agricultural. On the x-axes the elements are given and for each element the individual scenarios are shown as points. These points are horizontally separated (i.e. jittered) for visibility. The ratios of the maximum average concentration divided by the MPA are shown on the y-axes (see Table 5.6.1). These ratios are given as ^{10}log transformed values. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 years. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

7.16.2 Residential and industrial

For the scenarios with soils with concentrations at the level of the MV Residential or Industrial only a comparison with the MC is made since this value is more representative of the impact on current groundwater. The results of the ratio of the maximum average concentration of residential soils with the MC is shown in Figure 7.16.2.1 while those with soils for industrial areas is shown in Figure 7.16.2.2 These results cover only the 20 selected soil profiles.

Figure 7.16.2.1 shows a general increase of up to one order of magnitude, except for Cd, Pb and Zn after 500 years. For Cd and Zn one single scenario exceeds the MC ratio by a factor of 10; for Pb almost all peaty soils exceed this MC ratio. At 500 cm depth MC ratios stay below 10. However, for Zn and Ni concentrations in sandy soils increase by an order of magnitude of between 0.5 for Ni and 1 for Zn.

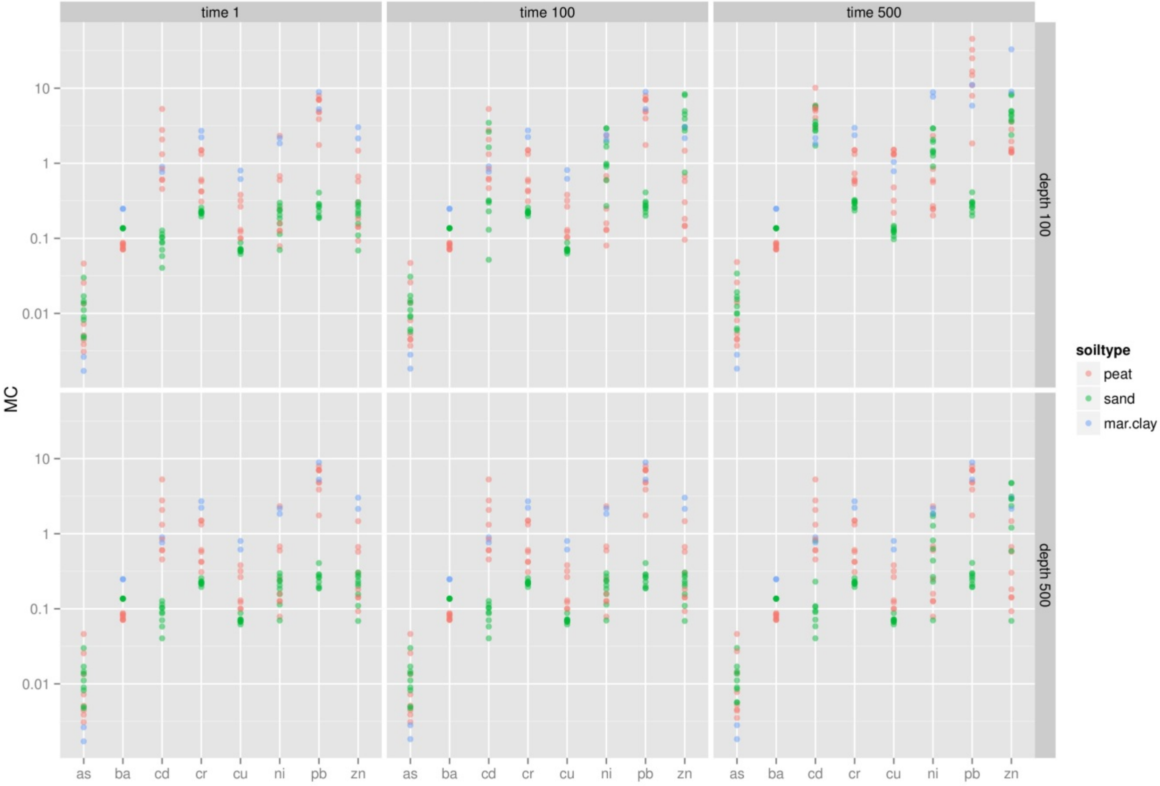


Figure 7.16.2.1: Results of the 20 scenarios with soil concentrations at the level of the MV Residential. On the x-axes the elements are given and for each element the individual scenarios are shown as points. The ratios of the maximum average concentration divided by the MC (MC.st) are shown on the y-axes (see Table 5.6.1). These ratios are given as ^{10}log transformed values. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 year. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

Figure 7.16.2.2 shows the scenarios with soils in industrial areas. After 100 years, at 100 cm depth, Cd, Ni and Zn have ratios, mainly in sandy soils, far above ten times the MC. After 500 years in clayey and peaty soils Cd and Pb are also above ten times MC. At 500 cm depth Cd and Zn show the highest ratios, above ten times MC.

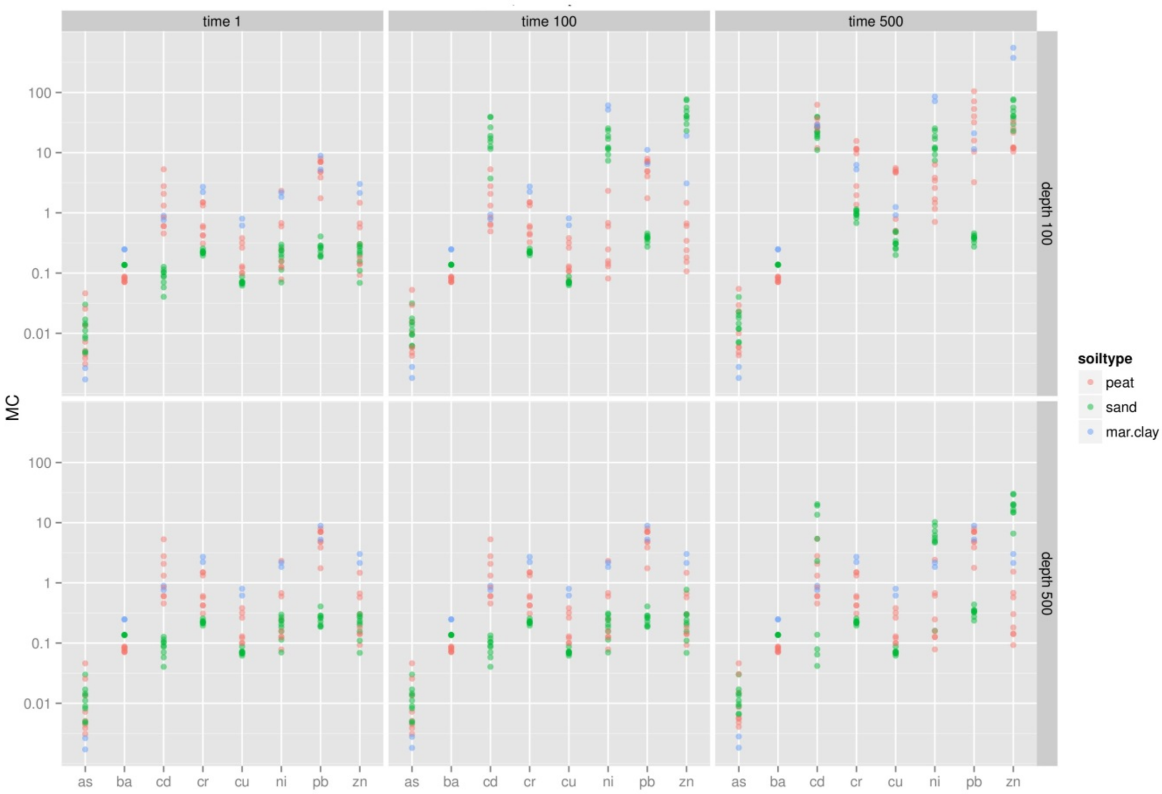


Figure 7.16.2.2: Results of the 20 scenarios with soil concentrations at the level of the MV Industrial. On the x-axes the elements are given and for each element the individual scenarios are shown as points. The ratios of the maximum average concentration divided by the MC (MC.st) are shown on the y-axes (see Table 5.6.1). These ratios are given as ^{10}log transformed values. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 year. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

7.16.3 *Comparing leaching from residential and industrial scenarios with agricultural scenarios*

To compare the increase in soil concentrations with clean situations as defined by the Soil Quality Decree the maximum average concentrations of the scenarios with the MVs Residential and Industrial are compared with the scenario with the MV Agricultural (see Table 5.6.1). Figure 7.16.3.1 shows the ratios of the MV Residential to the MV Agricultural.

Looking at the ratios at 100 cm depth after a time range of 100 years, concentrations of Sb, Cd, Mo, Co, Ni, Sn and Zn are clearly elevated, whereas for the other elements only slight increases occur, if any. Differences between soil types can also be discerned. For example, Cd, Co, Ni and Zn show the highest increases in sand, while Sb and Sn show the highest increases in peaty soils. For Sb it has already been stated that the modelling of the leaching is too uncertain. For Mo the MVs Residential and Industrial are too high for a realistic modelling of soil chemistry, as discussed in Section 7.9.

At the deeper layer (500 cm) after 500 years, Sb, Cd, Co, Mo, Ni and Sn clearly show increased ratios. These ratios mainly occur in sandy soils.

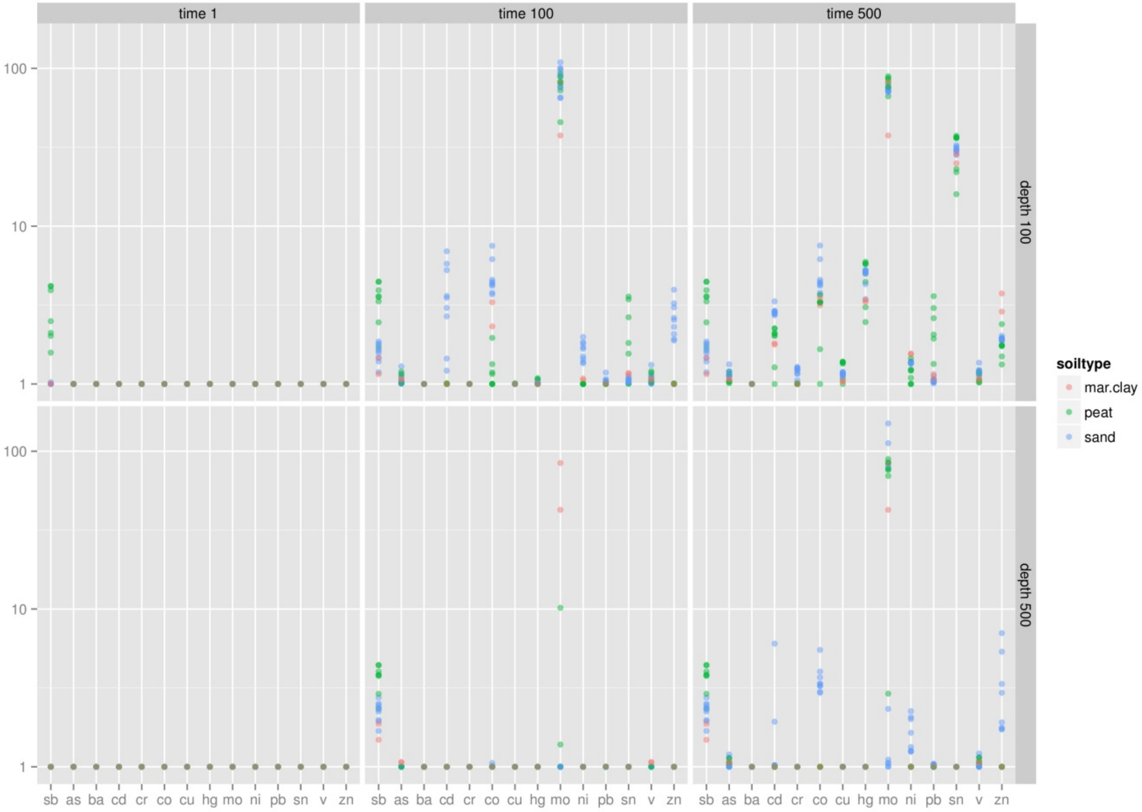


Figure 7.16.3.1: Results of the 20 scenarios with soil concentrations at the level of the MV Residential. On the x-axes the elements are given and for each element the individual scenarios are shown as points. The ratios of the maximum average concentration for soils to the Maximum Values Residential divided by the maximum average concentration for soil with MV Agricultural are shown on the y-axes (see Table 5.6.1). These ratios are given on a log-transformed scale. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 year. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

Figure 7.16.3.2 shows the ratios of the MV Industrial to the background situation, the MV Agricultural. Ratios of Cd, Co and Mo are up to two orders of magnitude above the situation of clean soils within 100 years. For Ni, Sn and Zn these ratios are one order of magnitude above the clean soil situation.

After 500 years the ratios of Cd and Co are much lower than after 100 years, while the ratios of Sn are increased. This is due to the dynamic behaviour of the estimated groundwater concentration in the reference scenarios with soils at the level of the MV Agricultural (the denominator in the ratio).

Also at deeper groundwater levels, after 500 years, a substantial increase in groundwater concentrations compared with the clean soil situation can be observed. Also here, Cd, Mo and Zn show ratios up to two orders of magnitude higher. Cobalt and Ni ratios are about one order of magnitude higher.

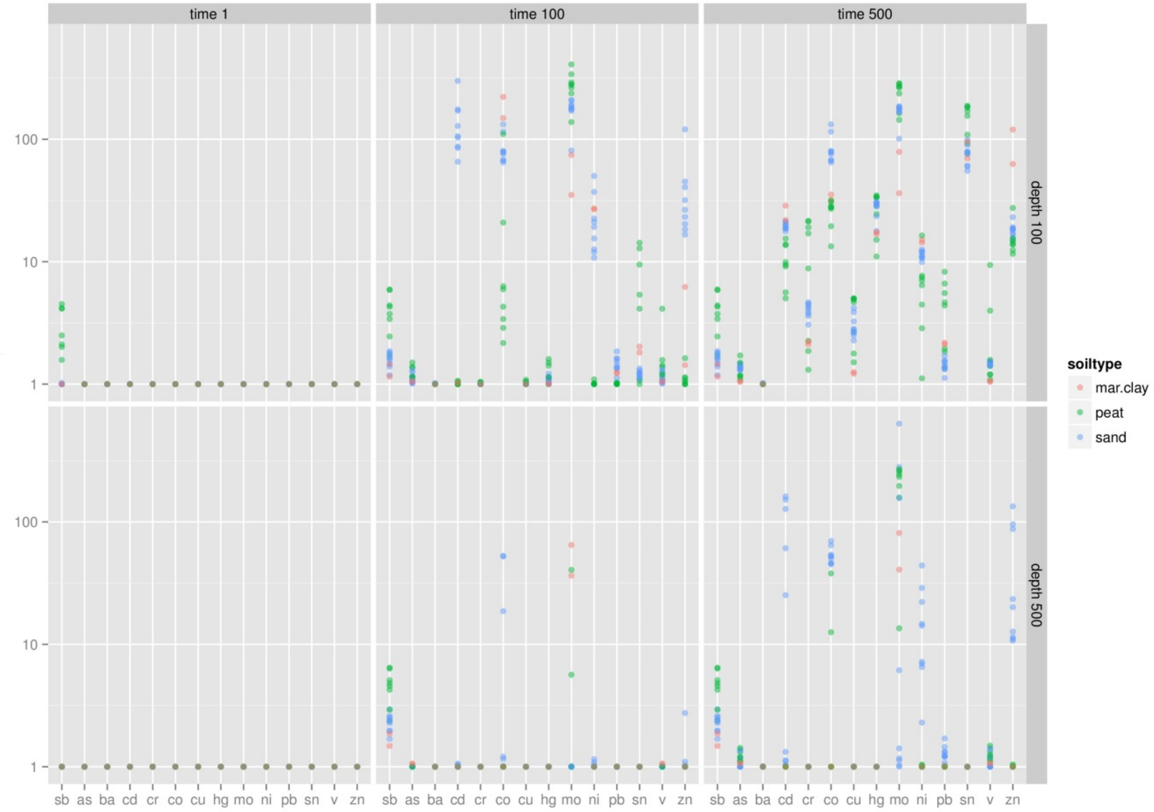


Figure 7.16.3.2: Results of the 20 scenarios with soil concentrations at the level of the MV Industrial. On the x-axes the elements are given and for each element the individual scenarios are shown as points. The ratio of the maximum average concentration for soils with the MV industrial divided by the maximum average concentration for soil to the MV Agricultural are shown on the y-axes (see Table 5.6.1). These ratios are given on a log-transformed scale. Each panel gives a time and depth range: columns show time ranges of 1, 100 and 500 year. Rows give depth ranges at 100 and 500 cm depth. Soil types are indicated by colour (see legend).

8 Discussion

8.1 Model assumptions

In this study we calculated the potential consequences of soil managed under the Dutch Soil Quality Decree on leaching towards groundwater, i.e. the groundwater concentrations arising from elevated soil concentrations. The geochemical multi-surface speciation and transport model requires highly detailed input parameterisation. Since a full parameterisation was not feasible within a reasonable budget, assumptions were made to simplify the modelling. These assumptions have their effect on how the data should be interpreted.

First of all, the added risk approach defines an anthropologically added concentration to soil as the part of the total concentration which determines the risk. In practice, this translates as the added concentration being equal to the reactive concentration. For Cd, Cu, Pb and Zn this assumption is valid (Spijker et al., 2011). For Sn and Sb this assumption largely overestimates the reactivity (Spijker, unpublished data) and this means that estimated groundwater concentrations of Sb and Sn should be treated with caution. For higher concentration levels, like the Dutch Intervention Value for soil pollution, it is expected that this assumption also overestimates reactivity in general (P. Romkens, B.-J. Groenenberg, pers. comm.).

Another source of overestimation is the decision to apply Maximum Values to soils. For our scenarios we set the concentration of each element in soil at the maximum concentration allowed by the Decree. In reality, such soils can be hardly be found. From experience it is known that contaminated soils in general have a few elements at polluted soil levels while others are at much lower levels than the Maximum Value. Since competition between elements is part of the model, this assumption can overestimate the transport of elements which are less retarded in the soil profile due to this competition.

In the model a mildly oxidising environment is assumed and the redox potential is fixed. Under these conditions many elements are at least partial mobile. It is generally known that the redox potential decreases with depth. This is particularly true in clayey and peaty soils. While this can be a cause of overestimation of leaching for many metals, for others, like As, it may lead to underestimation.

The hydrology in the model could be kept simple because the breakthrough point of elements was important only in a relative sense. For every soil profile the downward water transport was set at 300 mm/year. With a porosity of 1/3 this resulted roughly in a downward movement of water of 1 m per year. This value of 300 mm/a is realistic for the Pleistocene sandy soils. However, for clayey and peaty soils it overestimates the actual amount of groundwater recharge. Particular in the western part of country, with its low field levels, often below sea level, most of the precipitation excess is removed by surface run-off and discharge to surface waters. Considering that in many of these low-lying parts upward seepage is the main source of shallow groundwater, with a lesser contribution of water leached through soils, this probably leads to dilution and hence overestimation of the contribution of elevated levels in soil to the concentrations in groundwater in these areas.

In the model the concentration for Ca^{2+}, and its counter-anion SO_4^{2-}, was set at 10^{-3} M. This concentration is based on the data of Dijkstra (2004) and was also used in our previous study (Spijker et al., 2009). During this study field data became available (Groenenberg, pers. comm.) which show concentrations for Ca^{2+}/SO_4^{2-} of 10^{-4} M. Data from Mol (2012) confirm the concentration of 10^{-4} M Ca^{2+} in sandy soils. To test the impact of a tenfold decrease in Ca^{2+}/SO_4^{2} concentrations, the three standard profiles were parameterised with 10^{-4} M concentrations for these ions. Appendix C gives the results of the modelling. From the results the effect of Ca^{2+} on the competition with other cations is evident. For sand and peat the maximum average concentrations of elements like As, Cd, Co, Mo, Ni, V and Zn decrease by no more than one order of magnitude. In clayey soils this effect is still present but to a smaller extent. Overall, the current choice of Ca^{2+}/SO_4^{2-} concentration (i.e. 10^{-3} M) may lead to an overestimation of groundwater concentrations.

For As and other oxyanions the assumption that the competition with PO^{4+} is negligible probably results in an underestimation of the concentrations of these oxyanions. This assumption was also based on Dijkstra et al. (2004) and used in the studies of Verschoor et al. (2006) and Spijker et al. (2009).

8.2 Model evaluation

Overall, the observed deviations between (transport) model predictions and observed data are considered acceptable. The deviations between model and data seem to be caused by inadequate estimates of important parameters (e.g. availability) rather than by failure of the underlying model components (e.g. NICA-Donnan, GTLM, Donnan models).

It must be noted, however, that important parameters such as pH and DOC are not predicted but estimated from the column data itself. We are aware that in the practice of using the reactive transport model for e.g. establishing generic limit values, information on important parameters such as pH, amount of reactive POM and DOM and background concentrations of major elements is not always available in as much detail as was available for this study. For the purpose of large-scale (e.g. nationwide) generic risk evaluation, such information is not available, and it is impossible to generate such detailed information on soil and pore water characteristics. The result is that one has to rely on the quality of other information sources (monitoring data, extrapolations from other parameters), which is potentially a source of considerable uncertainty. It must also be accepted that a large degree of spatial heterogeneity may be an even greater source of uncertainty.

8.3 Concentration endpoints, thresholds and indicators

The results of the modelling are average groundwater concentrations over 1 m of soil profile which is variable over time. In general, the concentrations follow a curvature, the so-called breakthrough curve. The maximum concentration is the endpoint, which is compared with a threshold criterion. This approach has a drawback. If a concentration starts at its maximum value, at time step 0, and then decreases over time, then the initial concentration determines the maximum concentration. This happens with As and V in the peat soil profiles and with As in the sand profile. These maximum concentrations are not the result of a peak concentration due to leaching from an enriched soil but rather the result of ‘rinsing’ of the mobile fraction.

Three threshold levels were considered for the maximum average concentrations. Respectively, three indicators were derived by dividing the maximum average concentration by the three threshold value.

The first indicator was a comparison between the maximum average concentration and the MPA risk level. This approach was implemented during the derivation of the critical emission values for construction products (Verschoor et al., 2006) and during the prior leaching study (Spijker et al., 2009). The rationale for using the MPA is that the added concentration to groundwater as result of leaching should not lead to negative effects on the groundwater ecosystem or human health. However, the MPA is a risk level; it does not account for variability in (natural) groundwater concentrations. Based on the principles of the added risk approach (see Section 5.2.1), the MPA is fully bioavailable while the natural background is not. This approach is viable for soils since the background is relatively inert compared with the added fraction (enrichment, see Section 4.2). This is probably not true for (ground)water, where no distinction can be made between the speciation of the dissolved background concentration and the added concentration due to leaching – especially when groundwater concentrations are already enriched in certain elements, presumably due to anthropogenic activities. Also, as shown in Table 4.3.1, the background concentration (MC) is often above the MPA. The exceedance of the MPA in groundwater below these diffusely contaminated soils implies, in theory, that ecological effects are already to be expected. However, a discussion about the existence or extent of these effects on groundwater ecosystems is beyond the scope of this report, as is the question whether these exceedances of the MPA are acceptable or not. One could argue that there is no way of restoring these diffusely contaminated soils to the state they in were before our industrial age. Considering that, as a society, we have to accept the current anthropogenic imprint of contaminants, we must reflect on whether the MPA is a proper indicator for curative soil management to assess leaching due to existing diffuse contamination.

The second indicator was the actual groundwater concentration, in this report defined as the MAD criterion, a robust upper limit of the statistical distribution in ambient groundwater concentrations, comparable with a 95th percentile. Comparing leaching from diffusely contaminated soils with actual groundwater concentrations is closer to the reality of the current state of the soil–groundwater system than comparing with a theoretical risk level. However, the consequence is that no statements can be made about the, possibly adverse, effects of contaminants on groundwater ecosystems. As argued above, such statements are not within the scope of this report. A major disadvantage of this second threshold is the fact that the current measure of groundwater concentration, i.e. the MC, is regarded as a fixed concentration over time despite the fact that due to leaching of the diffuse contamination and as result of dissolution (i.e. weathering) of soil minerals, this groundwater concentration will vary over time.

The third indicator was based on the ratio of the maximum average concentration that results from the Maximum Value (MV) Residential or Industrial with the maximum average concentrations resulting from with concentrations at the level of the MV Agricultural. In formula form, in which I is the indicator and 'concentration' indicates the maximum average groundwater concentration:

I = concentration MV Residential / concentration MV Agricultural

Since the groundwater concentrations for both the MV Residential and the MV Agricultural vary over time, this indicator incorporates future groundwater concentrations that will result from the leaching of the diffuse contaminated soil. If the value for I is larger than 1, the scenario leads to an increase in groundwater concentrations compared with the estimated leaching of soils which, from a policy perspective, are regarded as clean. Comparing two values which are both an estimate from the model means that the uncertainty of the final value of the indicator is a combination of the uncertainty in both estimates. This uncertainty in the final value is not assessed in detail.

This study looks at the impact on groundwater of the curative management of diffusely contaminated soils, under the Dutch Soil Quality Decree. With this in mind it is considered that the third indicator is the most relevant for assessing this impact, since it compares the clean situation, as defined by the Soil Quality Decree, with a specific situation resulting from residential or industrial use. However, this indicator does not contain any information about current groundwater concentrations or information about risks to the ecosystem or human health.

8.4 Spatial overview

In the results we also give a spatial overview of leached concentrations compared with the MC for selected elements. As discussed above, comparison with the MC does not incorporate changes in groundwater composition over time. Therefore, these maps should be interpreted in terms of which areas are, over time, more vulnerable to the leaching of certain elements from soil to groundwater. However, the interpretation for peaty and clayey areas is impeded by the assumptions for the hydrological transport modelling. As already discussed, the value of 300 mm/year for water infiltration overestimates this transport. This can also be interpreted as speeding up time, so that calculated concentrations may appear later in reality. If we reduce the amount of infiltrating water, the peak concentrations will occur later. This extends the time horizon of the modelling far beyond the 500 years, which, in most cases, increases the effects of processes like diffusion and dilution, lowering the peak concentration.

For many clayey soil profiles the model is not able to find a numeric solution for the chemical speciation and therefore these profiles are automatically discarded by the algorithm. These discarded profiles are shown as grey areas on the maps. It is assumed that these clayey soils are in general soils with relatively high pH values (above pH7, see Figure 5.4.1). These high pH values probably result in very low dissolved concentrations of metal cations in the model. Considering that in reality the pH in these soils is indeed high and that leaching from the topsoil under these circumstances is not expected, then the discarding of these profiles is not problematic. While it should be possible to solve the modelling issues with these soil profiles, they are not regarded as relevant to the scope of this study.

8.5 Detailed discussion of some elements

Based on the evaluation of the model, or parts of the model (see Chapter 6), we infer that the prediction of the speciation of Ba, Cd, Co, Cu, Ni, Hg, Pb, Sn, V and Zn is sufficiently sound, with a somewhat lower model performance for oxyanions than for metal cations. The initial concentrations for Ni and Zn can be rather high due to the use of the Dutch Soil Type Correction. For As, Mo, Sb and Sn we have to make some reservations.

For As the prediction of the speciation is acceptable. However, the model presumes mildly oxic conditions and simplified PO^{4+} chemistry. The limited parameterisation of PO^{4+} results in an underestimation of As concentration (and that of other oxyanions). For soils with an anoxic environment, like some peaty and clayey soils, the leaching of As is further underestimated. The speciation of As is very dependent on the redox conditions and the concentration of organic matter, iron and sulphides. The modelling of this complex system was not possible within the constraints of this study.

The modelling of Mo is satisfactory but the input concentrations for scenarios with an MV Residential or Industrial are somewhat unrealistic. The MVs are based on human exposure and, as a result, the MVs for Mo are very high compared with the actual field concentrations. Compared with the areas within Europe with the highest concentrations of Mo, the input concentrations of Mo are about a factor of 20–40 times higher (Salminen et al., 2005). Under field conditions, these high input concentrations probably result in precipitation of Wulfenite ($PbMoO_4$), which sequesters both Mo and Pb from the dissolved phase. In the model the precipitation of Wulfenite was prevented so that the high Mo concentrations would not remove Pb, leaving the soil solution super-saturated with Mo. We do not expect that the Mo concentrations for the scenarios with MVs Residential or Industrial reflect reality.

Antimony concentrations from the model are highly uncertain due to a lack of a proper parameterisation of the thermodynamic models underlying our model. This is a general problem, since knowledge about the behaviour of this element is scarce (Filella et al., 2009). This is also evident from the model evaluation. In our results Sb shows almost no retention, which makes the results highly unlikely.

Tin also suffers from overestimated input values, despite the fact that the modelling of Sn is satisfactory. Using the principles of Chapter 5 and relying on the assumption that the added concentration is reactive, the input concentration for the scenarios with the MV Agricultural results in pore water concentrations at *t=0*, which are already one or two orders of magnitude higher than field values, resulting in an overestimated leaching.

9 Conclusions

In this report we predicted the groundwater concentrations below soils with assumed concentrations of As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni Pb, Sb, Sn, V and Zn at the level of the Maximum Values for agricultural, residential and industrial soil use, taken from the Dutch Soil Quality Decree. We created a model to calculate the groundwater concentrations which result from the leaching of the aforementioned elements. This model was based on a multi-surface geochemical speciation model including a simple transport model.

We evaluated the model and showed the suitability of the multi-surface model to predict the solubility of most metal cations in soils, with the exception of Sb. The precision of the predictions is highest for metals with a moderate to strong affinity for binding with organic matter. Generally, the model performance for oxyanions is lower than for metal cations. The results of hindcast modelling give confidence in the ability of the model to simulate the transport of metals adequately over long time scales on the basis of equilibrium chemistry.

The results of the column tests showed that the observed deviations between (transport) model and data are adequate. This is encouraging given the large differences between batch and column tests and the consistency in model performance under both test conditions. The deviations between model and data seem to be caused by inadequate estimates of important parameters (e.g. availability) rather than by failure of the underlying model components due to the very different loadings under transport conditions as a result of different L/S ratios. Also, transport-related physical features, such as the influence of non-equilibrium, do not seem to be a major source of deviation between model and data, as the sensitivity of the model curves for important chemical parameters is demonstrated to be very important.

The modelled scenarios were based on soil profiles from the STONE soil schematisation of the Netherlands. In this schematisation, Dutch soils are divided into 456 plots, each with its own soil profile. For each soil profile in the upper 50 cm, the concentrations of elements were set at the level of one of the Maximum Values, respectively in the various simulations.

Three soil profiles, representative of sand, peaty soils and clayey soils, were studied in detail. Soil profiles from the 20 largest plots in the STONE schematisation were studied at an aggregated level. The 456 soil profiles, covering the whole area of the Netherlands, were studied using maps showing binned results.

Leaching from the soil profiles was assessed in three ways. First, breakthrough curves showing changes in groundwater concentrations after several time spans at several depths were studied for the three main soil profiles. Second, for the 20 large-plot soil profiles, aggregated concentration ranges were studied. Third, for all 456 profiles the results were studied spatially using maps. For all soil profiles the maximum average concentration was calculated from the average concentration over a 1 m depth range for each time step. Then, for all the time steps, the maximum of these average values was determined. These maximum average concentrations were calculated after 1, 100 and 500 years and for 1 m (100–200 cm) and 5 m (500–600 cm) depths.

Three indicators were used to compare the maximum average concentration with a threshold value. The first indicator was based on the Maximum Permissible Addition (MPA). This MPA is a risk level and is used in risk assessments as the no effect level for an added concentration in the event that the substance also occurs naturally. The second indicator is based on the 95th percentile of current groundwater concentrations. The third indicator is the predicted groundwater concentrations below soils with the Maximum Value Agricultural. This is compared with the predicted maximum average groundwater concentrations of the Maximum Value Residential and the Maximum Value Industrial. This last indicator is representative of the predicted changes in the groundwater composition of soil with a ‘clean’ soil with a diffuse anthropogenic imprint of contaminants.

In this report, we argue that the MPA without considering background concentrations is not very useful as a reference to compare groundwater concentrations that result from the management of diffusely contaminated soils. The major reason is that it is hard to differentiate between the natural background concentration and the anthropogenically added part within ambient groundwater concentrations. These ambient groundwater concentrations are often above the MPA level already.

When comparing our results from the scenarios having soils with concentrations at the level of the Maximum Value Agricultural with current groundwater concentrations, we found that the elements Cd, Co, Cu Mo, Ni Sb, Sn and Zn can be considered mobile at the time range of 500 years. Cadmium, Co, Cu and Ni show mobility related to soil type. Antimony, Cd, Mo, Ni and Zn are also found at greater depths (5 m) and can be considered more mobile than the others.

For the scenarios with Maximum Value Residential and Maximum Value Industrial, Cd, Ni and Zn show enrichment when compared with current groundwater concentrations. Lead also shows elevated concentrations in peat and clay areas but this is due to the relatively low, and possibly biased, current groundwater concentrations together with an overestimation by the model.

Comparing the maximum average concentrations of the scenarios with Maximum Values Residential and Industrial with those of the scenarios with Maximum Value Agricultural (i.e. ‘clean’ soils), we found that higher concentrations occur for Cd, Co, Mo, Ni, Sn, Zn and Sb. For Mo, Sn and Sb these increases are expected to be a result of modelling artefacts.

10 Recommendations

Considering the results of this modelling study we make the following recommendations for further research and the improvement of the model and methodology presented in this report.

1. One of the main assumptions in the methodology is that the added concentrations of metals/metalloids are regarded as geochemically reactive. This added concentration is determined by a geochemical baseline to calculate the background concentration and the Maximum Values corrected for soil type using the Dutch Soil Type Correction (STC). In an earlier study Spijker (2012) concluded that the underlying model of the STC needs to be updated. It is known that the assumption of full availability (reactivity) in most cases overestimates actual reactivity. For both issues, the limitations of STC and the overestimation of reactivity, alternative methods became available during the course of this study. We recommend studying how these alternative methods can improve the estimation of reactive concentrations for input into the overall model.

2. In this study we assumed a relatively simple hydrology, a constant downward water flux of 300 mm recharge per year at field level. For clay and peat areas this overestimates leaching from the soil. The hydrology can be improved by either using area-specific groundwater recharge or incorporating dynamic soil hydrology models like SWAP. The first option is relatively simple to implement in the model, if the data is available. The second option requires refactoring of the model and increases its complexity. We recommend studying which option is more feasible and implementing that option.

3. New data on the concentrations of major elements like Ca^{2+}, PO^{4+} and SO_4^{2-} show that the concentrations used in our model for some cations and oxyanions can be improved. We recommend further investigation to establish which concentrations of major elements are appropriate for the different soil types.

4. In this model we defined three modelling scales: a scale with high detail but a limited number (3) of soil profiles, an aggregated scale (20) and a binned scale with all available profiles. The reasons for these choices were the calculation time required for simulation of a single soil profile and the time needed for interpretation of the data. During this study, these calculation and interpretation steps were increasingly automated. A rerun of the model in which all the profiles are modelled in detail would still require significant computation facilities but far less labour time than at the start of the study. Considering the aforementioned recommendations we recommend applying these improvements and rerunning the model using all available soil profiles. With the available data it is possible to discern the most sensitive areas or situations with regard not only to current groundwater concentrations but also to estimated future concentrations.

5. The data underlying our model have their origin in rural areas. For example the baseline model, the Soil Type Correction, models concerning estimating the DOC fractions and the STONE schematisation are all based on datasets obtained from non-urban, often agricultural, soil. In urban soils, hydrology

and groundwater composition are distinctly different from those in rural areas. We recommend researching the availability of data on urban soil–groundwater systems and determining how the model in this study can be applied in the urban setting.

6. A major argument for choosing a multi-surface speciation model in previous studies (e.g. Verschoor, et al., 2006) was that this kind of model is the proper model in situations with many elements and, consequently, chemical competition. Also, this kind of model was assumed to perform better when considering the wide ranges of important soil properties like pH and organic matter content. However, data input and calculation times are quite large for this kind of model. Considering the already available data on many soil profiles and conditions we might be able to construct a simplified meta-model. This meta-model could be based on already calculated cases with only a few variables needed as input. For example, only soil concentration and water transport. In Dutch soil policy a toolbox is used so that local soil managers can assess different options for soil management and the consequences for humans and the ecosystem. We recommend investigating the need for including a groundwater model in this toolbox to assess the impact of soil management options on groundwater and, if appropriate, developing a meta-model for this purpose based on the results from this study.

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11 Appendix A: Estimation of input parameters

11.1 Extending STONE profiles

ORCHESTRA uses a schematisation in layers of 10–15 cm depth to a maximum depth of 600 cm. The STONE database has a different schematisation in soil layers, with depths varying from 5 cm to 25 cm, up to a depth of 100 cm. To match the STONE schematisation with the ORCHESTRA schematisation, the STONE layers were expanded in layers of 5 cm, duplicating layers within the same original layer. For example, if a STONE layer had a thickness of 15 cm, this resulted in three identical layers. To each layer in the ORCHESTRA schematisation, the corresponding 5 cm layers were assigned. For example, the first ORCHESTRA layer of 10 cm comprises the first two layers of the 5 cm schematisation. The concentrations of the 5 cm layers were averaged within the ORCHESTRA layer. For the ORCHESTRA layers between 100 and 600 cm, the 100 cm layer from the STONE database was duplicated.

The above procedure resulted in a profile with 10 cm layers to 600 cm depth, except one 15 cm layer at 20 cm depth. Each layer in the profile contained clay content, concentrations of Fe- and Al-hydroxides, pH and organic matter. The first 50 cm was assigned to the (enriched) topsoil, the layers between 50 and 100 cm were assigned to the subsoil (no enrichment) and layers deeper than 100 cm were assigned to groundwater.

11.2 Calculating metal concentrations

For the model two types of metal concentration were defined: the natural concentration and the enriched concentration. The enriched concentration is at the level of a Maximum Value given as standard soil concentration is corrected using the Soil Type Correction formula (see Spijker, 2012):

$$C = \frac{C_{b,s} \cdot \beta_0 + \beta_1 L + \beta_2 O}{\beta_0 + 25\,\beta_1 + 10\,\beta_2}$$

Where $C_{b,s}$ is the concentration for a standard soil with 10 wt-% organic matter and 25 wt-% clay (grain size fraction <2 um), C is the concentration for the specific soil, and L and O are the clay and organic matter fractions (wt-%) for the specific soil. Values for L and O are based on the organic matter and clay fraction of the STONE plot. The $\beta_{0,1,2}$ values are the regression parameters according to the Soil Quality Decree (see Spijker, 2012, p.23).

For the model the 'reactive' concentration is used as input. This reactive concentration for the upper (enriched) soil layer is derived according to:

reactive concentration = Maximum Value – natural background concentration

The natural background concentration was derived using the geochemical baseline model:

Me = Al_2O_3 ** bl.slope + bl.interc*

in which Me is the natural background concentration [mg/kg], Al_2O_3 is the concentration [wt-%] and bl.slope (b1) and bl.interc (b0) are respectively the slope and intercept of the model (see Table A.1.1). In the STONE database no information is present about Al_2O_3, so this concentration is calculated using:

Al_2O_3 *[wt-%] = (gf2 [wt-%] + 15.42) / 4.76 (Spijker, 2005)*

If no baseline was present (e.g. for Hg) then the median subsoil value from the Geochemical Atlas was used instead. In the case of clay content <5%, the value for sand was used; for clay content >=5%, the value for marine clay was used. When the median value was not present (e.g. Co), another representative value was applied.

Table A.1.1 Regression parameter ($\beta_{0,1}$), regression error (ε) and robust correlation coefficient (r) of the relation between total metal concentrations and aqua-regia extraction (see equation (x)).

Element	β_1	β_0	ε	**r**
As	0.81	1.15	0.57	0.98
Ba	0.50	-84.0	12.0	0.52
Be	1.0	-0.350	0.052	0.99
Cd	1.1	-0.107	0.018	0.74
Cr	1.4	-56.0	2.9	0.99
Cu	1.00	-0.00167	0.11	0.91
Pb	1.2	-6.52	0.93	0.98
V	0.85	-2.25	1.6	0.99
Zn	0.98	13.1	1.4	1.00
Mo	1.0	-0.115	0.038	0.97
Ni	0.92	0.486	0.85	0.98
Sb	0.47	0.00730	0.028	0.82
Se	0.89	-0.268	0.037	0.97
Sn	0.78	-0.260	0.12	0.84
Tl	0.96	-0.081	0.046	0.82

In cases where the natural background was greater than the Maximum Value (e.g. for Ba and Cr) this procedure resulted in negative reactive concentrations. In that case the reactive concentration was derived by applying the topsoil partition coefficient to the natural background concentration and the reactive concentration is representative of the natural, not enriched, situation. This is tenable because the enriched case, a Maximum Value below the natural concentration, is somewhat awkward.

11.3 Calculating humic substances in the solid phase

At the time of modelling no data on the representative values of reactive humic substances (HS) for each soil type were available. Therefore, a generic value of HS=50% of solid organic matter (SOM) was assumed. This is the same value as used in earlier model studies (Verschoor et al., 2006; Spijker e.a. , 2009)

11.4 Humic substances in liquid phase

The binding of elements to SOM and dissolved organic matter is modelled as binding to humic substances, the principal reactive fraction in organic matter for ion binding.

The concentration of reactive SOM modelled as generic humic acid (HA) was estimated from the organic matter content assuming that 50% of organic matter is reactive (Dijkstra et al., 2009; Groenenberg et al., 2012).

Regression functions were developed to relate the concentration of dissolved humic substances (HS-diss), i.e. the sum of fulvic acid (FA) and humic acid, to soil properties. These relations were based on measurements of DOC and sub-fractions of HA and FA in 10^{-3}M $CaCl_2$ extractions of 66 top- and subsoil samples from major Dutch soil types (sand, peat and clay) from the archive of samples of the Geochemical Soil Atlas of the Netherlands (Mol et al., 2012). The dried samples were incubated for one month, after being re-moisturised to field capacity, prior to the extraction and fractionation procedure, in order to limit the previously observed effects of soil drying on DOC. Extractions were done at a liquid to solution ratio (LS) of 10. Fractions of FA, HA and Hy were determined according to the procedure of van Zomeren and Comans (Van Zomeren and Comans, 2007).

Here we use a regression function which relates the concentration of dissolved HS to the organic matter content (as determined with loss on ignition, LOI) and the reactive iron oxide content extracted with 0.43 M HNO_3:

$$Log(HS\text{-}diss) = -5.130 + 0.707 * log(LOI) - 0.192 * log(Fe_{re})$$

$$R^2_{adj} = 0.60 \; SE_y = 0.29$$

where HS-diss = concentration HS in solution (kgC.L^{-1}), %LOI = weight % LOI, Fe_{re} = reactive content iron in soil (mg/kg).

To calculate the Fe_{re} concentration from the Fe-oxide (Fe_{ox}) oxalate extracted concentrated given in the STONE profiles we use the equation (Groenenberg, unpublished results)

$$Log(Fe_{re}) = -0.335+0.946*log(Fe_{ox})$$

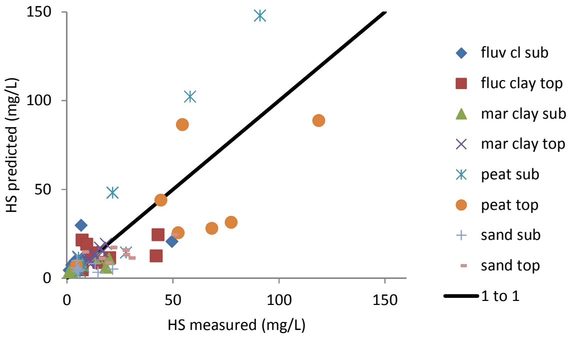

Figure A.4.1: Comparison of concentrations of HS calculated using the regression relation (Equation 1) with measured concentrations for the 66 soil samples used in the derivation of the relation

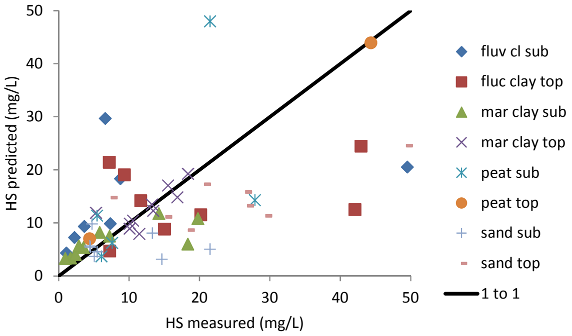

Figure A.4.2: Comparison of concentrations of HS (kg/L) calculated with Equation 1 with measured concentrations of the 66 soil samples (left: all data; right: lower concentration range)

The liquid to solution ratio (LS) of the extraction has a distinct effect on the concentration of dissolved organic matter and subfractions (Fest et al., 2008). Therefore, the HS-diss concentrations obtained with Equation 1 were corrected with a generic factor of 3 to estimate the HS-diss concentration under field conditions. This correction factor was based on the average ratio of HS-diss obtained by centrifugation of field moist soils to HS-diss extracted with $CaCl_2$ in the incubated soils for a total of six soils including top- and subsoils of a sandy, clayey and peaty soil (Groenenberg, unpublished results).

The concentration of reactive solid organic matter modelled as generic humic acid (HA) was estimated from the organic matter content assuming that 50% of organic matter is reactive (Dijkstra et al., 2009; Groenenberg et al., 2012).

11.4.1 *Calculating pH and pe*

pH and pe were estimated using the equation:

$pH_{sol} + pe = 15,$

in which pH_{sol} is the pH in the soil solution. To calculate this pH_{sol} from the pH, derived after a KCl extraction (pH_{KCl}), in the STONE database we use the equation (Bonten and Brus, 2006):

$pHsol = 0.82\ pH_{KCl} + 1.79$

11.5 Model output and data processing

The model output for each cell in the profile and for each time step was saved to a raw data file. Due to the large amount of raw data a selection was made, using every tenth time step, for further data processing. If the model was not able to converge to a solution (i.e. no equilibrium could be reached within the model), the scenario was rejected and the model output was discarded.

Data processing was done in the R statistical software (R Core Team, 2013 using the *sp*, *maptools*, *parallel*, *compiler*, *MASS* and *lattice* libraries. For each scenario, reports with detailed data tables and graphs were generated using *SWeave*.

A full model run, using 499 scenarios, took about six days on eight CPU cores. A single run of the model took about 1.5 hours on two CPU cores.

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12 Appendix B: Detailed results

12.1 Detailed results for arsenic (As)

12.1.1 *Breakthrough curves*

Figures B.1.1.1 to B.1.1.3 show the breakthrough curves for As. The breakthrough curve in the sand profile shows somewhat unexpected behaviour. However, considering that the concentration range between up- and downward peaks is about 0.0003 ug/l, this behaviour is not relevant. The same goes for the clayey profiles. In the peat profile the concentration of As diminishes over time in the 100 cm depth soil layer.

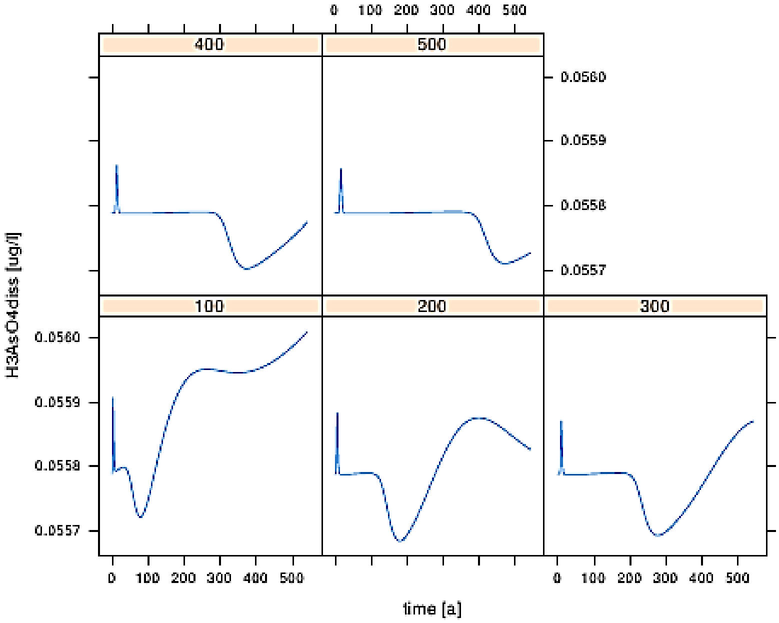


Figure B.1.1.1: Breakthrough curve for dissolved As (H3AsO4diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

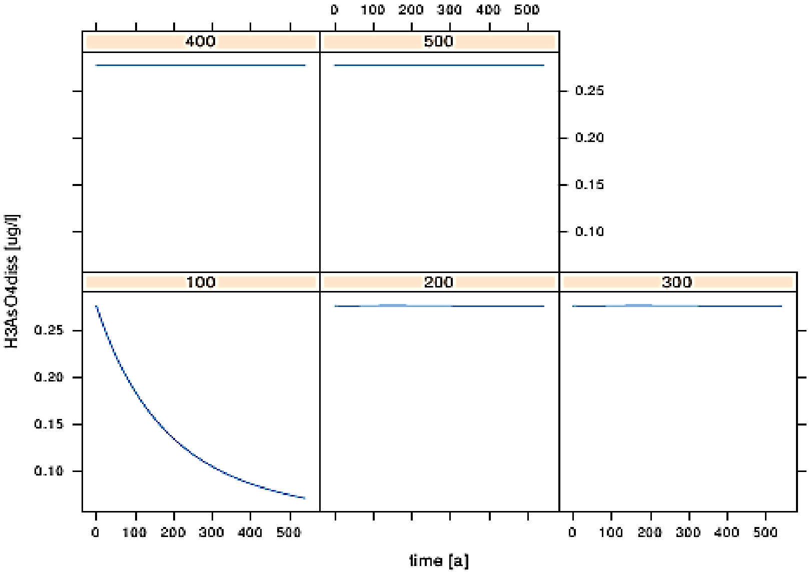


Figure B.1.1.2: Breakthrough curve for dissolved As (H3AsO4diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

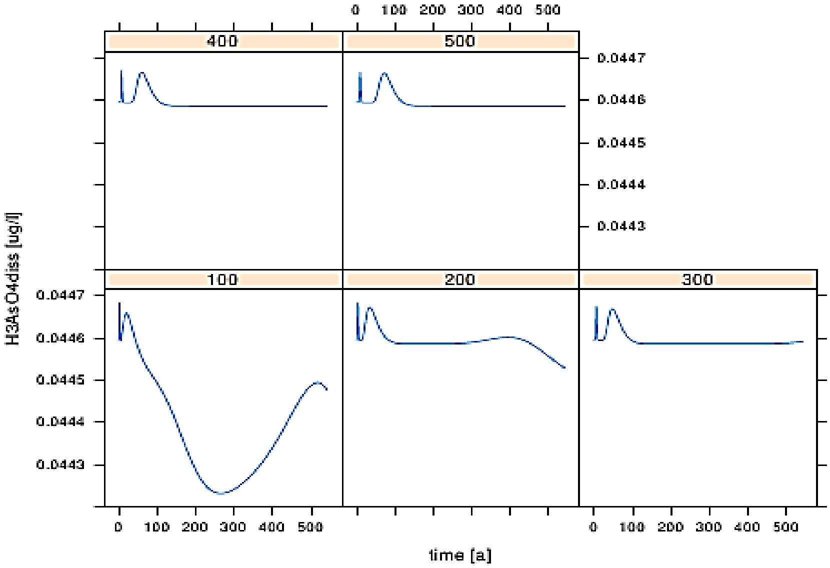


Figure B.1.1.3: Breakthrough curve for dissolved As (H3AsO4diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.1.2 *Soil profile*

Figures B.1.2.1 to B.1.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. The sand and peat profiles show some higher soluble concentrations of As in the upper layer, which rapidly decrease in the subsequent layer. For peat this variability of As over depth in the solid phase is related to the Fe-ox content in the standard soil profile. These Fe-ox values are high in the upper part of the profile (around 200 mg/kg) but decrease to values of 13 mg/kg in the lower part (>100 cm depth).

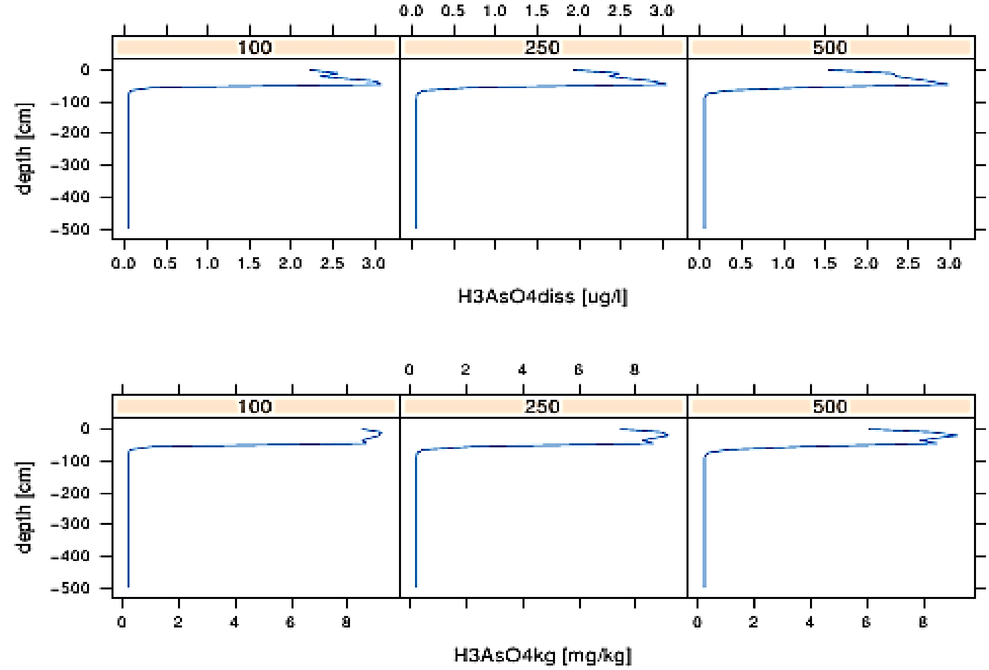


Figure B.1.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved As (H3AsO4diss) is given in the top figure; the lower figure gives As in the solid phase (H3AsO4kg).

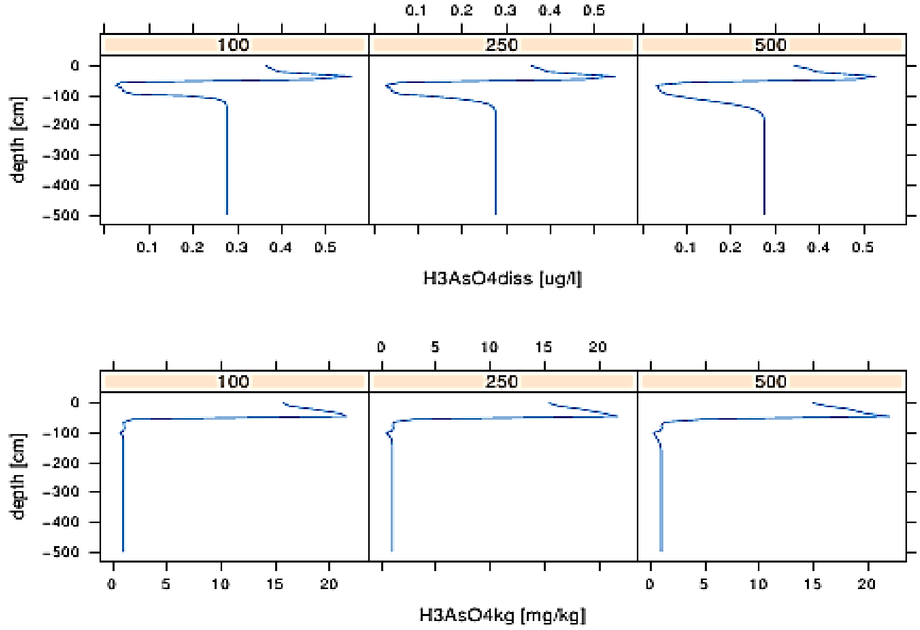


Figure B.1.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved As (H3AsO4diss) is given in the top figure; the lower figure gives As in the solid phase (H3AsO4kg).

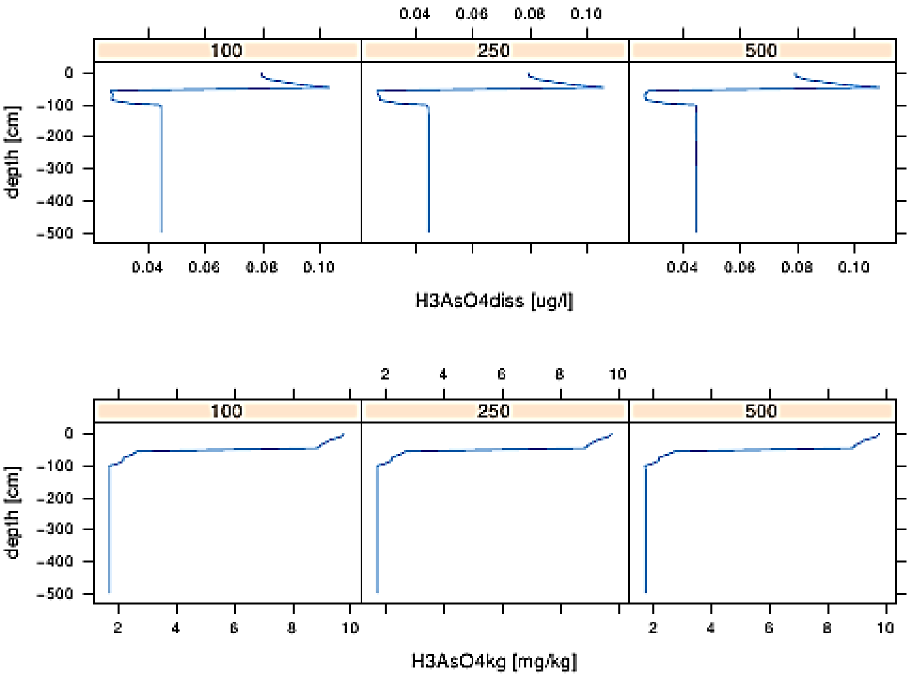


Figure B.1.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved As (H3AsO4diss) is given in the top figure; the lower figure gives As in the solid phase (H3AsO4kg).

12.1.3 Results standard scenario

Table B.1.3.1 gives the exact values for the three standard soil profiles. The values of peak concentration and exceedance of the MC are so minute that they are given as zero in this table. These values are corroborated further in the next paragraph.

Table B.1.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
residential	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
industrial	*sand*	0.02	3.8	24	0	0
	peat	0.17	10.8	24	0.02	0
	clay	0.07	26.1	24	0	0
time: 500 yr, depth: 100 cm						
agricultural	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
residential	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
industrial	*sand*	0.03	3.8	24	0	0
	peat	0.25	10.8	24	0.02	0
	clay	0.07	26.1	24	0	0
time: 500 yr, depth: 500 cm						
agricultural	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
residential	*sand*	0.02	3.8	24	0	0
	peat	0.15	10.8	24	0.01	0
	clay	0.07	26.1	24	0	0
industrial	*sand*	0.03	3.8	24	0	0
	peat	0.16	10.8	24	0.02	0
	clay	0.07	26.1	24	0	0

12.2 Detailed results for barium (Ba)

12.2.1 Breakthrough curves

Figures B.2.1.1 to B.2.1.3 show the breakthrough curves for Ba. The variability in concentrations over time is rather low. For sand and peat these concentration ranges are 0.005 ug/l and 0.004 ug/l, respectively. For peat the range is somewhat larger, 0.015 ug/l, but still minute.

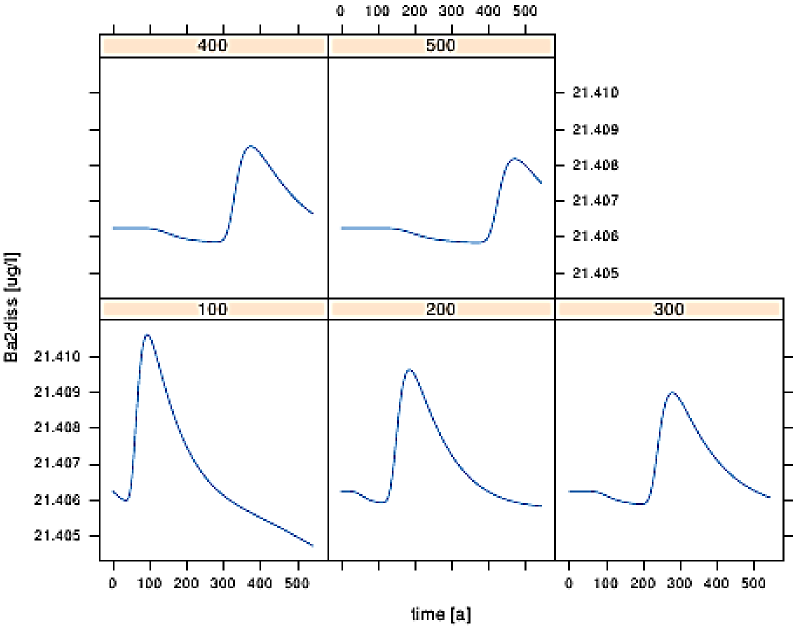


Figure B.2.1.1: Breakthrough curve for dissolved Ba (Ba2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

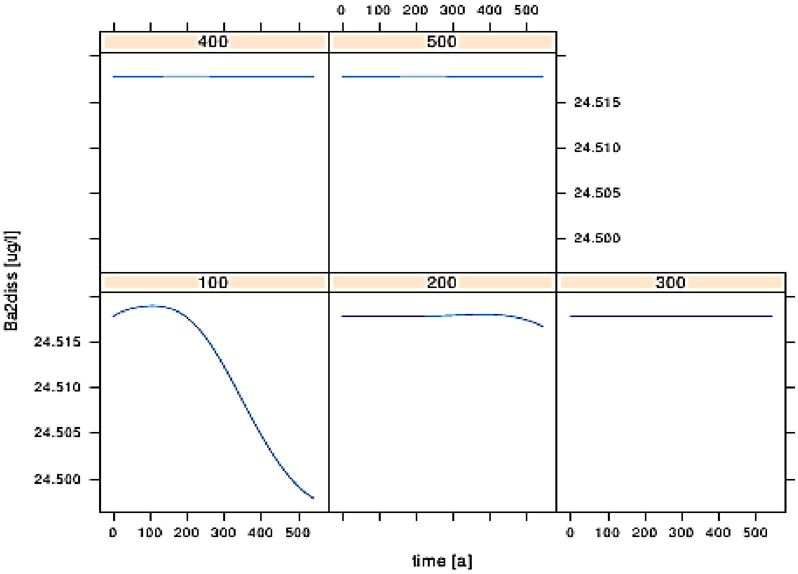


Figure B.2.1.2: Breakthrough curve for dissolved Ba (Ba2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

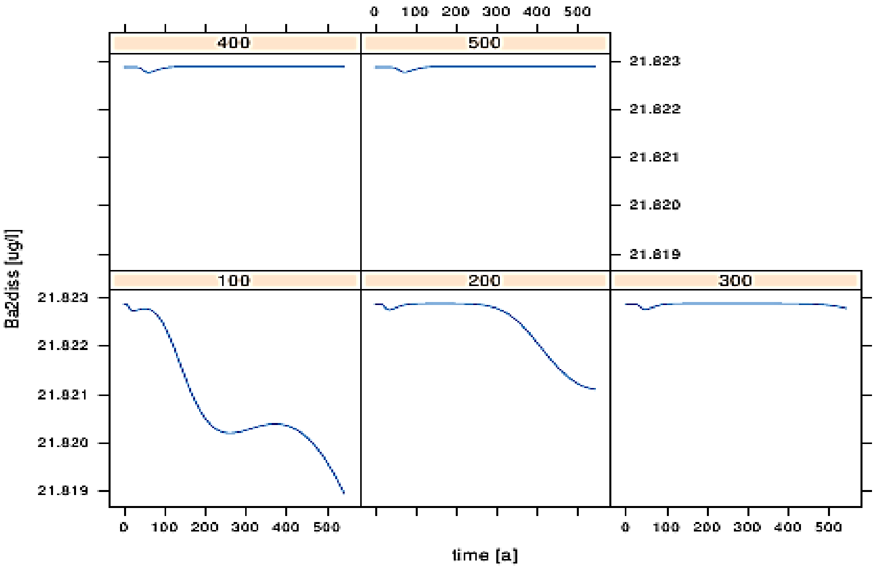


Figure B.2.1.3: Breakthrough curve for dissolved Ba (Ba2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.2.2 *Soil profile*

Figures B.2.2.1 to B.2.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. In the leaching profiles almost no change over time can be discerned. Only after 500 years do the solid concentrations indicate some minor displacement of Ba in the upper layer.

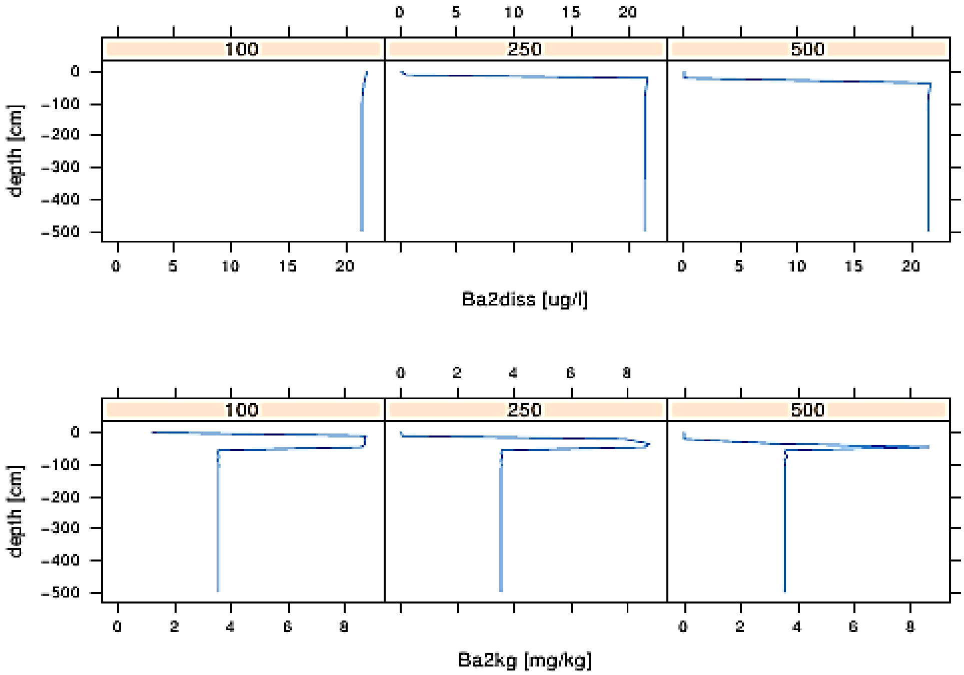


Figure B.2.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Ba (Ba2diss) is given in the top figure; the lower figure gives Ba in the solid phase (Ba2disskg).

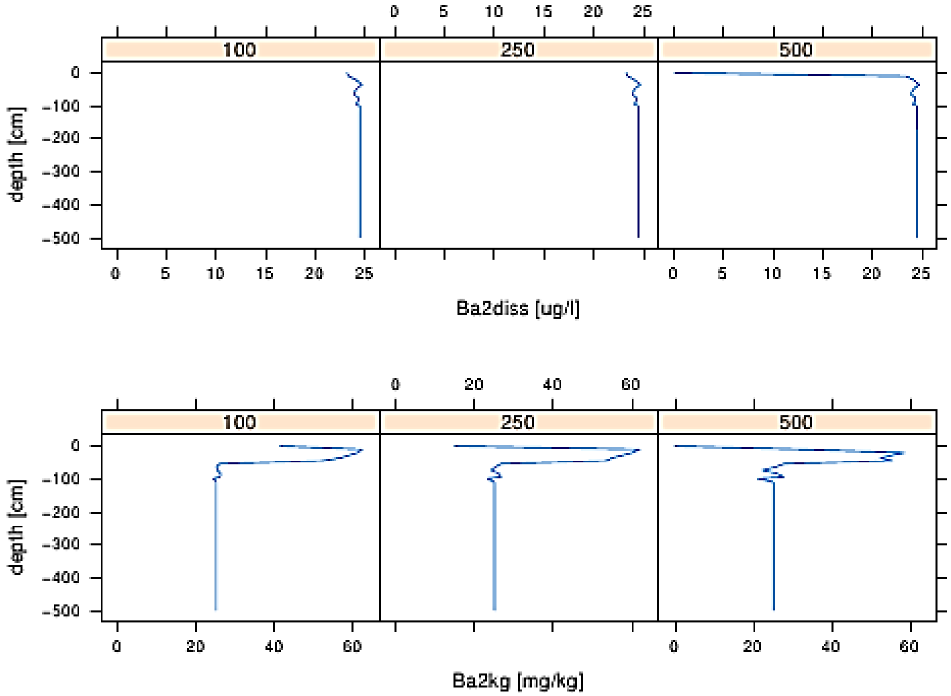
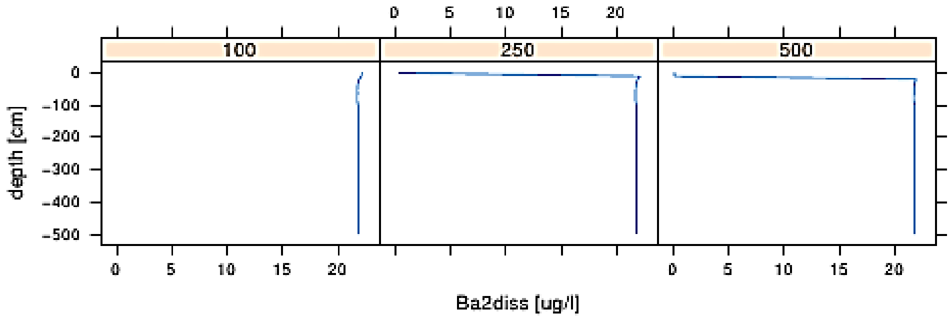


Figure B.2.2.2: *Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Ba (Ba2diss) is given in the top figure; the lower figure gives Ba in the solid phase (Ba2kg).*



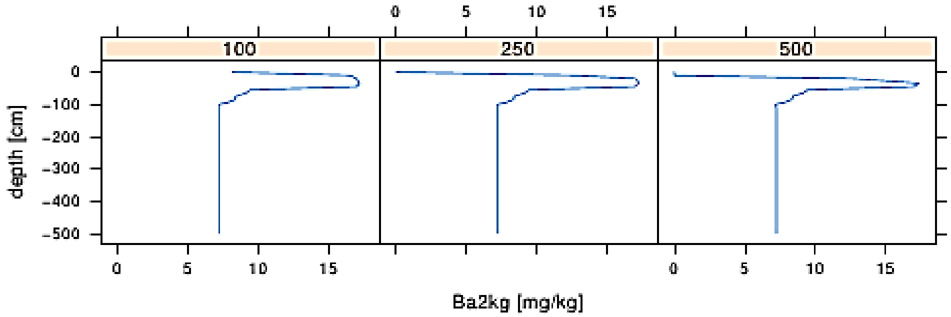


Figure B.2.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Ba (Badiss) is given in the top figure; the lower figure gives Ba in the solid phase (Ba2kg).

12.2.3 *Results standard scenario*

Table B.2.3.1 gives the exact values for the three standard soil profiles. Both MC and MPA are not exceeded in all the used scenarios. However, for the Maximum Value Industrial the ratio of predicted concentration to MPA gets close to 1. Peak values are the same for the different scenarios. The selected time frame and depth have the same peak concentrations. Only difference in soil type results in different peak values.

Table B.2.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
residential	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
industrial	*sand*	21.7	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.7
time: 500 yr, depth: 100 cm						
agricultural	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
residential	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
industrial	*sand*	21.7	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
time: 500 yr, depth: 500 cm						
agricultural	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
residential	*sand*	21.4	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8
industrial	*sand*	21.7	157.2	29	0.14	0.7
	peat	26.1	302.6	29	0.09	0.9
	clay	22.0	88.5	29	0.25	0.8

12.3 Detailed results for cadmium (Cd)

12.3.1 Breakthrough curves

Figures B.3.1.1 to B.3.1.3 show the breakthrough curves for Cd. For clay and peat increasing concentration is only predicted for the top layer. At 100 cm concentrations rise but do not reach a peak level. For the sandy profile an increase in concentration can be seen up to 300 cm depth, although at 300 cm this increase is relatively small compared with the layers above.

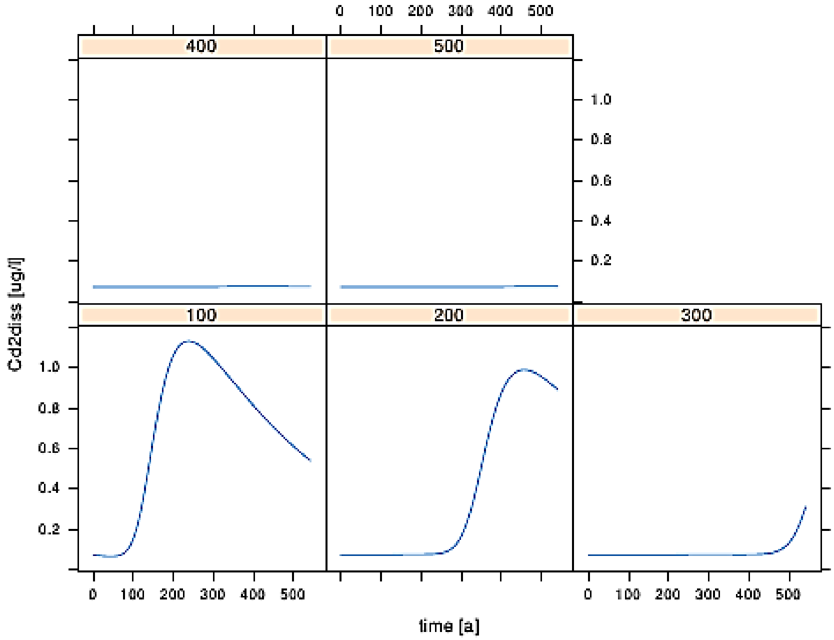


Figure B.3.1.1: Breakthrough curve for dissolved Cd (Cd2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

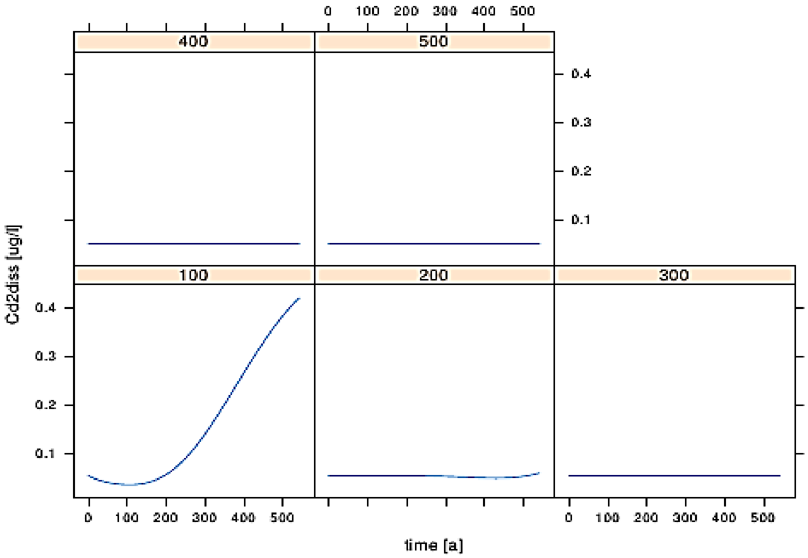


Figure B.3.1.2: Breakthrough curve for dissolved Cd (Cd2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

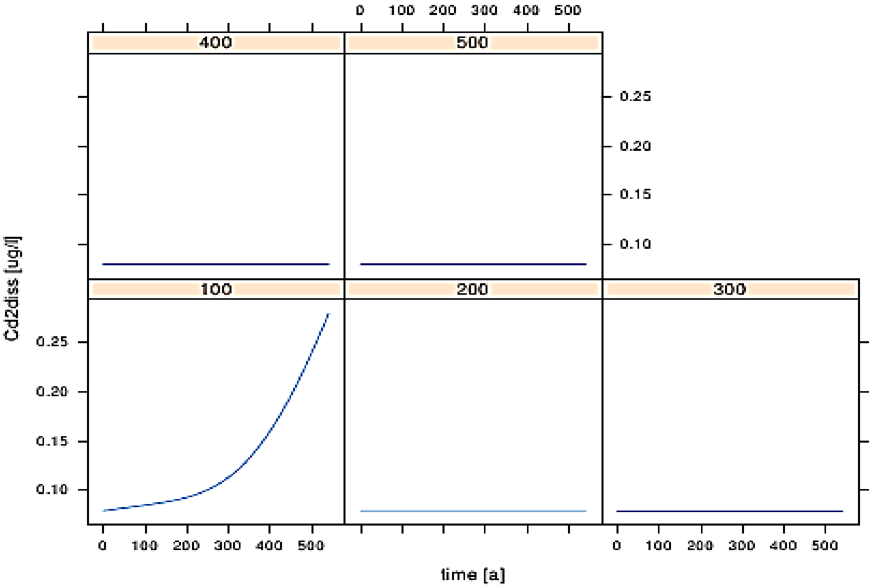


Figure B.3.1.3: Breakthrough curve for dissolved Cd (Cd2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.3.2 Soil profile

Figures B.3.2.1 to B.3.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. In the sandy profile, transport of Cd is evident, including some chromatographic separation in the solid phase. The other profiles show some leaching but within the time frame of 500 years the transport of Cd is limited to the upper layers (<200 cm).

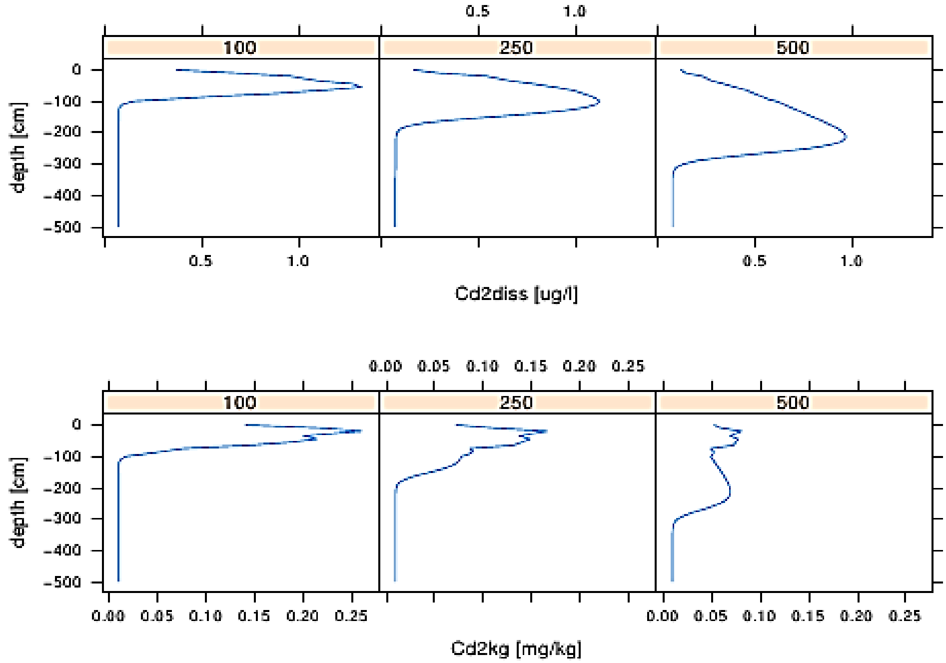


Figure B.3.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cd (Cd2diss) is given in the top figure; the lower figure gives Cd in the solid phase (Cd2kg).

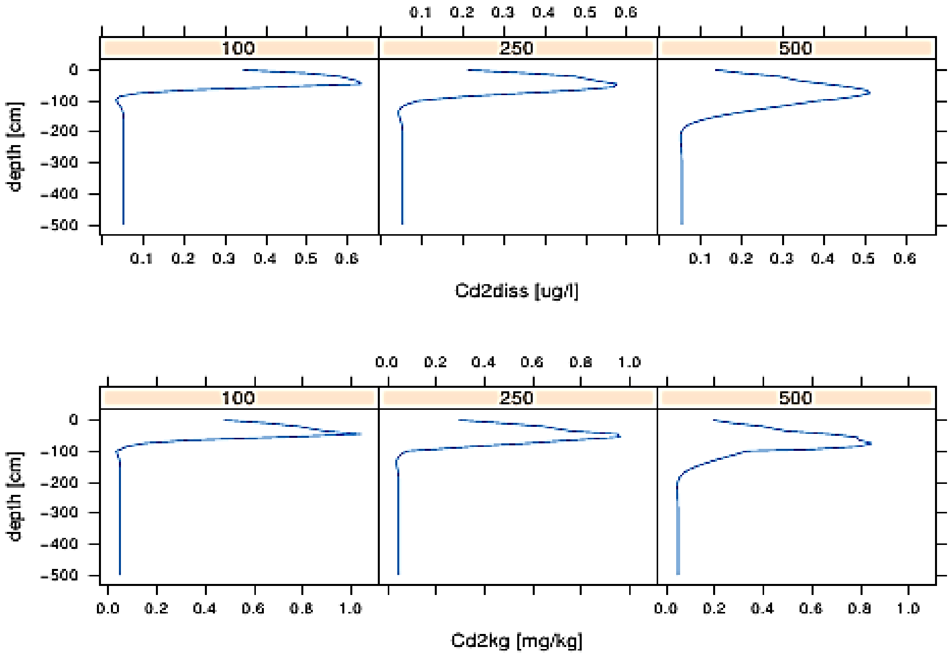
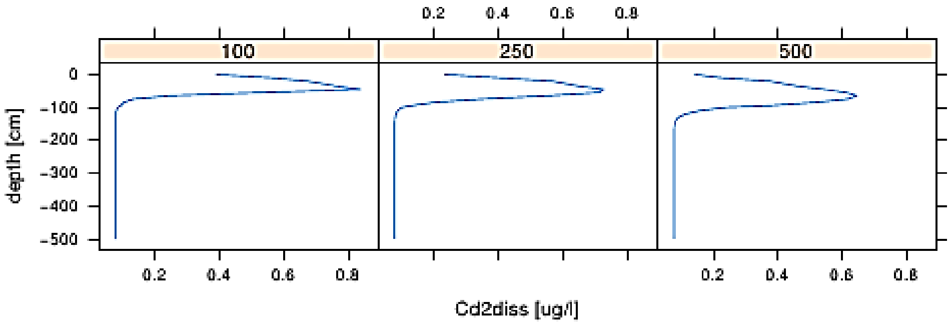


Figure B.3.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cd (Cd2diss) is given in the top figure; the lower figure gives Cd in the solid phase (Cd2kg).



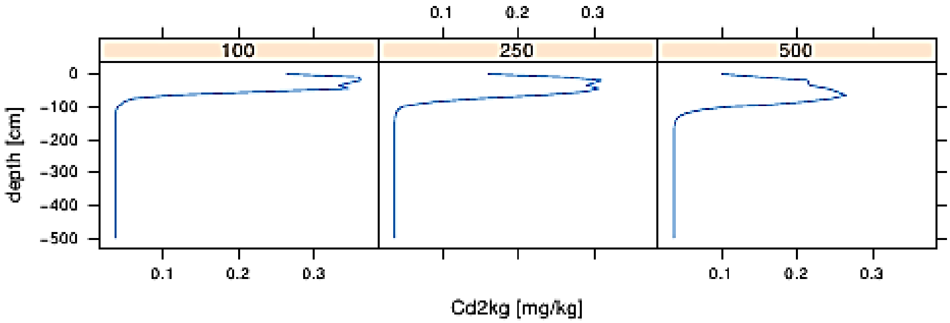


Figure B.3.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cd (Cd2diss) is given in the top figure; the lower figure gives Cd in the solid phase (Cd2kg).

12.3.3 *Results standard scenario*

Table B.3.3.1 gives the exact values for the three standard soil profiles. The table indicates that the MC and the MTT are exceeded for the Maximum Value Industrial in the sand profile at 100 cm depth. For the MC value this ratio is about 20 while for the MPA this ratio is around 50. In the peat and clay profiles, after 500 years and at 100 cm depth, the Maximum Value Industrial also results in values larger than the MC and MPA.

Table B.3.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0.05	0.82	0.34	0.07	0.2
	peat	0.03	0.06	0.34	0.49	0.1
	clay	0.09	0.10	0.34	0.96	0.3
residential	*sand*	0.20	0.82	0.34	0.24	0.6
	peat	0.03	0.06	0.34	0.50	0.1
	clay	0.09	0.10	0.34	0.96	0.3
industrial	*sand*	15.7	0.82	0.34	19.3	46.2
	peat	0.03	0.06	0.34	0.53	0.1
	clay	0.10	0.10	0.34	0.10	0.3
time: 500 yr, depth: 100 cm						
agricultural	*sand*	0.95	0.82	0.34	1.2	2.8
	peat	0.20	0.06	0.34	3.3	0.6
	clay	0.13	0.10	0.34	1.3	0.4
residential	*sand*	2.0	0.82	0.34	3.3	7.9
	peat	0.42	0.06	0.34	1.1	1.2
	clay	0.24	0.10	0.34	2.5	0.7
industrial	*sand*	18.0	0.82	0.34	22.7	54.4
	peat	18.0	0.06	0.34	31.4	5.6
	clay	28.1	0.10	0.34	28.8	8.3
time: 500 yr, depth: 500 cm						
agricultural	*sand*	0.05	0.82	0.34	0.06	0.1
	peat	0.03	0.06	0.34	0.48	0.1
	clay	0.09	0.10	0.34	0.95	0.3
residential	*sand*	0.05	0.82	0.34	0.06	0.1
	peat	0.03	0.06	0.34	0.48	0.1
	clay	0.09	0.10	0.34	0.95	0.3
industrial	*sand*	0.05	0.82	0.34	0.07	0.2
	peat	0.03	0.06	0.34	0.48	0.1
	clay	0.09	0.10	0.34	0.95	0.3

12.4 Detailed results for cobalt (Co)

12.4.1 Breakthrough curves

Figures B.4.1.1 to B.4.1.3 show the breakthrough curves for Co. The breakthrough curve of the sandy profile only shows decreasing concentrations.

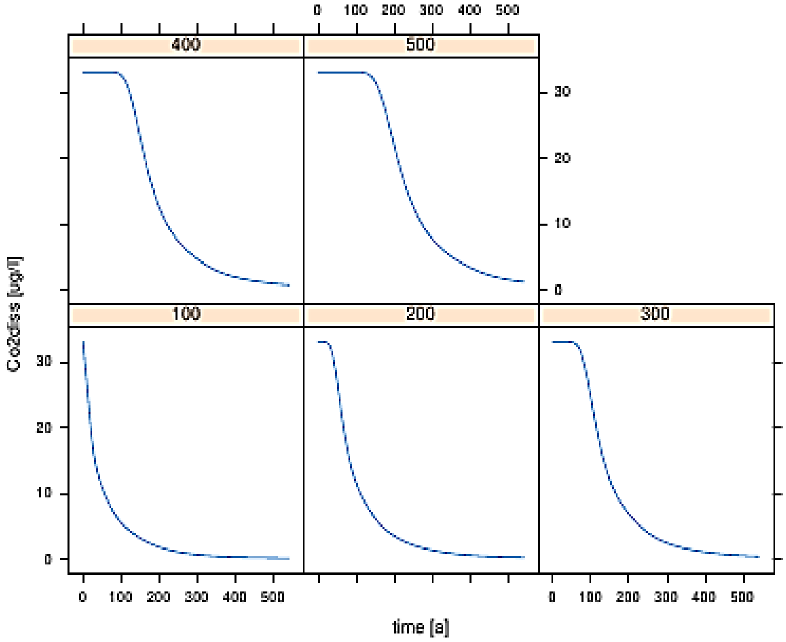
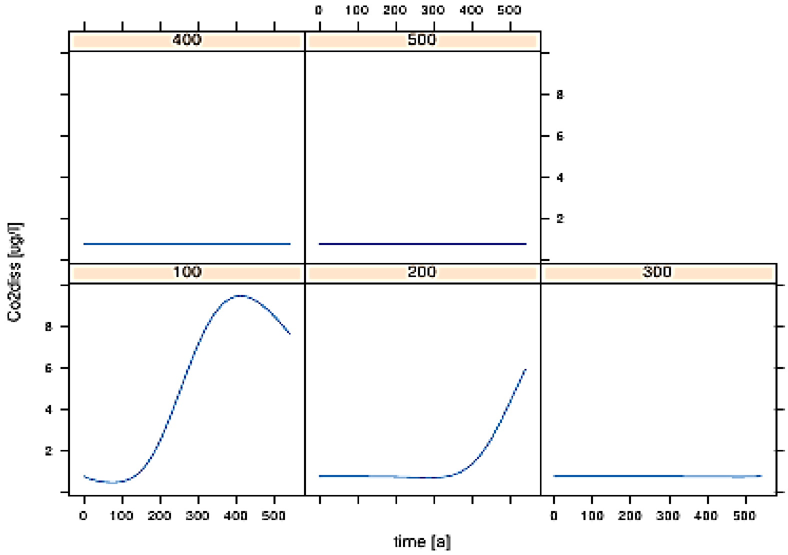


Figure B.4.1.1: Breakthrough curve for dissolved Co (Co2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.



Figuur 2.11: breakthrough curves of co for specified cells (depths).

Figure B.4.1.2: Breakthrough curve for dissolved Co (Co2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

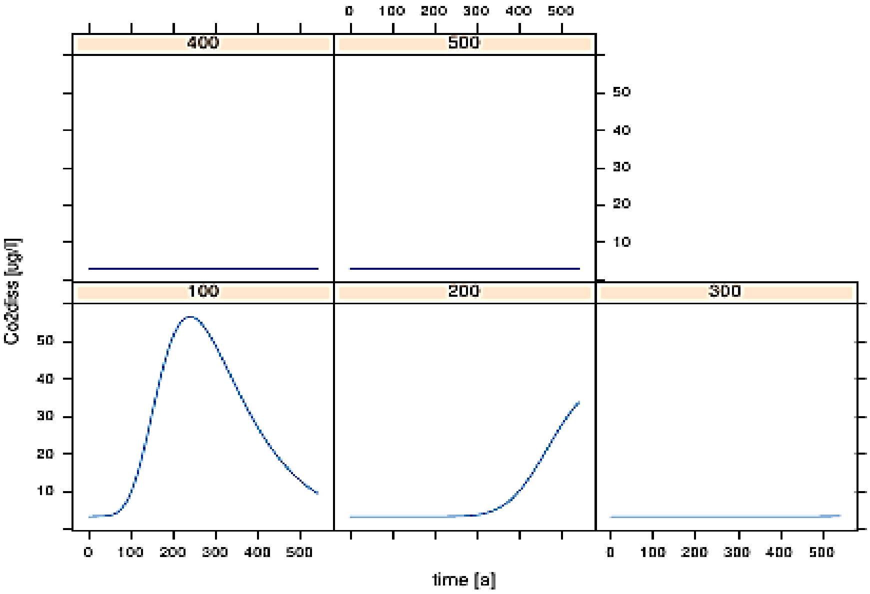


Figure B.4.1.3: Breakthrough curve for dissolved Co (Co2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.4.2 *Soil profile*

Figures B.4.2.1 to B.4.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles.

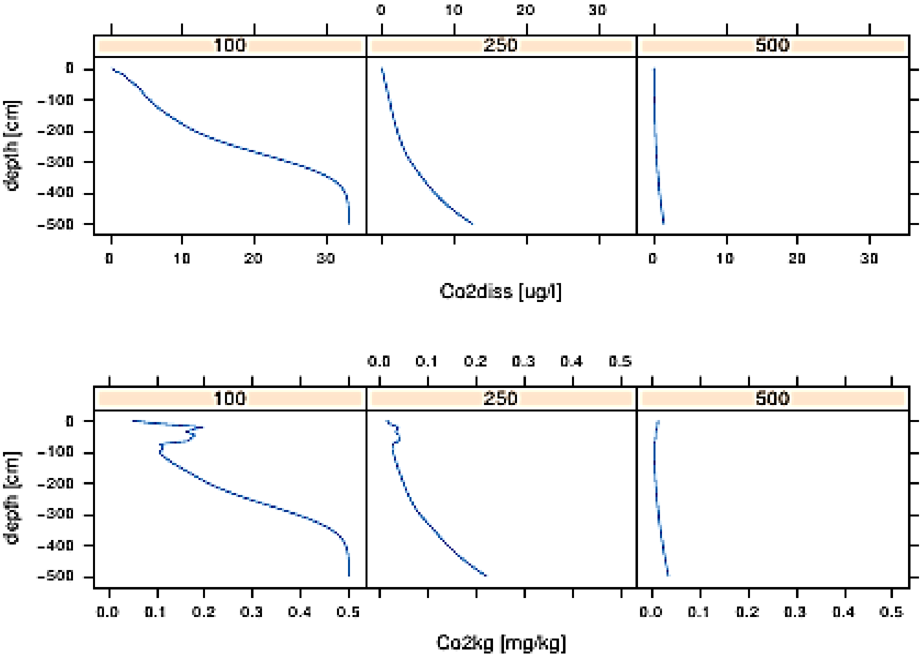


Figure B.4.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Co (Co2diss) is given in the top figure; the lower figure gives Co in the solid phase (Co2kg).

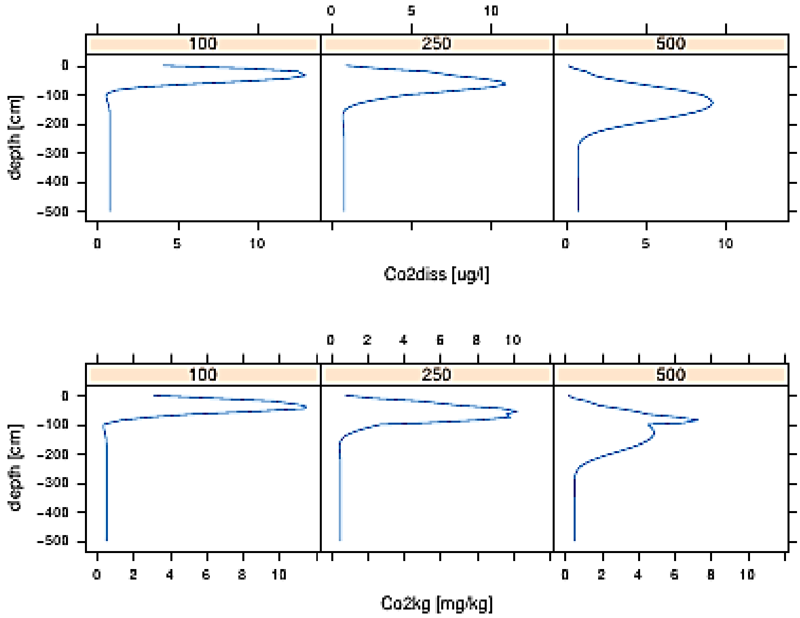


Figure B.4.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Co (Co2diss) is given in the top figure; the lower figure gives Co in the solid phase (Co2kg).

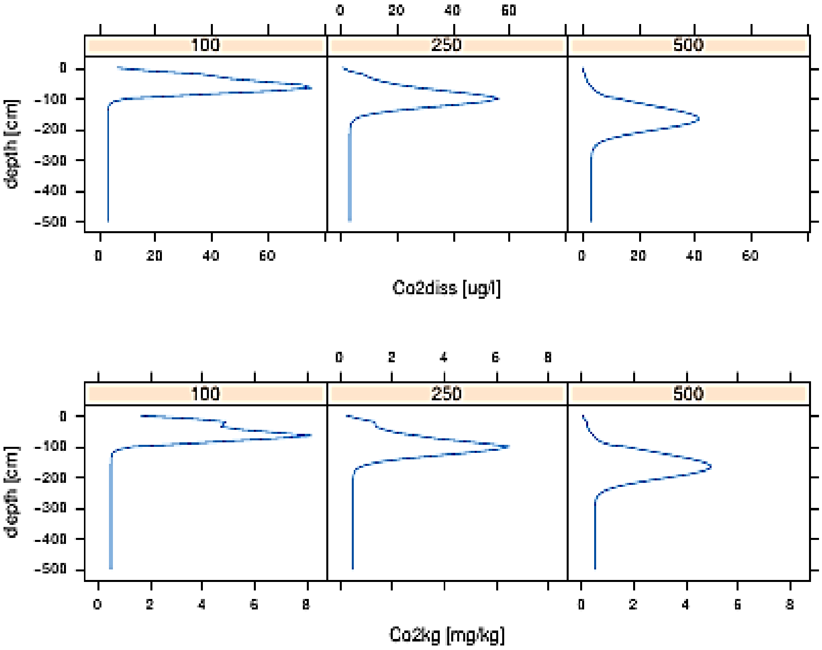


Figure B.4.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved C0 (C02diss) is given in the top figure; the lower figure gives Co in the solid phase (Co2kg).

12.4.3 Results standard scenario

Table B.4.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	24.2	-	2.6	-	9.3
	peat	0.43	-	2.6	-	0.2
	clay	3.7	-	2.6	-	1.4
residential	*sand*	148.9	-	2.6	-	57.3
	peat	0.52	-	2.6	-	0.2
	clay	12.0	-	2.6	-	4.6
industrial	*sand*	3194.2	-	2.6	-	1228.5
	peat	3.0	-	2.6	-	1.1
	clay	797.6	-	2.6	-	306.8
time: 500 yr, depth: 100 cm						
agricultural	*sand*	24.2	-	2.6	-	9.3
	peat	12.5	-	2.6	-	4.8
	clay	48.8	-	2.6	-	18.8
residential	*sand*	148.9	-	2.6	-	57.3
	peat	40.6	-	2.6	-	15.6
	clay	153.0	-	2.6	-	58.9
industrial	*sand*	3194.2	-	2.6	-	1228.5
	peat	322.8	-	2.6	-	124.1
	clay	1539.2	-	2.6	-	592.0
time: 500 yr, depth: 500 cm						
agricultural	*sand*	24.2	-	2.6	-	9.3
	peat	0.4	-	2.6	-	0.2
	clay	2.1	-	2.6	-	0.8
residential	*sand*	97	-	2.6	-	37.2
	peat	0.4	-	2.6	-	0.2
	clay	2.1	-	2.6	-	0.8
industrial	*sand*	1557.7	-	2.6	-	599.1
	peat	0.4	-	2.6	-	0.2
	clay	2.1	-	2.6	-	0.8

12.5 Detailed results for chromium (Cr)

12.5.1 Breakthrough curves

Figures B.5.1.1 to B.5.1.3 show the breakthrough curves for Cr. The sand and peat profiles show first a decrease in concentration and then an increase.

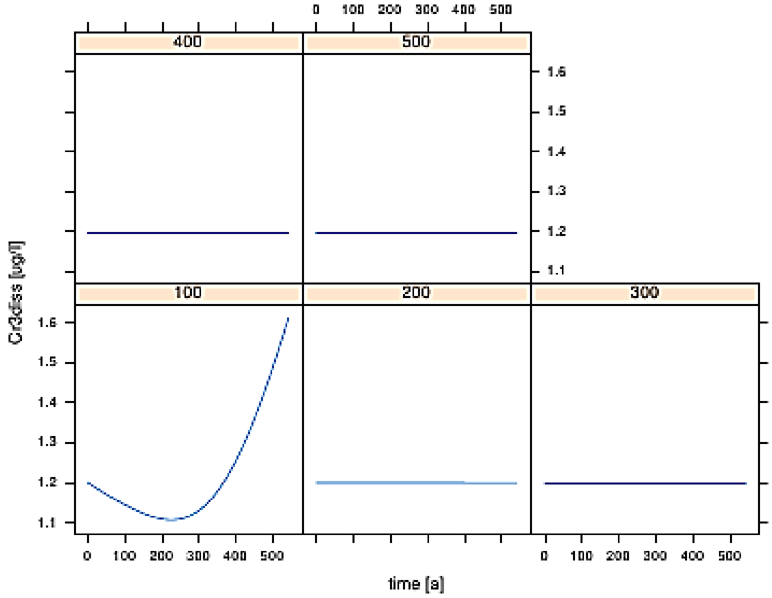


Figure B.5.1.1: Breakthrough curve for dissolved Cr (Cr3diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

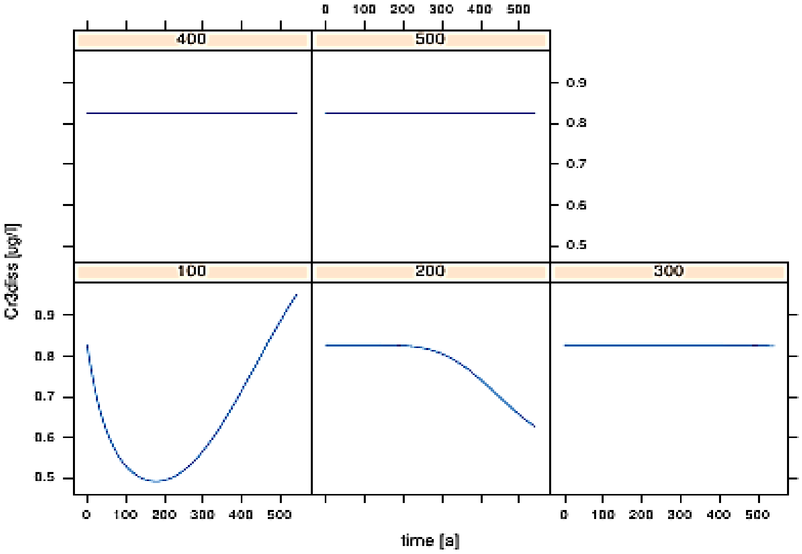


Figure B.5.1.2: Breakthrough curve for dissolved Cr (Cr3diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

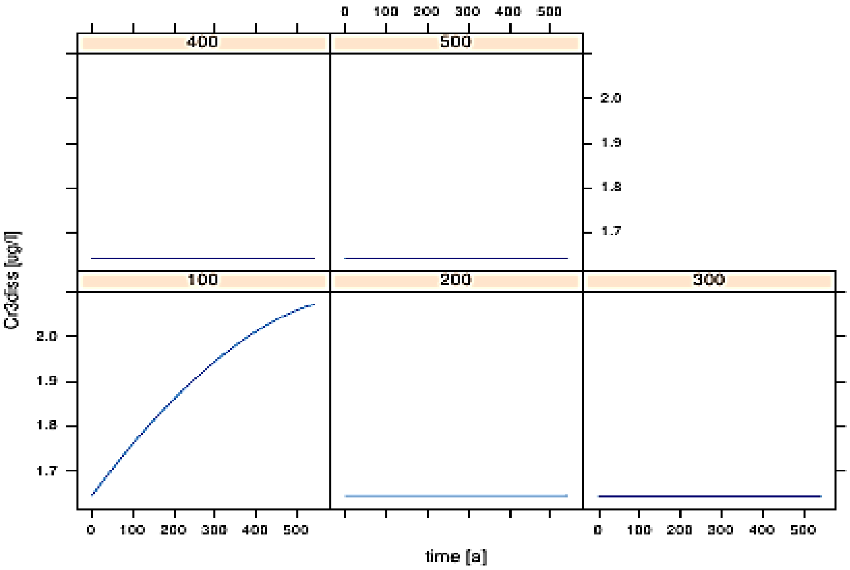


Figure B.5.1.3: Breakthrough curve for dissolved Cr (Cr3diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.5.2 *Soil profile*

Figures B.5.2.1 to B.5.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles.

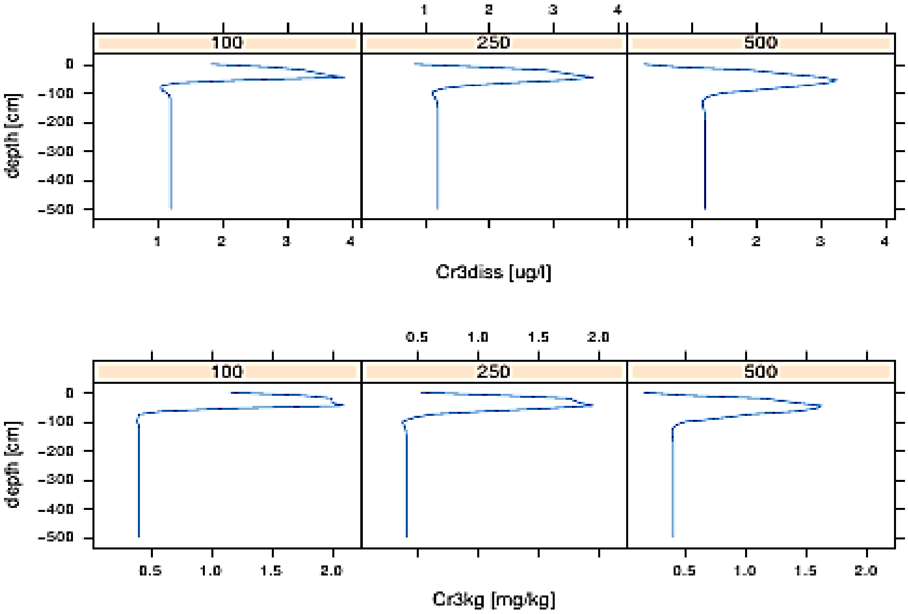


Figure B.5.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cr (Cr3diss) is given in the top figure; the lower figure gives Cr in the solid phase (Cr3kg).

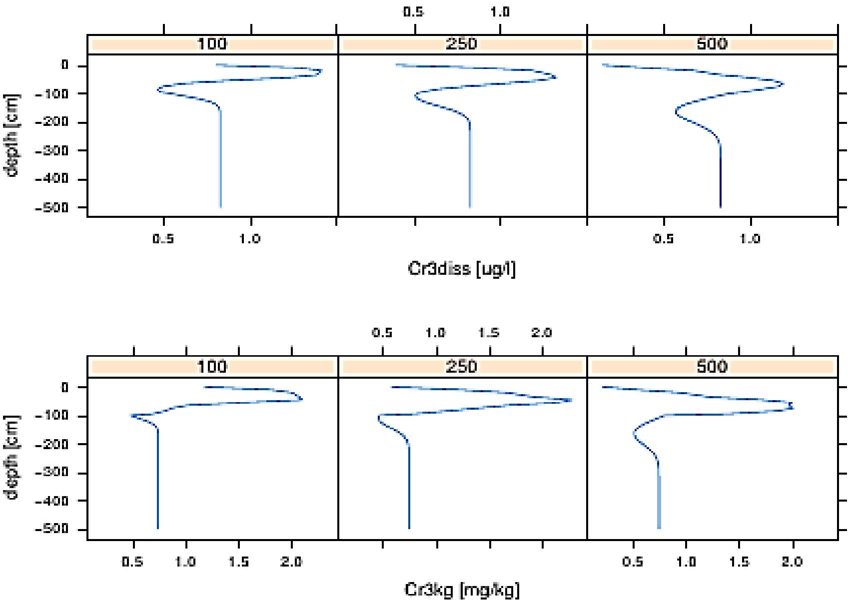


Figure B.5.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cr (Cr3diss) is given in the top figure; the lower figure gives Cr in the solid phase (Cr3kg).

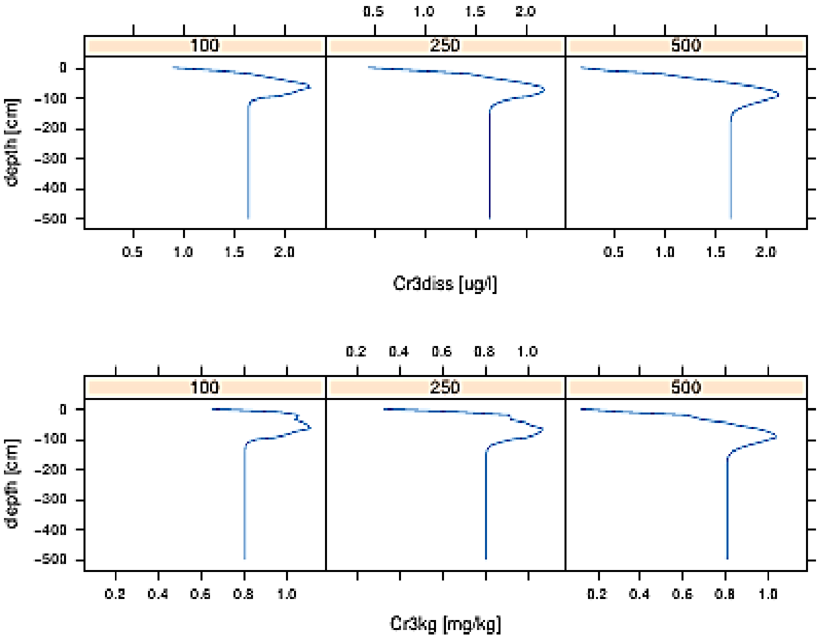


Figure B.5.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cr3 (Cr3diss) is given in the top figure; the lower figure gives Cr in the solid phase (Cr3kg).

12.5.3 *Results standard scenarios*

Table B.5.3.1 gives the exact values for the three standard soil profiles.

Table B.5.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.45	1.4	8.7	0.33	0.1
	clay	2.0	0.7	8.7	2.9	0.2
residential	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.45	1.4	8.7	0.33	0.1
	clay	2.0	0.7	8.7	2.9	0.2
industrial	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.45	1.4	8.7	0.35	0.1
	clay	2.0	0.7	8.7	2.9	0.2
time: 500 yr, depth: 100 cm						
agricultural	*sand*	1.4	5.2	8.7	0.27	0.2
	peat	0.81	1.4	8.7	0.6	0.1
	clay	2.2	0.7	8.7	3.2	0.3
residential	*sand*	1.8	5.2	8.7	0.35	0.2
	peat	0.81	1.4	8.7	0.6	0.1
	clay	2.2	0.7	8.7	3.2	0.3
industrial	*sand*	7.0	5.2	8.7	1.3	0.8
	peat	19.4	1.4	8.7	14.2	2.2
	clay	5.3	0.7	8.7	7.5	0.6
time: 500 yr, depth: 500 cm						
agricultural	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.4	1.4	8.7	0.33	0.1
	clay	2.0	0.7	8.7	2.9	0.2
residential	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.45	1.4	8.7	0.33	0.1
	clay	2.0	0.7	8.7	2.9	0.2
industrial	*sand*	1.2	5.2	8.7	0.23	0.1
	peat	0.45	1.4	8.7	0.33	0.1
	clay	2.0	0.7	8.7	2.9	0.2

12.6 Detailed results for copper (Cu)

12.6.1 Breakthrough curves

Figures B.6.1.1 to B.6.1.3 show the breakthrough curves for Cu. An increase in concentration can be seen at the soil depth of 100 cm. However, no peak concentration is achieved. The concentration is about a factor of two to three higher in the peat profile than in the sand and clay profile. Also, the peat profile has the highest reactive input concentration.

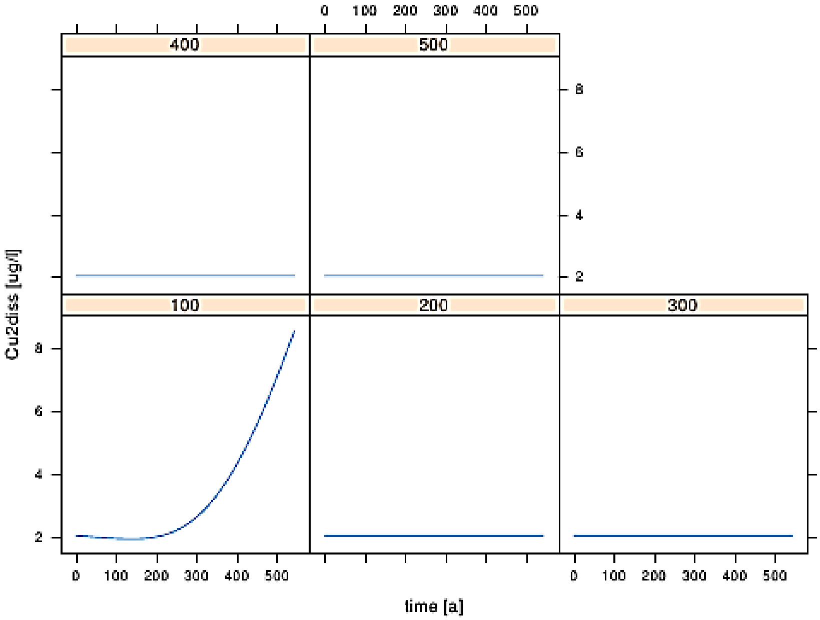


Figure B.6.1.1: Breakthrough curve for dissolved Cu (Cu2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

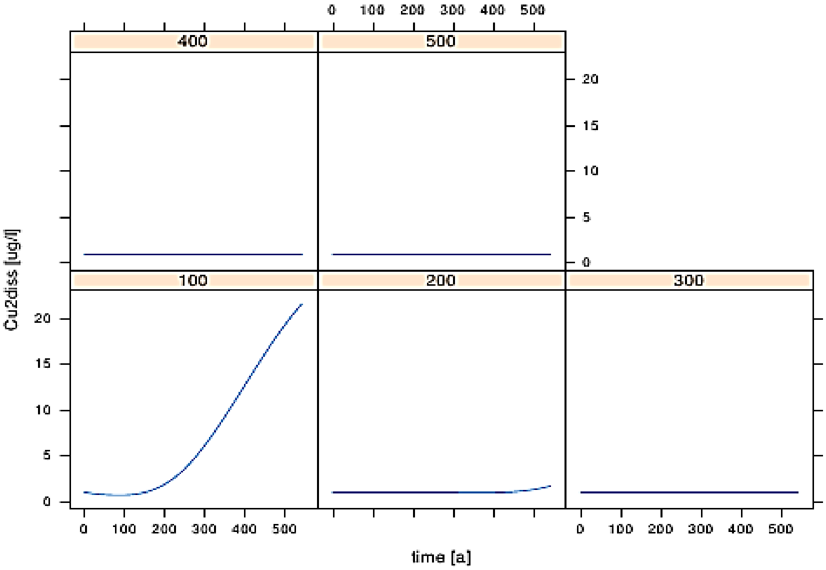


Figure B.6.1.2: Breakthrough curve for dissolved Cu (Cu2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

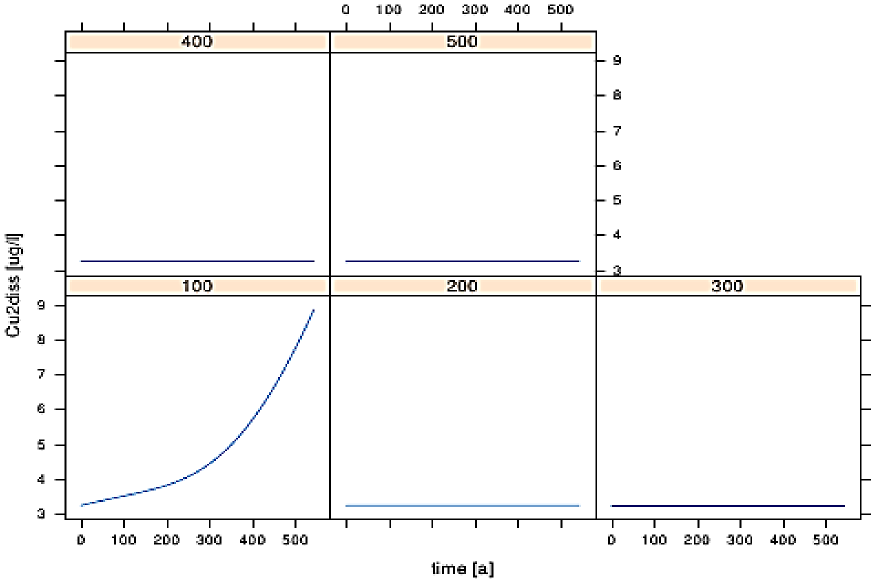


Figure B.6.1.3: Breakthrough curve for dissolved Cu (Cu2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.6.2 *Soil profile*

Figures B.6.2.1 to B.6.2.3 show the concentrations in the dissolved and solid phases in the soil profile of the three soil profiles. These profiles show some downward migration of Cu within the first 2 m. The dissolved peak concentrations of Cu are almost equal for three soil profiles, peat showing the highest value.

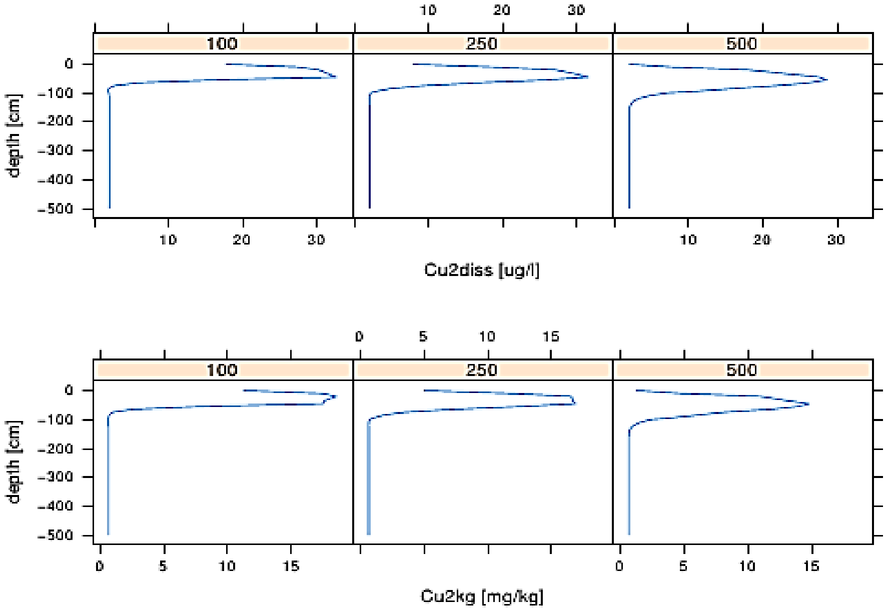


Figure B.6.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of *dissolved Cu (Cu2diss) is given in the top figure; the lower figure gives Cu in the solid phase (Cu2kg).*

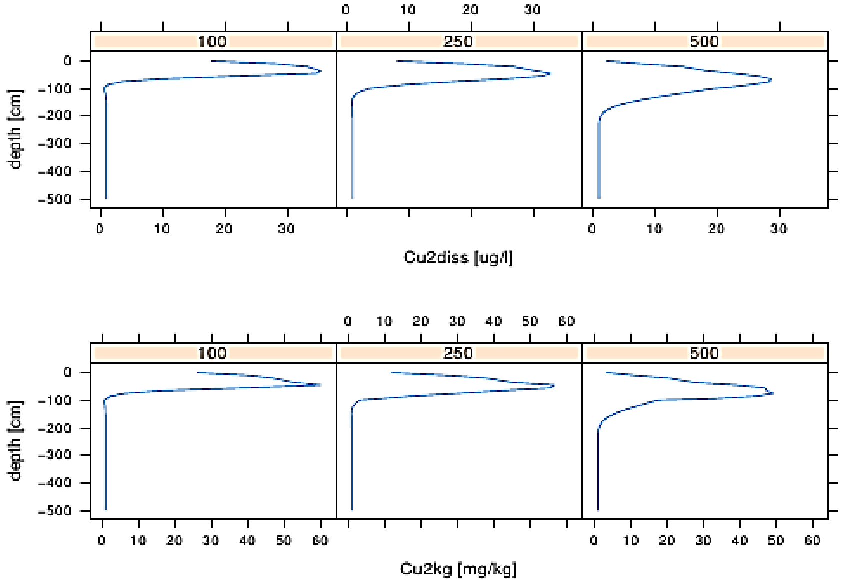


Figure B.6.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cu (Cu2diss) is given in the top figure; the lower figure gives Cu in the solid phase (Cu2kg).

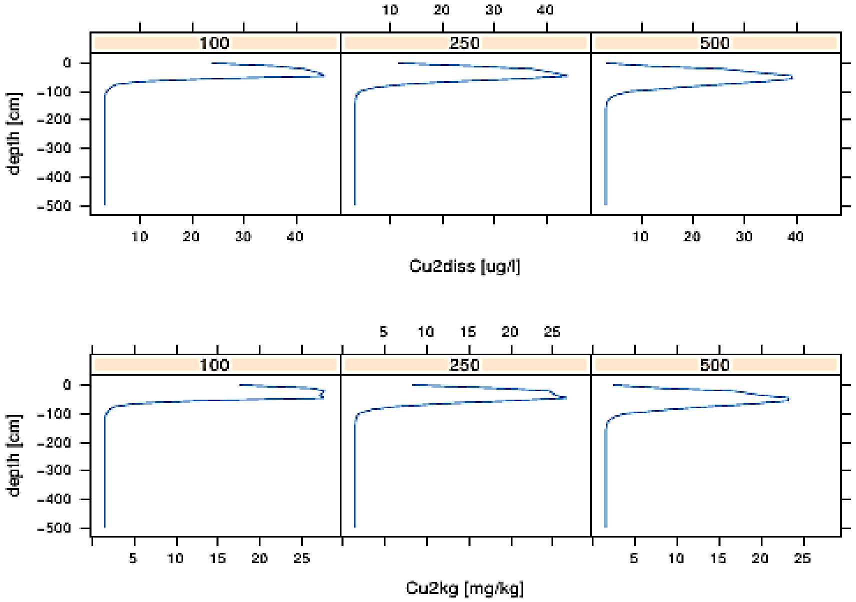


Figure B.6.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Cu (Cu2diss) is given in the top figure; the lower figure gives Cu in the solid phase (Cu2kg).

12.6.3 *Results standard scenarios*

Table B.6.3.1 give the exact values for the three standard soil profiles. The exceedance of the MC is limited but for the MPA predicted peak concentrations are often above this level. The scenario of 500 years, 5m depth shows no difference in concentration between the different Maximum Values, indicating that the results of this scenario only shows equilibrium background concentrations from the model.

Table B.6.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.55	7.3	1.1	0.07	0.5
	clay	4.3	5.0	1.1	0.86	3.9
residential	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.55	7.3	1.1	0.07	0.5
	clay	4.3	5.0	1.1	0.86	3.9
industrial	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.61	7.3	1.1	0.08	0.6
	clay	4.3	5.0	1.1	0.86	3.9
time: 500 yr, depth: 100 cm						
agricultural	*sand*	3.6	28.2	1.1	0.13	3.2
	peat	9.7	7.3	1.1	1.3	8.9
	clay	5.4	5.0	1.1	1.1	4.9
residential	*sand*	4.3	28.2	1.1	0.15	3.9
	peat	13.5	7.3	1.1	1.9	12.2
	clay	5.7	5.0	1.1	1.1	5.2
industrial	*sand*	10.6	28.2	1.1	0.38	9.7
	peat	49.4	7.3	1.1	6.8	45
	clay	7.1	5.0	1.1	1.4	6.4
time: 500 yr, depth: 500 cm						
agricultural	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.53	7.3	1.1	0.07	0.5
	clay	4.2	50	1.1	0.85	3.8
residential	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.53	7.3	1.1	0.07	0.5
	clay	4.2	50	1.1	0.85	3.8
industrial	*sand*	2.0	28.2	1.1	0.07	1.8
	peat	0.53	7.3	1.1	0.07	0.5
	clay	4.2	5.0	1.1	0.84	3.8

12.7 Detailed results for mercury (Hg)

12.7.1 Breakthrough curves

Figures B.7.1.1 to B.7.1.3 show the breakthrough curves for Hg. For all three soil profiles a change in groundwater concentration is visible only for the first soil layer at 100 cm depth. This concentration increases but does not reach a peak level within 500 years.

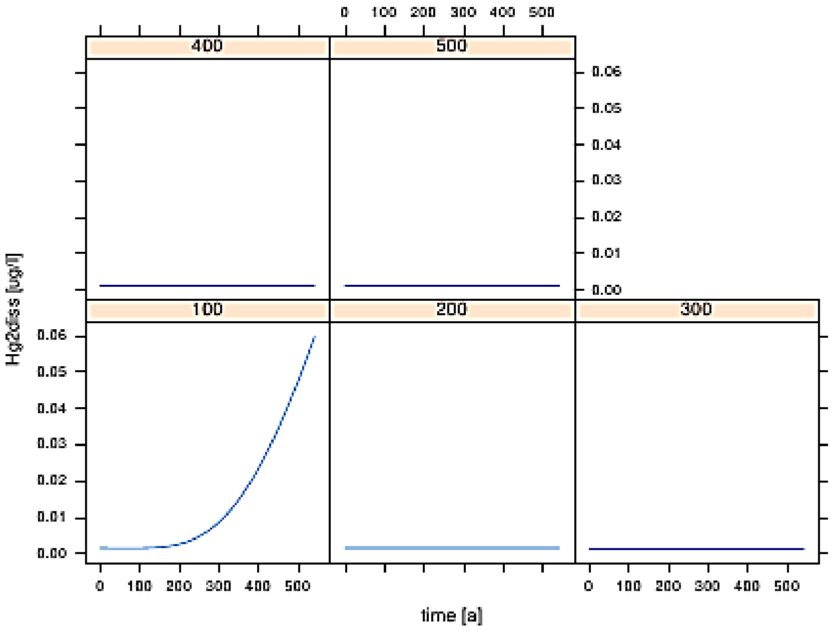


Figure B.7.1.1: Breakthrough curve for dissolved Hg (Hg2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

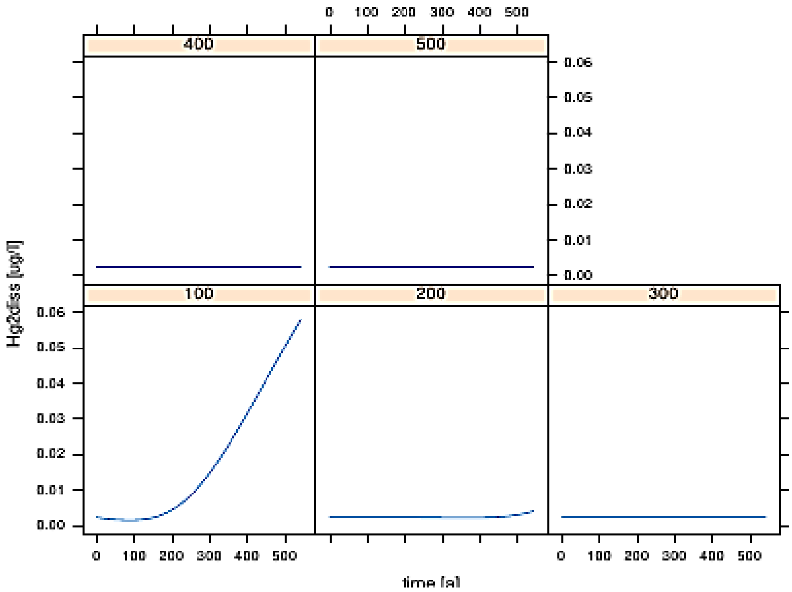


Figure B.7.1.2: Breakthrough curve for dissolved Hg (Hg2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

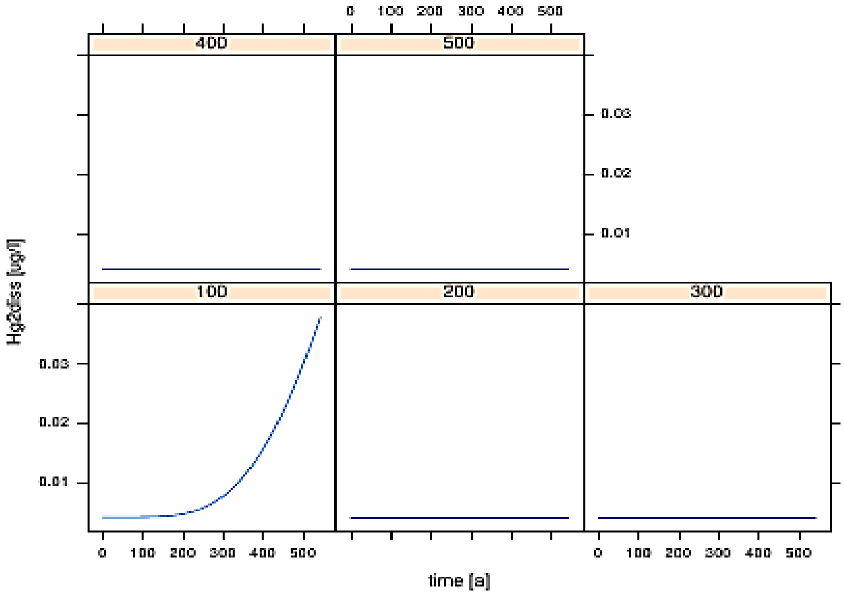


Figure B.7.1.3: Breakthrough curve for dissolved Hg (Hg2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.7.2 *Soil profile*

Figures B.7.2.1 to B.7.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. From these soil profiles it is apparent that almost no downward migration of Hg occurs. Slight migration can be seen in the soil profiles after 500 years.

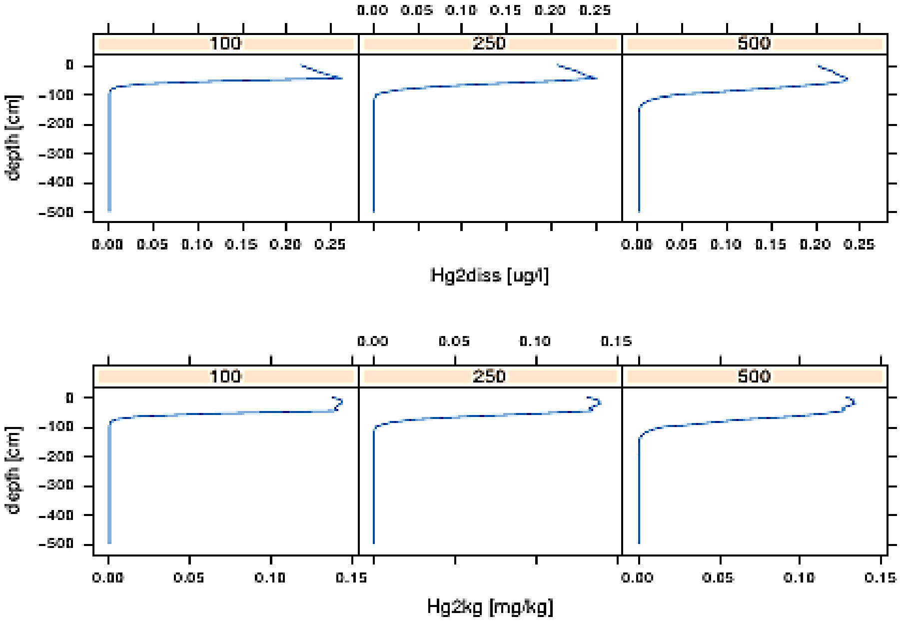


Figure B.7.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Hg (Hg2diss) is given in the top figure; the lower figure gives Hg in the solid phase (Hg2kg).

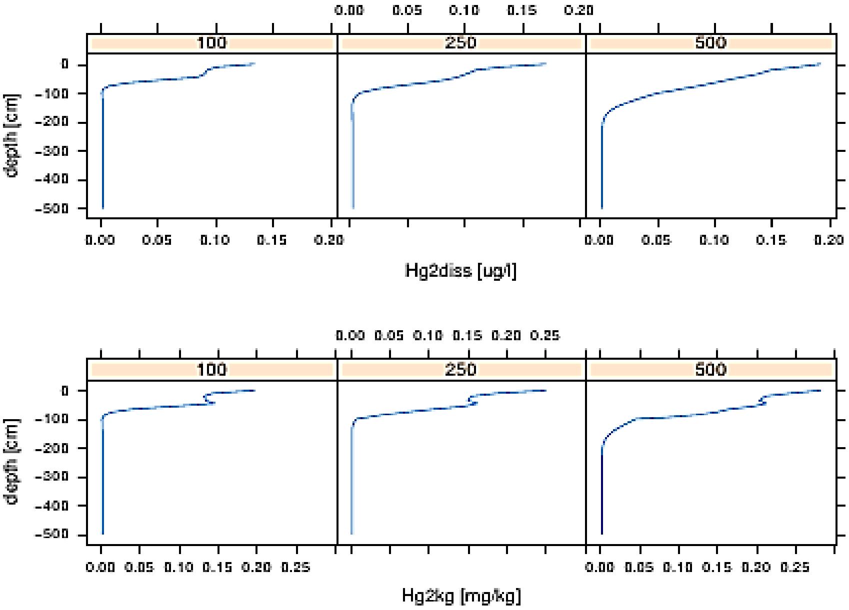


Figure B.7.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Hg (Hg2diss) is given in the top figure; the lower figure gives Hg in the solid phase (Hg2kg).

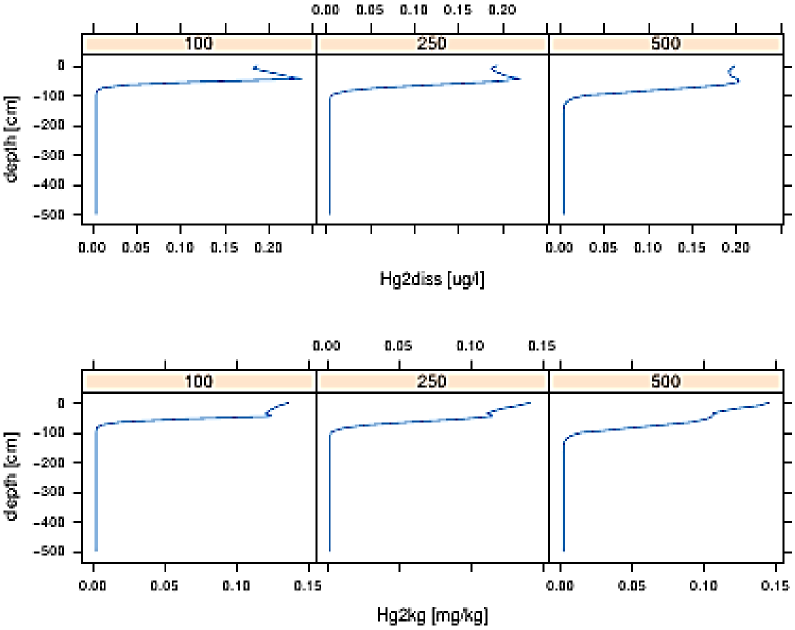


Figure B.7.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Hg (Hg2diss) is given in the top figure; the lower figure gives Hg in the solid phase (Hg2kg).

12.7.3 Results standard scenario

Table B.7.3.2: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are give for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0
residential	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0
industrial	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0
time: 500 yr, depth: 100 cm			-		-	
agricultural	*sand*	0.01	-	0.23	-	0
	peat	0.01	-	0.23	-	0
	clay	0	-	0.23	-	0
residential	*sand*	0.09	-	0.23	-	0.4
	peat	0.1	-	0.23	-	0.5
	clay	0.02	-	0.23	-	0.1
industrial	*sand*	0.57	-	0.23	-	2.5
	peat	0.6	-	0.23	-	2.6
	clay	0.14	-	0.23	-	0.6
time: 500 yr, depth: 500 cm			-		-	
agricultural	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0
residential	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0
industrial	*sand*	0	-	0.23	-	0
	peat	0	-	0.23	-	0
	clay	0	-	0.23	-	0

12.8 Detailed results for molybdenum (Mo)

12.8.1 Breakthrough curves

Figures B.8.1.1 to B.8.1.3 show the breakthrough curves for Mo. While most elements are more mobile in the sand profile, for Mo it is the other way around. The sand profiles show some migration until a depth of 300–400 cm in 500 years. For peat and clay a full breakthrough is visible at all depths. For peat the peak concentration occurs between 100 and 200 years, while for clay it is within the first 100 years.

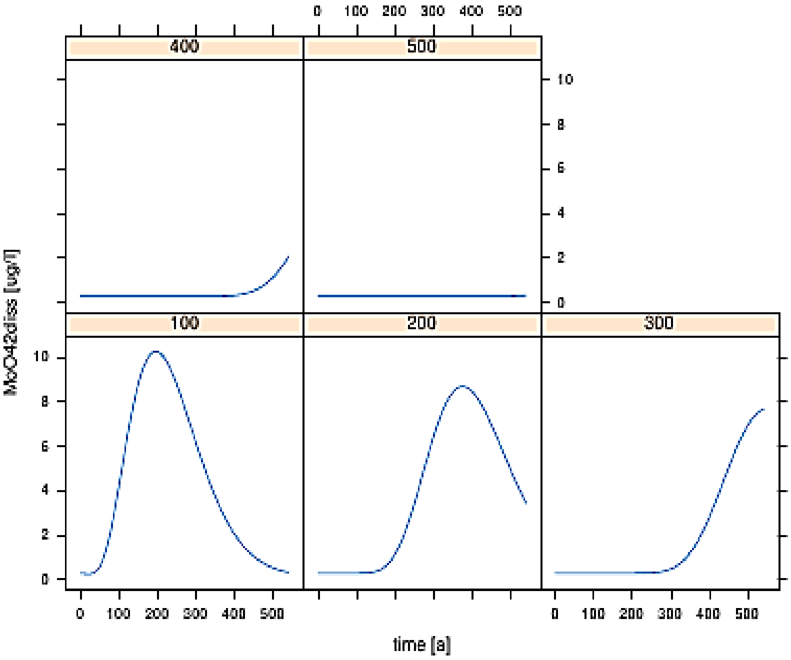


Figure B.8.1.1: Breakthrough curve for dissolved MoO4 (MoO42diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

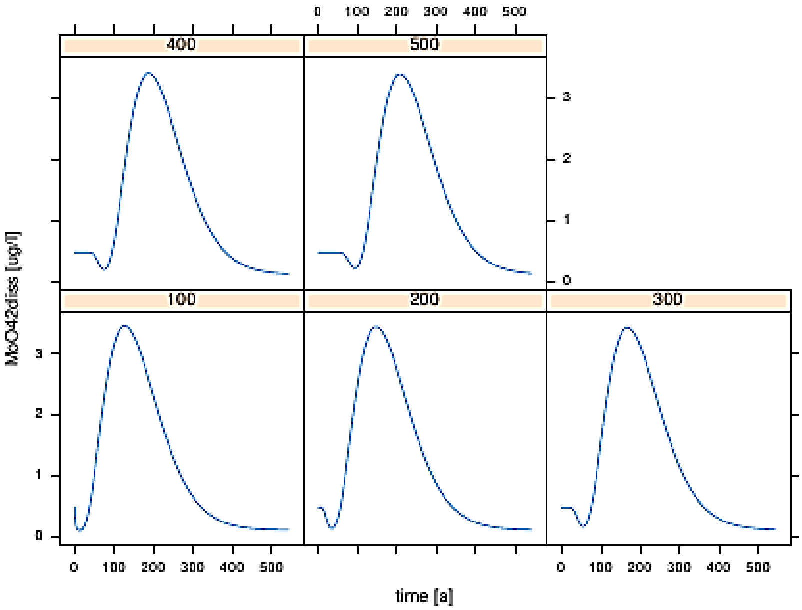


Figure B.8.1.2: Breakthrough curve for dissolved MoO4 (MoO42diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

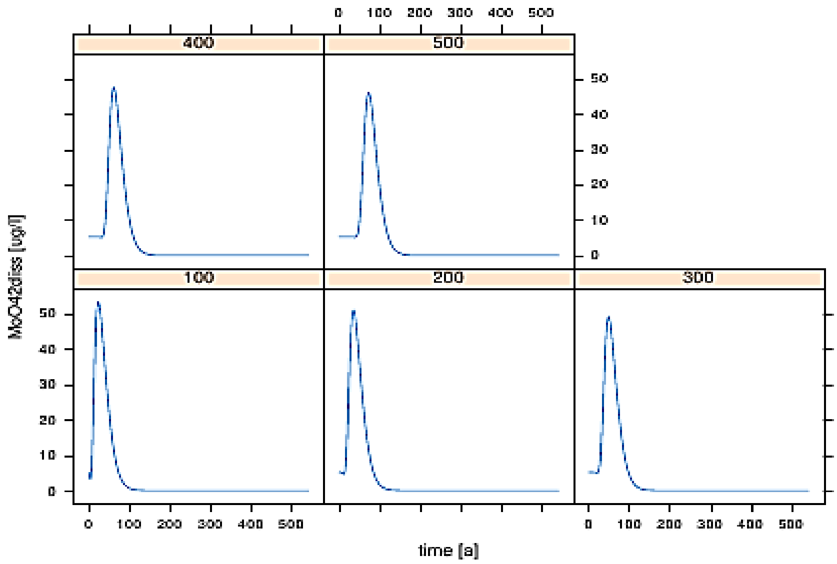


Figure Figure B.8.1.3: Breakthrough curve for dissolved MoO4 (MoO42diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.8.2 *Soil profile*

Figures B.8.2.1 to B.8.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. In these soil profiles a clear downward migration of Mo is visible, as already indicated by the breakthrough curves. For peat and clay almost all the added Mo is lost to deeper layers (>500 cm).

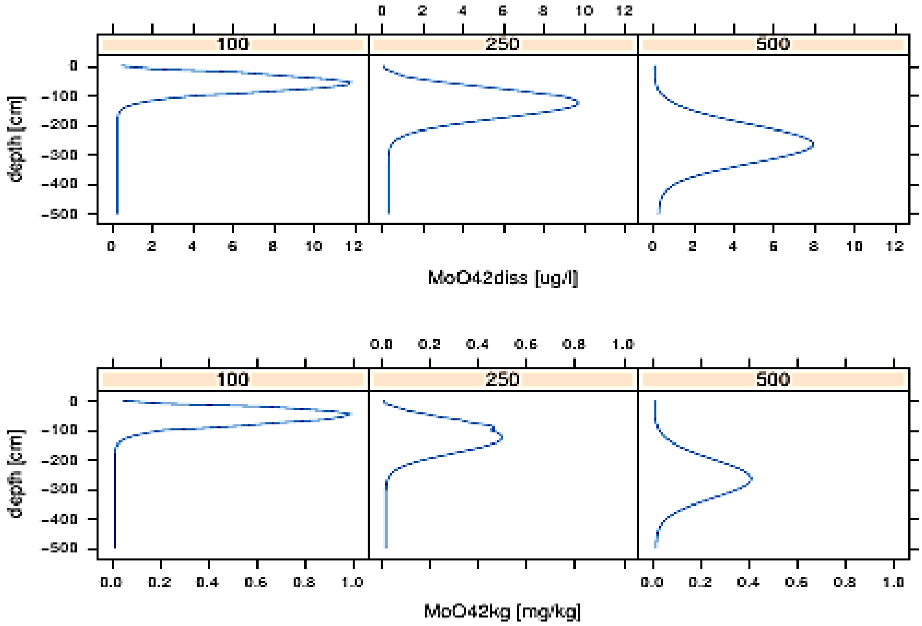


Figure B.8.1.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Mo (MoO42diss) is given in the top figure; the lower figure gives Mo in the solid phase (MoO42kg).

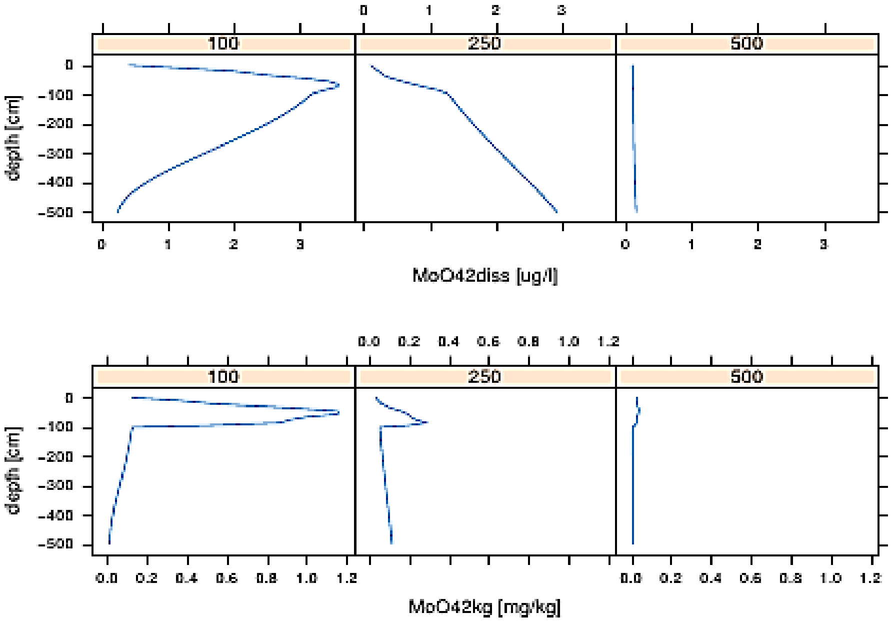


Figure B.8.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Mo (MoO42diss) is given in the top figure; the lower figure gives Mo in the solid phase (MoO42kg).

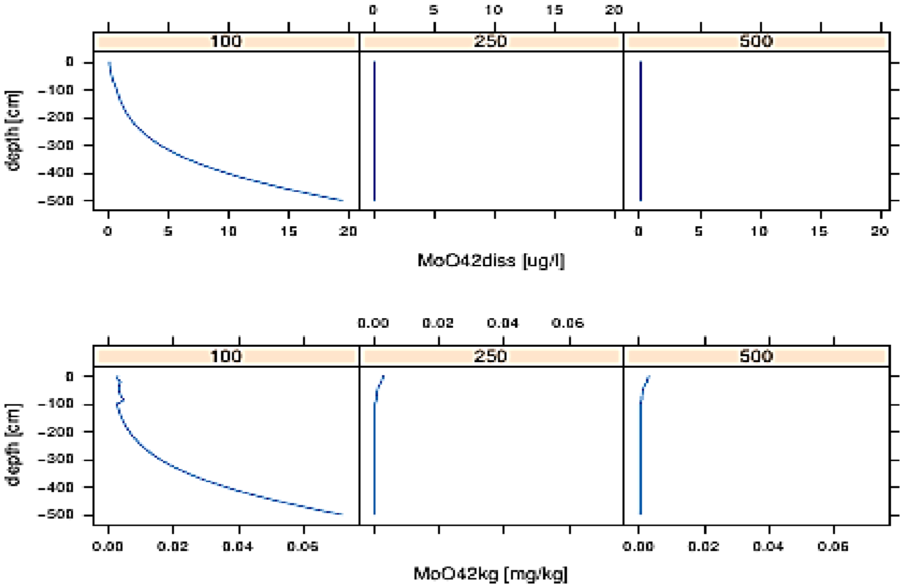


Figure B.8.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Mo (MOO42diss) is given in the top figure; the lower figure gives Hg in the solid phase (MoO42kg).

12.8.3 Results standard scenario

Table B.8.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	15.7	-	29	-	0.5
	peat	2.0	-	29	-	0.1
	clay	22.9	-	29	-	0.8
residential	*sand*	1.241	-	29	-	42.8
	peat	173	-	29	-	6.0
	clay	1872.1	-	29	-	64.6
industrial	*sand*	1272.6	-	29	-	43.9
	peat	666.0	-	29	-	23.0
	clay	1704.8	-	29	-	58.8
time: 500 yr, depth: 100 cm			-		-	
agricultural	*sand*	18.7	-	29	-	0.6
	peat	2.3	-	29	-	0.1
	clay	22.9	-	29	-	0.8
residential	*sand*	1405.1	-	29	-	48.5
	peat	199.5	-	29	-	6.9
	clay	1872.1	-	29	-	64.6
industrial	*sand*	1.893	-	29	-	65.3
	peat	666.0	-	29	-	23.0
	clay	1808.3	-	29	-	62.4
time: 500 yr, depth: 500 cm			-		-	
agricultural	*sand*	10.2	-	29	-	0.4
	peat	2.0	-	29	-	0.1
	clay	21.9	-	29	-	0.8
residential	*sand*	823.0	-	29	-	28.4
	peat	167.9	-	29	-	5.8
	clay	1846.5	-	29	-	63.7
industrial	*sand*	1591.5	-	29	-	54.9
	peat	496.9	-	29	-	16.8
	clay	1.777	-	29	-	61.3

12.9 Detailed results for nickel (Ni)

12.9.1 Breakthrough curves

Figures B.9.1.1 to B.9.1.3 show the breakthrough curves for Ni. The propagation of Ni concentrations through the soil profile over time in the sandy soils is clear. In the peat profile at 1 m depth the concentration decreases before it increases. This shows a leaching of the background input concentration. For peaty and clayey soils no breakthrough can be seen from 3 m over the time span of 500 years. In sandy soils a breakthrough is predicted for each depth and time span while the top of the peak is just reached in the layer at 5 m after 500 years.

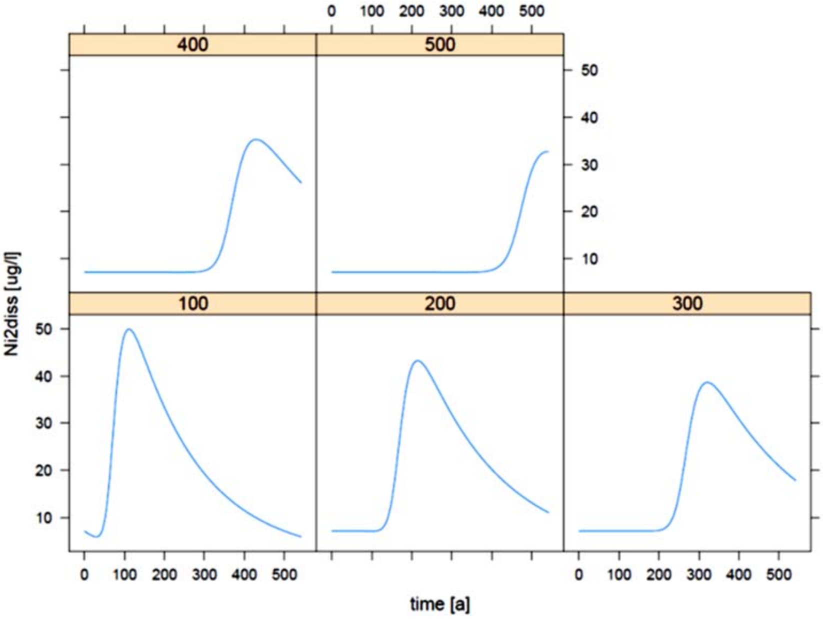


Figure B.9.1.1: Breakthrough curve for dissolved Ni (Ni2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

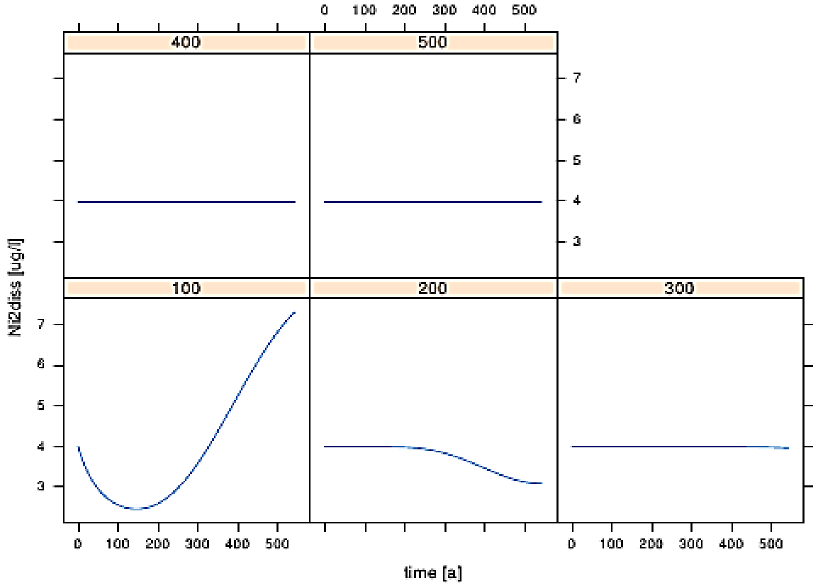


Figure B.9.1.2: Breakthrough curve for dissolved Ni (Ni2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

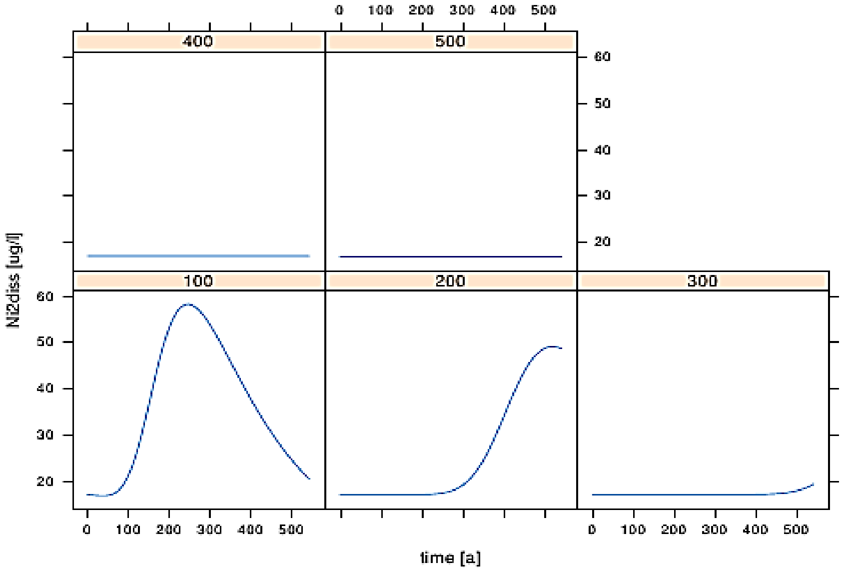


Figure B.9.1.3: Breakthrough curve for dissolved Ni (Ni2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.9.2 *Soil profile*

Figures B.9.2.1 to B.9.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. Ni is clearly leaching downwards. The profiles of sandy and clayey soils show in the solid phase a chromatic separation between a mobile and a less mobile Ni-specie. This is not apparent form the peaty soil profile.

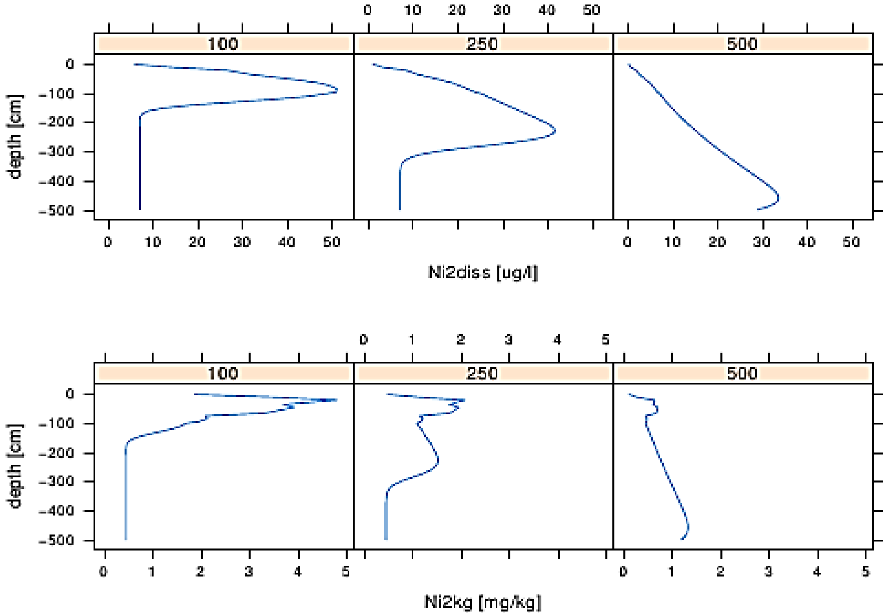


Figure B.9.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Ni (Ni2diss) is given in the top figure; the lower figure gives Ni in the solid phase (Ni2kg).

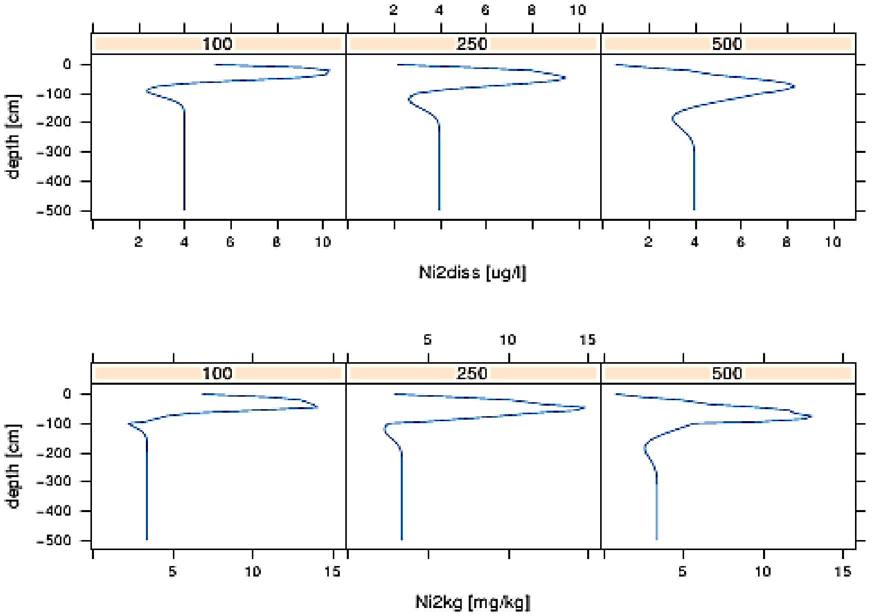


Figure B.9.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Zn (Ni2diss) is given in the top figure; the lower figure gives Ni in the solid phase (Ni2kg).

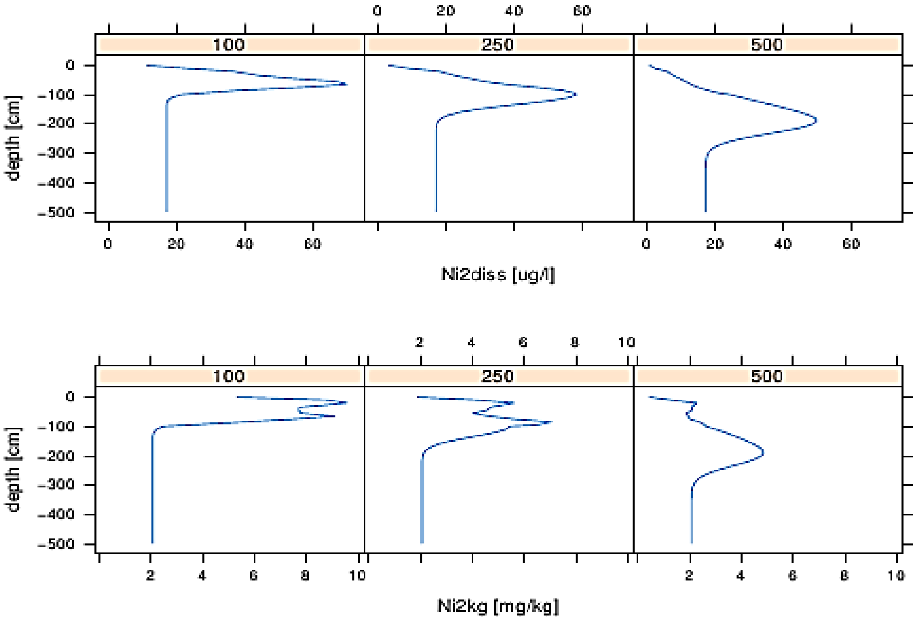


Figure B.9.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Ni (Ni2diss) is given in the top figure; the lower figure gives Ni in the solid phase (Ni2kg).

12.9.3 Results standard scenario

Table B.9.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	32.7	38.2	1.9	0.86	17.2
	peat	2.0	23.8	1.9	0.08	1.1
	clay	21.2	9.2	1.9	2.3	11.1
residential	*sand*	41.6	38.2	1.9	1.1	21.9
	peat	2.0	23.8	1.9	0.08	1.1
	clay	21.7	9.2	1.9	2.4	11.4
industrial	*sand*	654.3	38.2	1.9	17.1	344.4
	peat	2.1	23.8	1.9	0.09	1.1
	clay	512.1	9.2	1.9	55.7	269.5
time: 500 yr, depth: 100 cm						
agricultural	*sand*	57.7	38.2	1.9	1.5	30.4
	peat	5.3	23.8	1.9	0.22	2.8
	clay	52.9	9.2	1.9	5.8	27.9
residential	*sand*	56.6	39.2	1.9	1.5	29.8
	peat	5.0	23.8	1.9	0.21	2.6
	clay	56.6	9.2	1.9	6.2	29.8
industrial	*sand*	654.3	38.2	1.9	17.1	344.4
	peat	36.2	23.8	1.9	1.5	19.1
	clay	729.3	9.2	1.9	79.4	383.9
time: 500 yr, depth: 500 cm						
agricultural	*sand*	4.4	38.2	1.9	0.12	2.3
	peat	2.0	23.8	1.9	0.08	1.0
	clay	20.2	9.2	1.9	2.2	10.6
residential	*sand*	5.2	38.2	1.9	0.14	2.7
	peat	2.0	23.8	1.9	0.08	1.0
	clay	20.2	9.2	1.9	2.2	10.6
industrial	*sand*	177.6	38.2	1.9	4.7	93.5
	peat	2.0	23.8	1.9	0.08	1.0
	clay	20.2	9.2	1.9	2.2	10.6

12.10 Detailed results for lead (Pb)

12.10.1 Breakthrough curves

Figures B.10.1.1 to B.10.1.3 show the breakthrough curves for Pb. At shallow depth (100 cm) dissolved concentrations increase over time. For the sand and peat profiles this is within a range of 0.1 ug/l. For peat this range is about 10 ug/l. Only in the soil profile can some minor changes in the dissolved concentration be observed at deeper layers (200–500 cm).

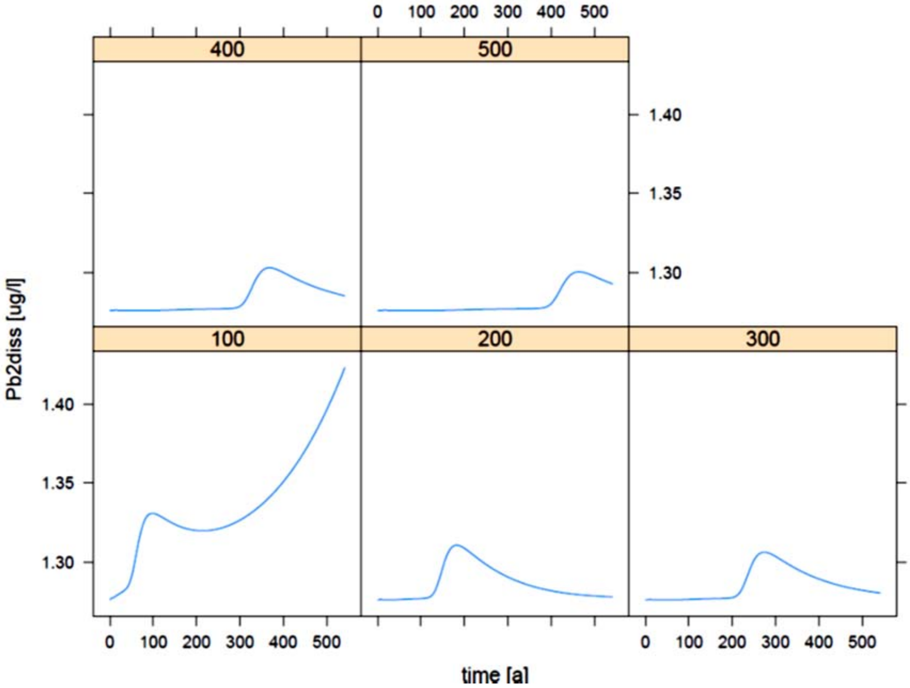


Figure B.10.1.1: Breakthrough curve for dissolved Pb (Pb2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

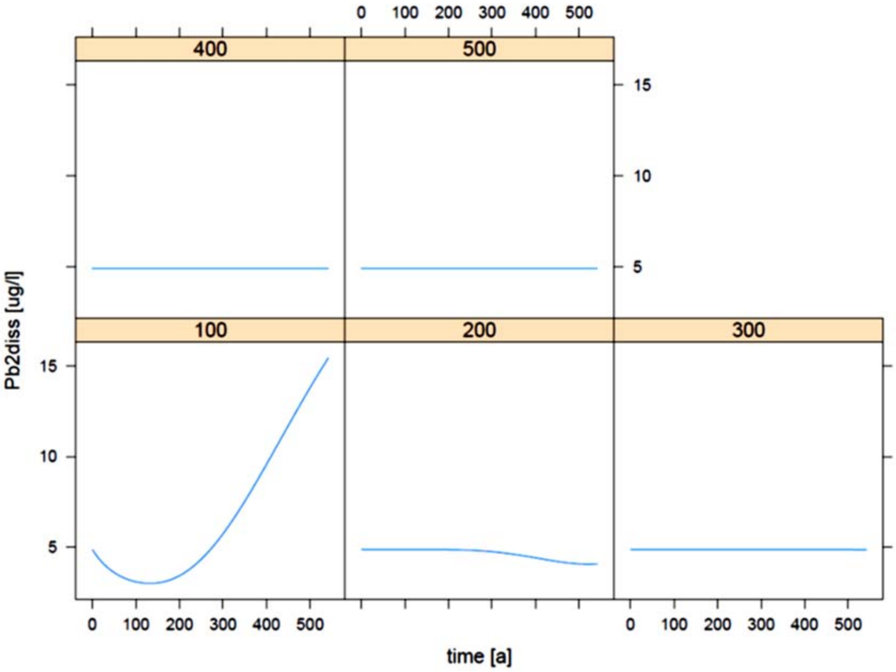


Figure B.10.1.2: Breakthrough curve for dissolved Pb (Pb2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

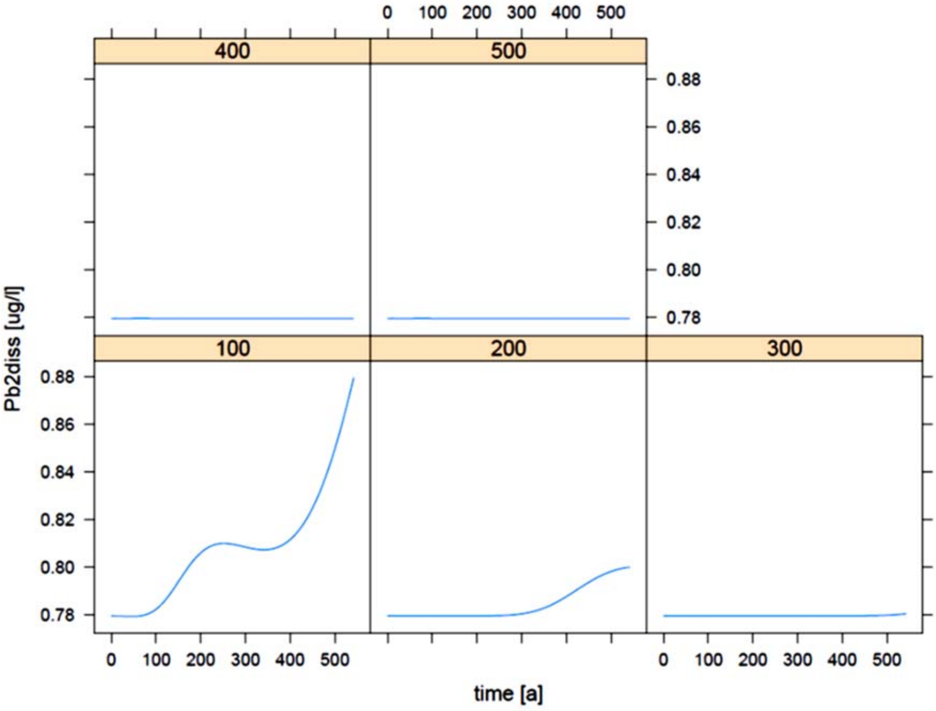


Figure B.10.1.3: Breakthrough curve for dissolved Pb (Pb2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.10.2 Soil profile

Figures B.10.2.1 to B.10.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. In the sandy and clayey soil profiles almost no downward migration can be observed. The peaty profile does show some leaching but not beyond 200 cm depth in 500 years.

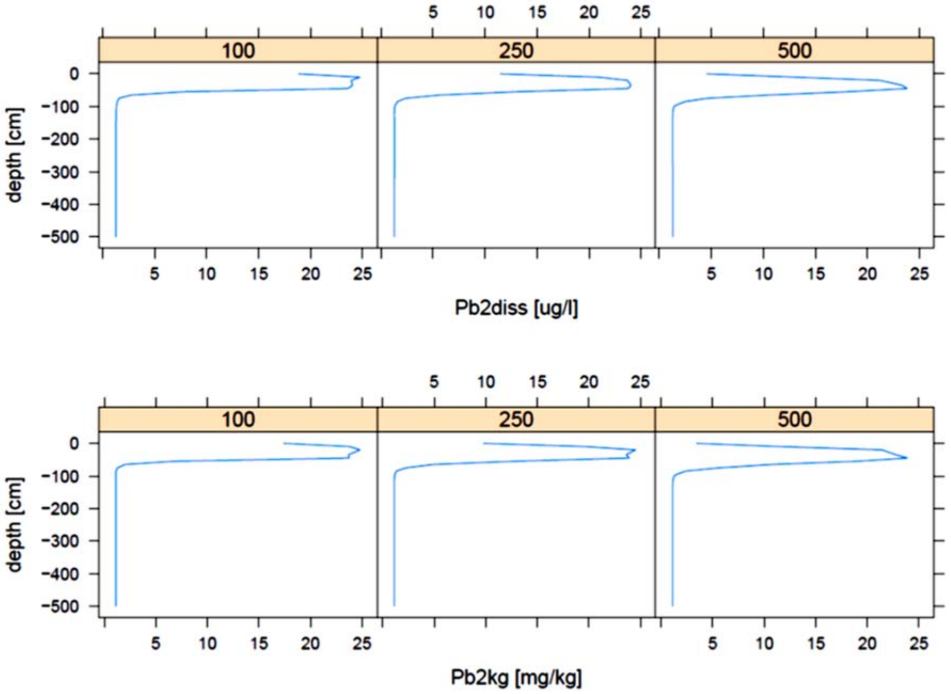


Figure B.10.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Pb (Pb2diss) is given in the top figure; the lower figure gives Pb in the solid phase (Pb2kg).

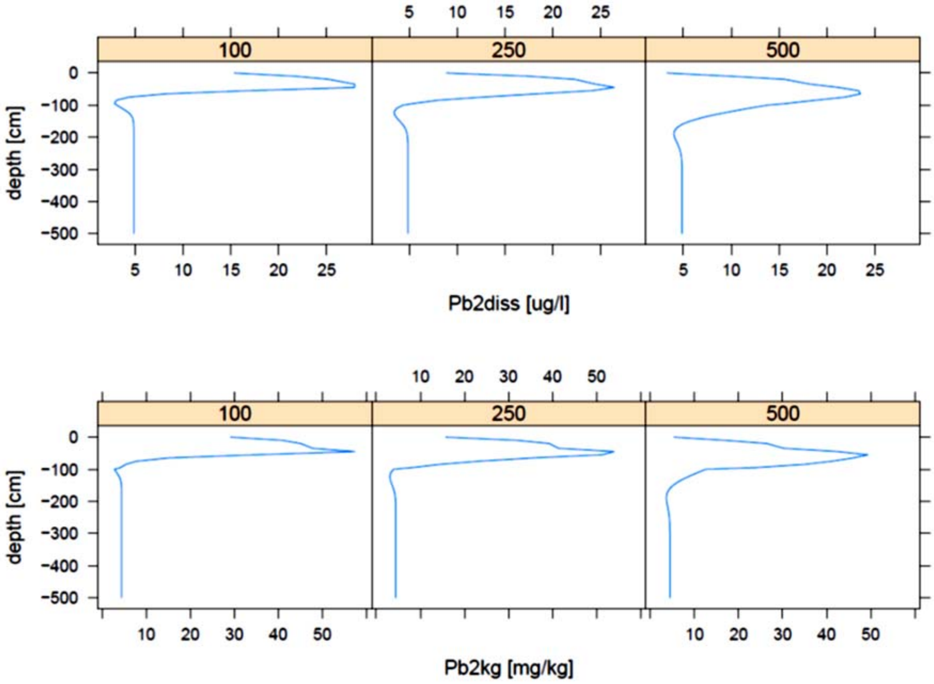


Figure B.10.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Pb (Pb2diss) is given in the top figure; the lower figure gives Pb in the solid phase (Pb2kg).

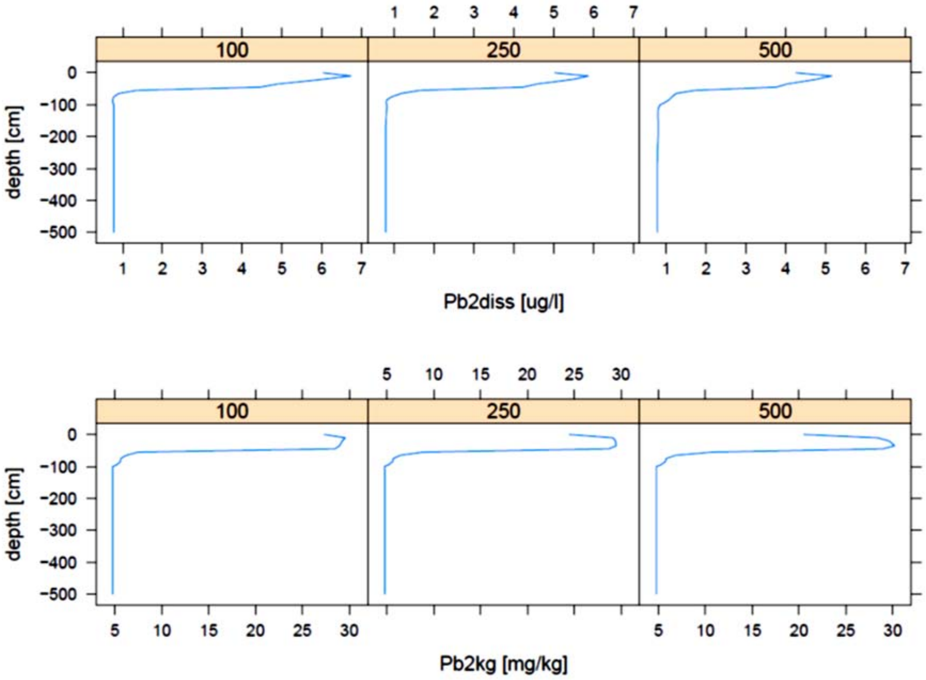


Figure B.10.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Pb (Pb2diss) is given in the top figure; the lower figure gives Pb in the solid phase (Pbkg).

12.10.3 Results standard scenario

Table B.10.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0.95	4.3	11	0.22	0
	peat	2.7	0.66	11	4.1	0.2
	clay	1.3	0.14	11	9.4	0.1
residential	*sand*	1.1	4.3	11	0.26	0.1
	peat	2.8	0.66	11	4.2	0.3
	clay	1.3	0.14	11	9.5	0.1
industrial	*sand*	1.7	4.3	11	0.41	0.2
	peat	2.9	0.66	11	4.3	0.3
	clay	1.6	0.14	11	11.7	0.1
time: 500 yr, depth: 100 cm						
agricultural	*sand*	1.0	4.3	11	0.24	0
	peat	9.7	0.66	11	14.8	0.9
	clay	1.4	0.14	11	10.2	0.1
residential	*sand*	1.2	4.3	11	0.27	0.1
	peat	36.4	0.66	11	55.1	3.3
	clay	1.6	0.14	11	11.8	0.1
industrial	*sand*	1.7	4.3	11	0.41	0.2
	peat	84.4	0.66	11	127.8	7.7
	clay	3.1	0.14	11	22.2	0.3
time: 500 yr, depth: 500 cm						
agricultural	*sand*	0.85	4.3	11	0.2	0.1
	peat	2.7	0.66	11	4.1	0.2
	clay	1.3	0.14	11	9.4	0.1
residential	*sand*	0.89	4.3	11	0.21	0.1
	peat	2.7	0.66	11	4.1	0.2
	clay	1.3	0.14	11	9.4	0.1
industrial	*sand*	1.5	4.3	11	0.34	0.1
	peat	2.7	0.66	11	4.1	0.2
	clay	1.3	0.14	11	9.4	0.1

12.11 Detailed results for antimony (Sb)

12.11.1 Breakthrough curves

Figures B.11.1.1 to B.11.1.3 show the breakthrough curves for Sb. For all three soil profiles no retention is predicted, resulting in one single spike, appearing almost simultaneously at each depth. The height of the peak does differ for the three soil types, peat having the lowest peak height and clay the highest.

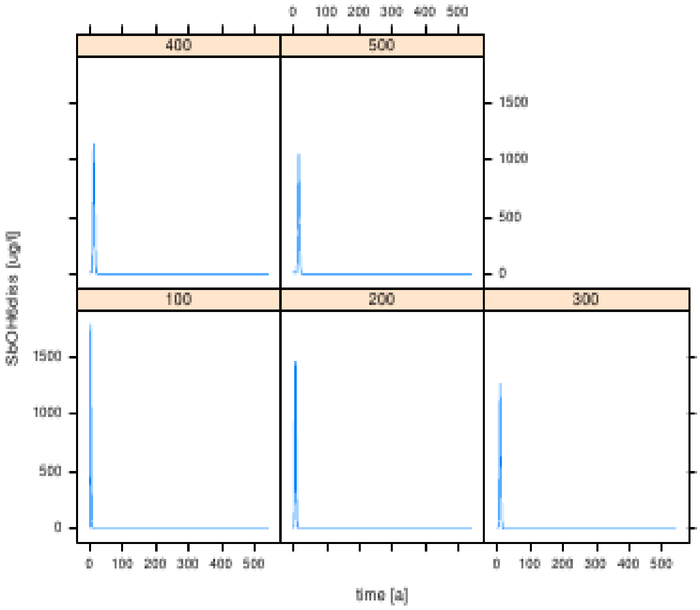


Figure B.11.1.1: Breakthrough curve for dissolved Sb (SbOH6diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

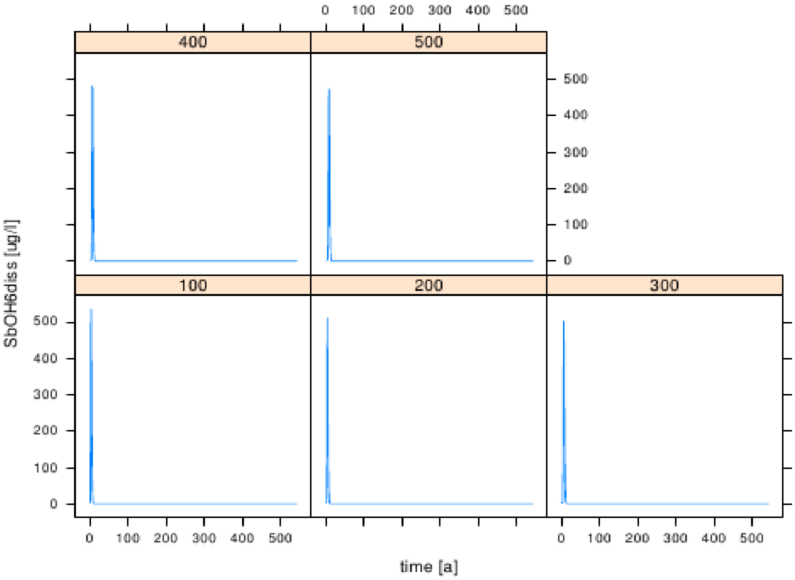


Figure B.11.1.2: Breakthrough curve for dissolved Sb (SbOH6diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

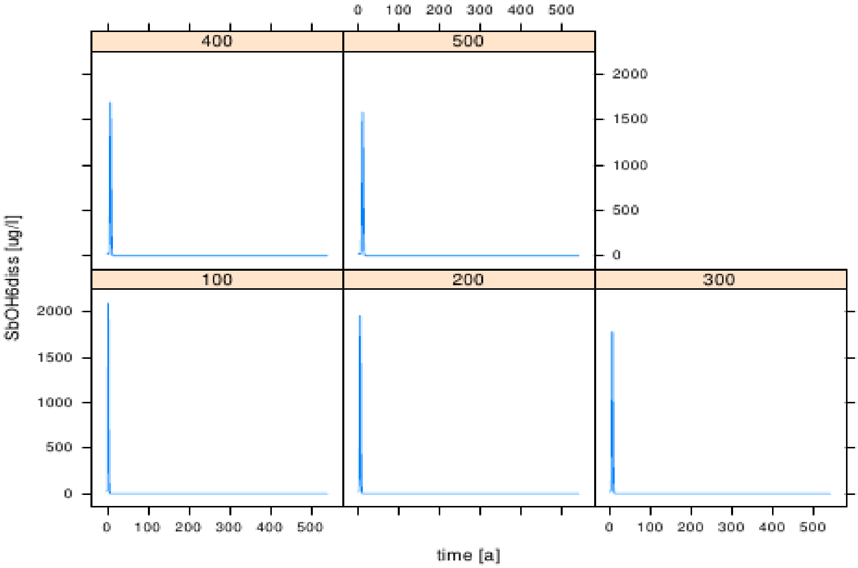


Figure B.11.1.3: Breakthrough curve for dissolved Sb (SbOH6diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.11.2 Soil profile

Figures B.11.2.1 to B.11.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. The variability of the soil concentrations over time and over depth is very small, in general within an order of 10^{-4} ug/l or 10^{-4} mg/kg. From Figures 1 to 3 it was already clear that the peak concentration fell within the first 10–20 years so after time spans of 100, 250 and 500 years no variability is expected, which Figures B.11.2.1 to B.11.2.3 do indeed show.

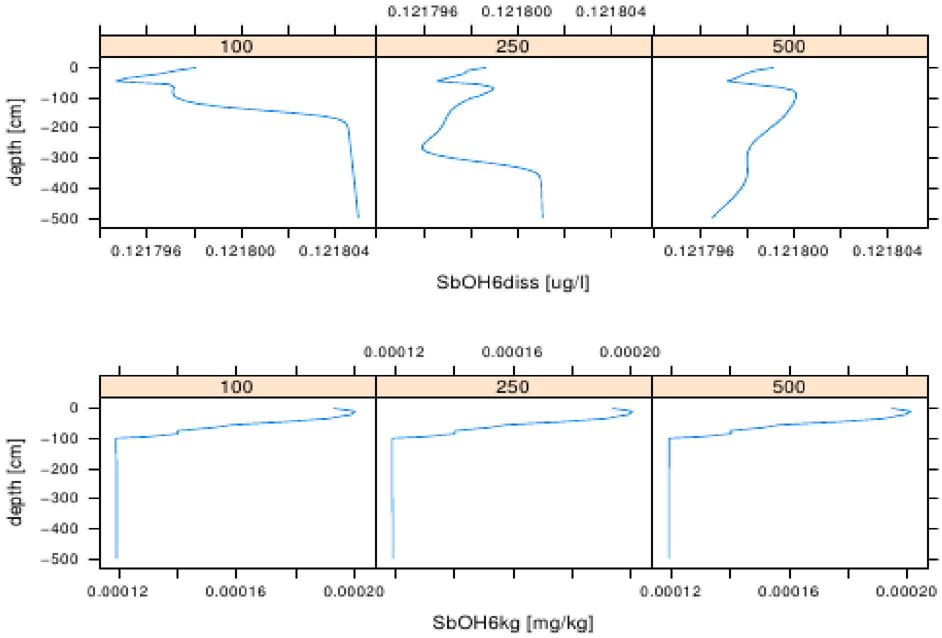


Figure B.11.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sb (SbOH6diss) is given in the top figure; the lower figure gives Sb in the solid phase (SbOH6kg).

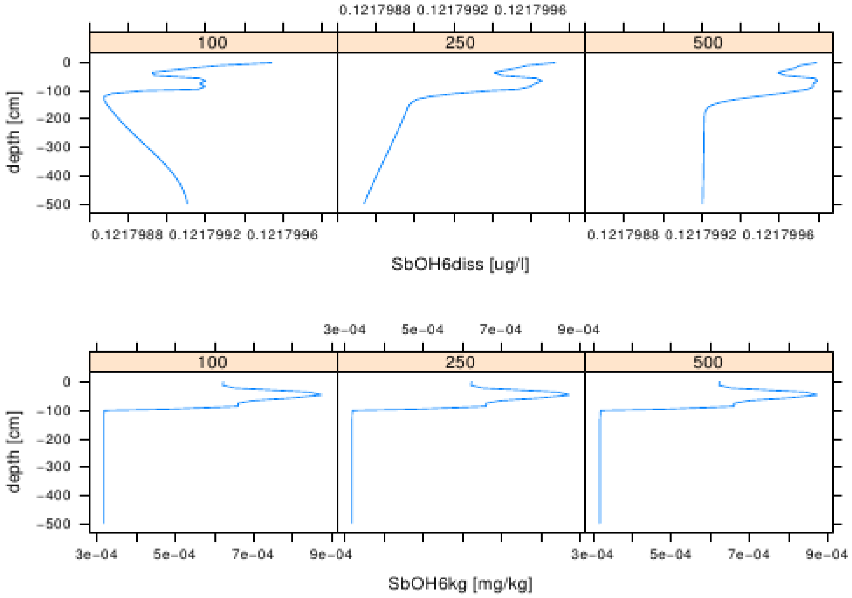


Figure B.11.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sb (SbOH6diss) is given in the top figure; the lower figure gives Sb in the solid phase (SbOH6kg).

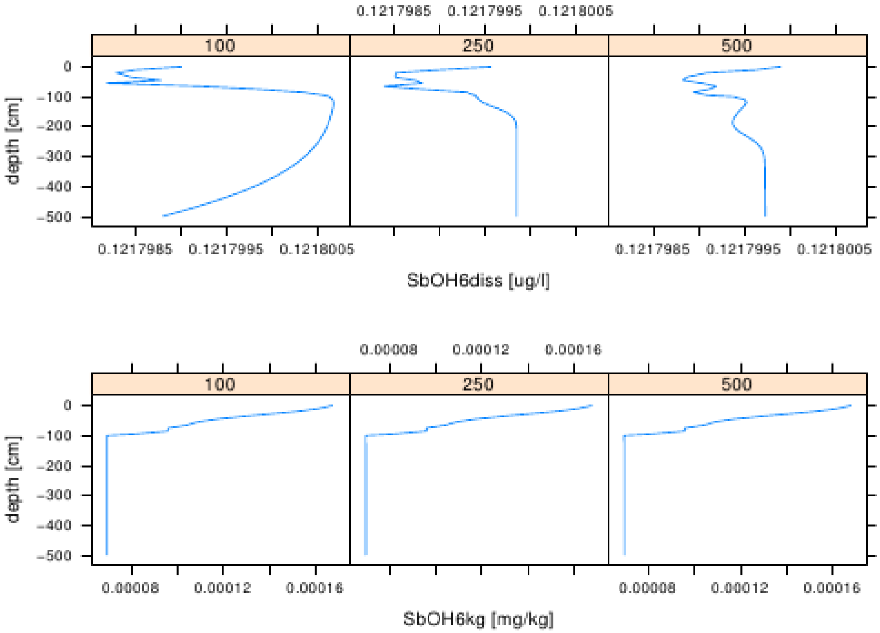


Figure B.11.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sb (SbOH6diss) is given in the top figure; the lower figure gives Sb in the solid phase (SbOH6kg).

12.11.3 *Results standard scenario*

Table B.11.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	1795	-	6.2	-	289.5
	peat	382.1	-	6.2	-	61.6
	clay	1458.9	-	6.2	-	235.3
residential	*sand*	2132	-	6.2	-	343.9
	peat	1695.2	-	6.2	-	273.4
	clay	2146	-	6.2	-	346.1
industrial	*sand*	2128.8	-	6.2	-	343.4
	peat	2256.2	-	6.2	-	363.9
	clay	2135.3	-	6.2	-	344.4
time: 500 yr, depth: 100 cm			-		-	
agricultural	*sand*	1795	-	6.2	-	289.5
	peat	382.1	-	6.2	-	61.6
	clay	1458.9	-	6.2	-	235.3
residential	*sand*	2132	-	6.2	-	343.9
	peat	1695.2	-	6.2	-	273.4
	clay	2146	-	6.2	-	346.1
industrial	*sand*	2128.8	-	6.2	-	343.4
	peat	2256.2	-	6.2	-	363.9
	clay	2135.3	-	6.2	-	344.4
time: 500 yr, depth: 500 cm			-		-	
agricultural	*sand*	1261.6	-	6.2	-	203.5
	peat	310.3	-	6.2	-	50
	clay	1146.5	-	6.2	-	184.9
residential	*sand*	2130.1	-	6.2	-	343.6
	peat	1368.1	-	6.2	-	220.7
	clay	2144.7	-	6.2	-	345.9
industrial	*sand*	2128.8	-	6.2	-	343.4
	peat	2000.4	-	6.2	-	322.6
	clay	2135.5	-	6.2	-	344.4

12.12 Detailed results for tin (Sn)

12.12.1 Breakthrough curves

Figures B.12.1.1 to B.12.1.3 show the breakthrough curves for Sn. An increase in the concentration of Sn can be seen in all profiles at a soil depth of 100 cm, but no peak concentration is obtained. The highest achieved concentrations in the three different soil profiles are within the same order of magnitude.

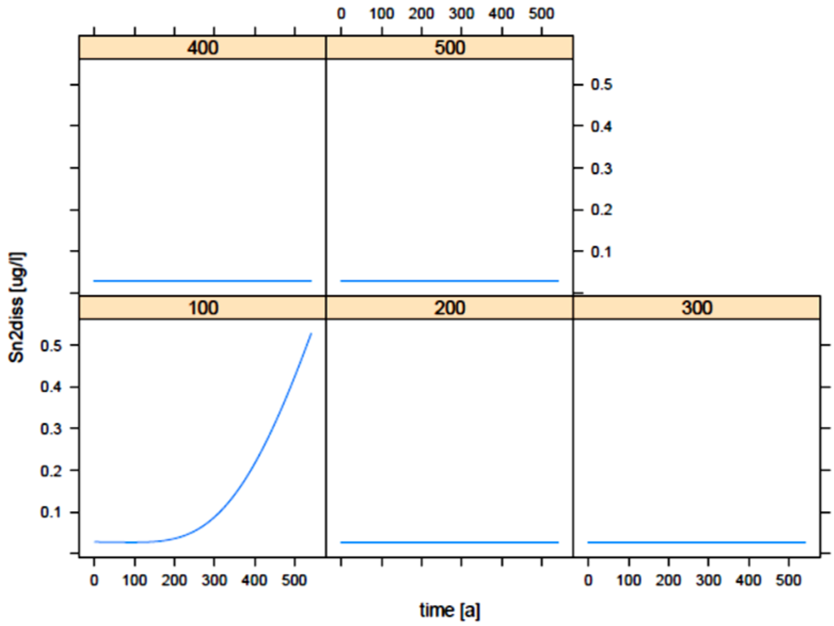


Figure B.12.1.1: Breakthrough curve for dissolved Sn (Sn2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

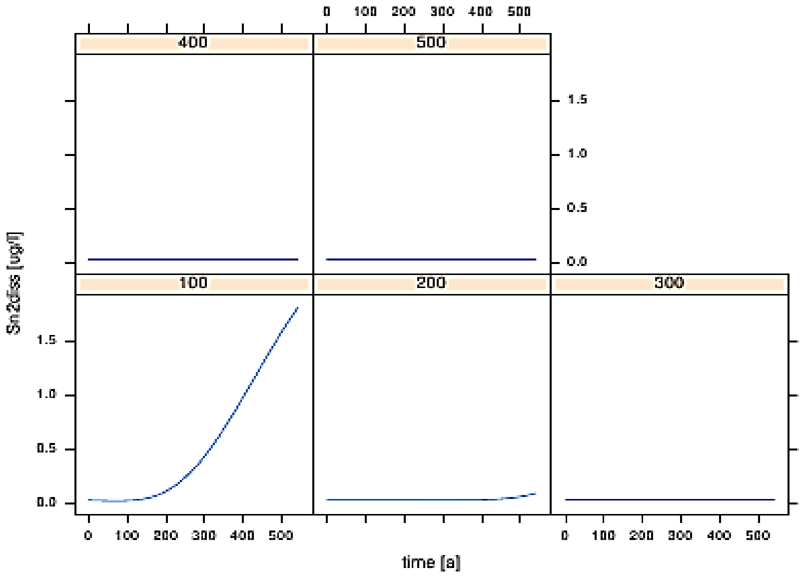


Figure B.12.1.2: Breakthrough curve for dissolved Sn (Sn2diss) in the peat profile. The figure gives the concentration over time at five different depths, cmbelow surface as indicated in the bars above the figure.

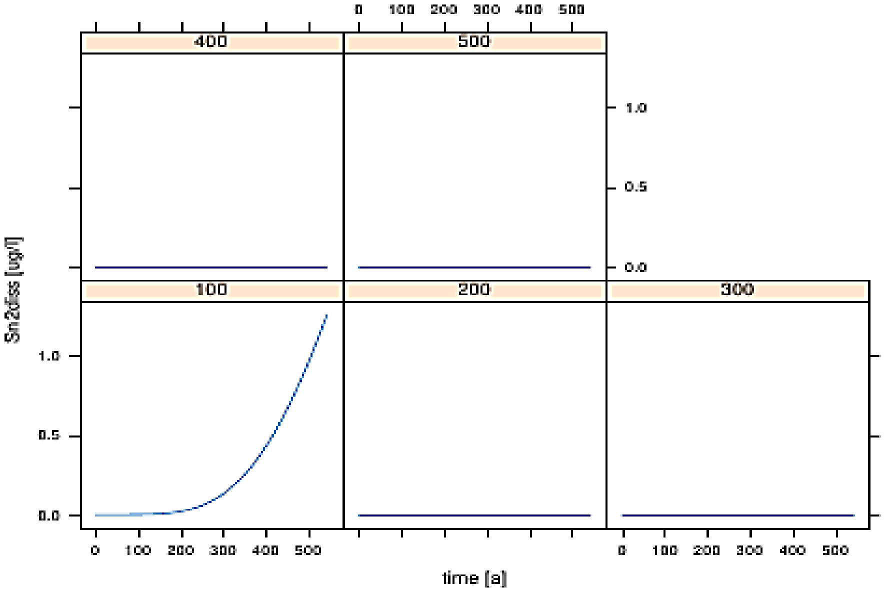


Figure B.12.1.3: Breakthrough curve for dissolved Sn (Sn2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.12.2 *Soil profile*

Figures B.12.2.1 to B.12.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. Here too, downward migration is not visible in most of the profiles, although within the 500-year time frame some migration is visible at 100 cm depth.

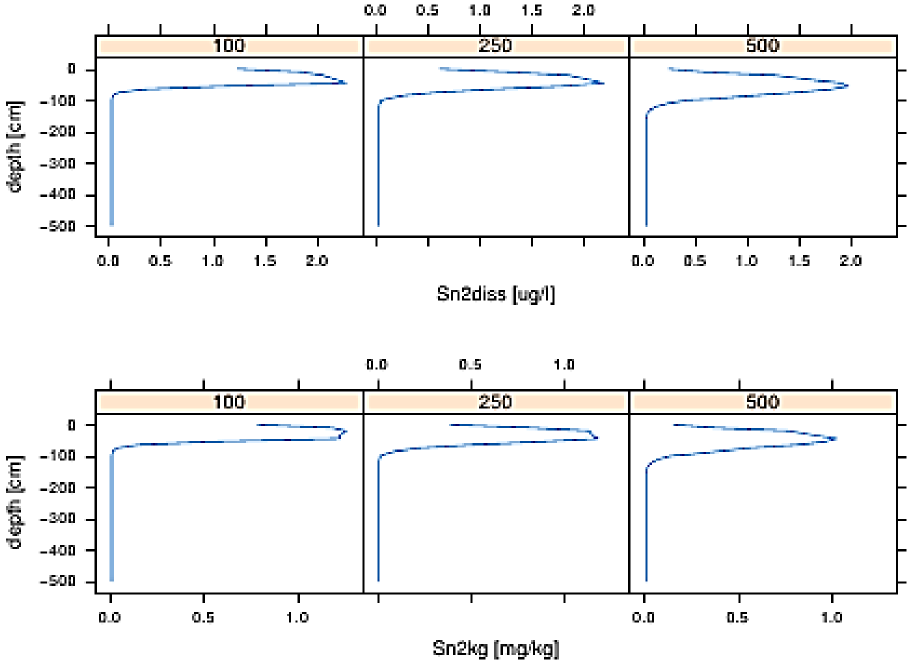


Figure B.12.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sn (Sn2diss) is given in the top figure; the lower figure gives Sn in the solid phase (Sn2kg).

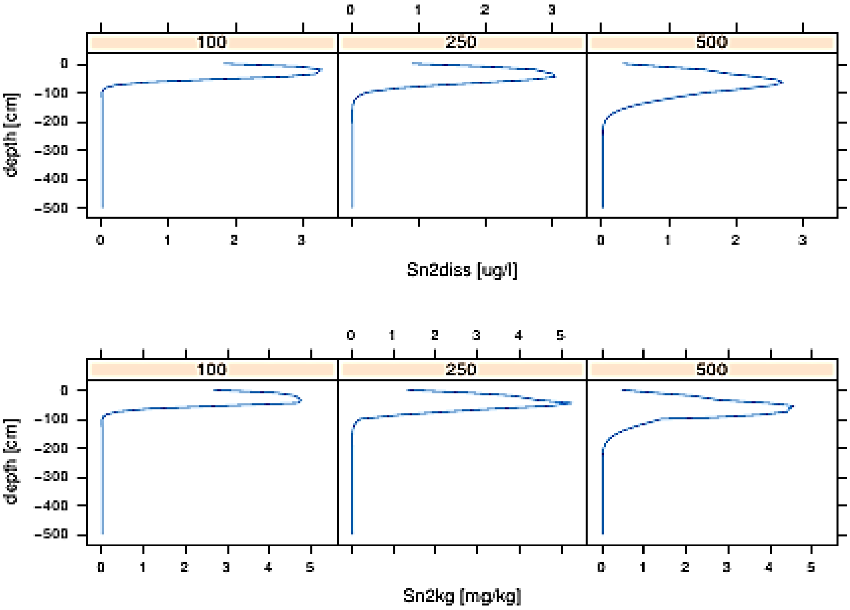


Figure B.12.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sn (Sn2diss) is given in the top figure; the lower figure gives Sn in the solid phase (Sn2kg).

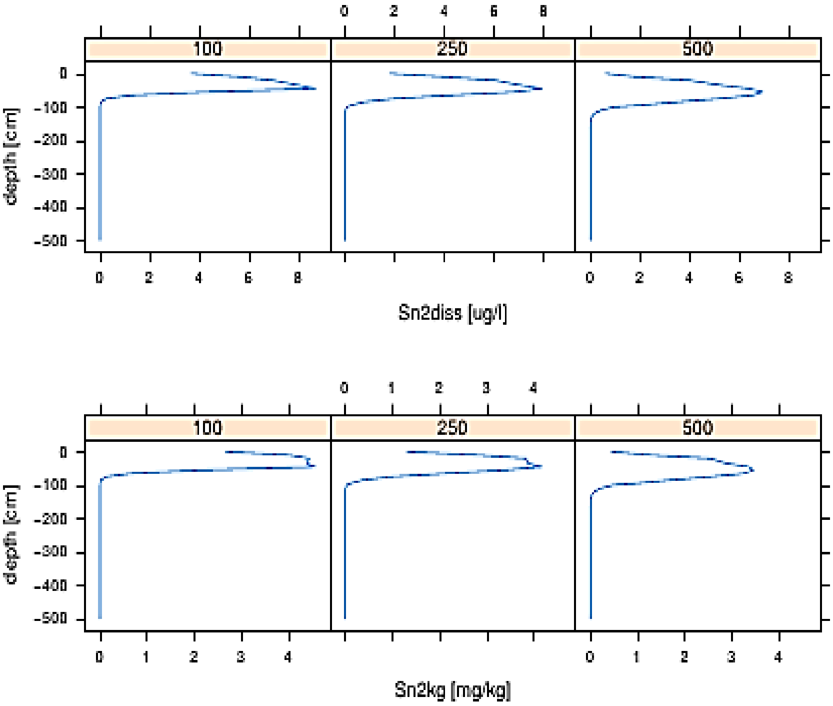


Figure B.12.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Sn (Sn2diss) is given in the top figure; the lower figure gives Sn in the solid phase (Sn2kg).

12.12.3 Results standard scenario

Table B.12.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0.03	-	20	-	0
	peat	0.01	-	20	-	0
	clay	0.01	-	20	-	0
residential	*sand*	0.03	-	20	-	0
	peat	0.06	-	20	-	0
	clay	0.01	-	20	-	0
industrial	*sand*	0.04	-	20	-	0
	peat	0.26	-	20	-	0
	clay	0.02	-	20	-	0
time: 500 yr, depth: 100 cm			-		-	
agricultural	*sand*	0.16	-	20	-	0
	peat	0.98	-	20	-	0
	clay	0.23	-	20	-	0
residential	*sand*	5.312	-	20	-	0.3
	peat	36.187	-	20	-	1.8
	clay	5.721	-	20	-	0.3
industrial	*sand*	1.228	-	20	-	0.6
	peat	181.888	-	20	-	9.1
	clay	15.214	-	20	-	0.8
time: 500 yr, depth: 500 cm			-		-	
agricultural	*sand*	0.03	-	20	-	0
	peat	0.01	-	20	-	0
	clay	0.01	-	20	-	0
residential	*sand*	0.03	-	20	-	0
	peat	0.01	-	20	-	0
	clay	0.01	-	20	-	0
industrial	*sand*	0.03	-	20	-	0
	peat	0.01	-	20	-	0
	clay	0.01	-	20	-	0

12.13 Detailed results for vanadium (V)

12.13.1 Breakthrough curves

Figures B.13.1.1 to B.13.1.3 show the breakthrough curves for V. For sand and peat some variation in the curves is shown. However, in an absolute sense the variability in concentration is negligible and in the range of 10^{-3} ug/l. For peat the concentration declines in the first soil layers.

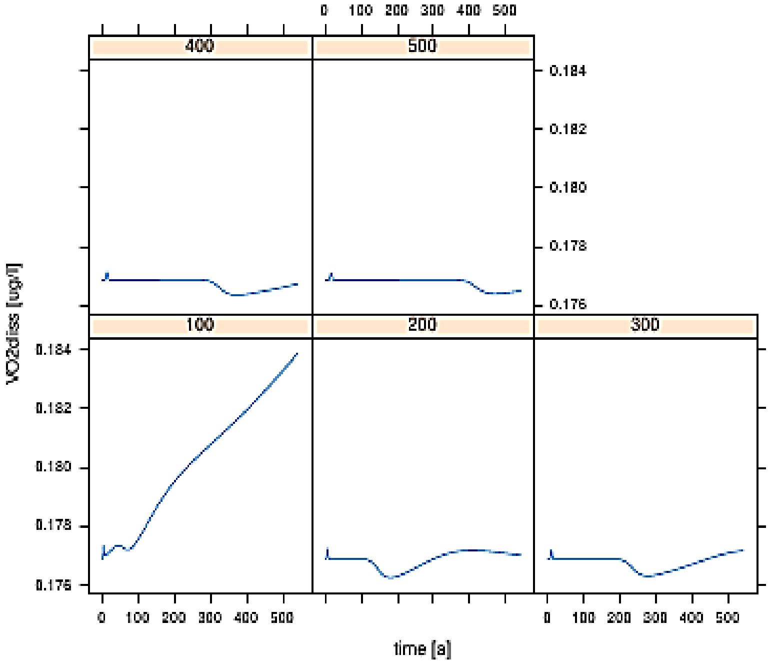


Figure B.13.1.1: Breakthrough curve for dissolved V (VO2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

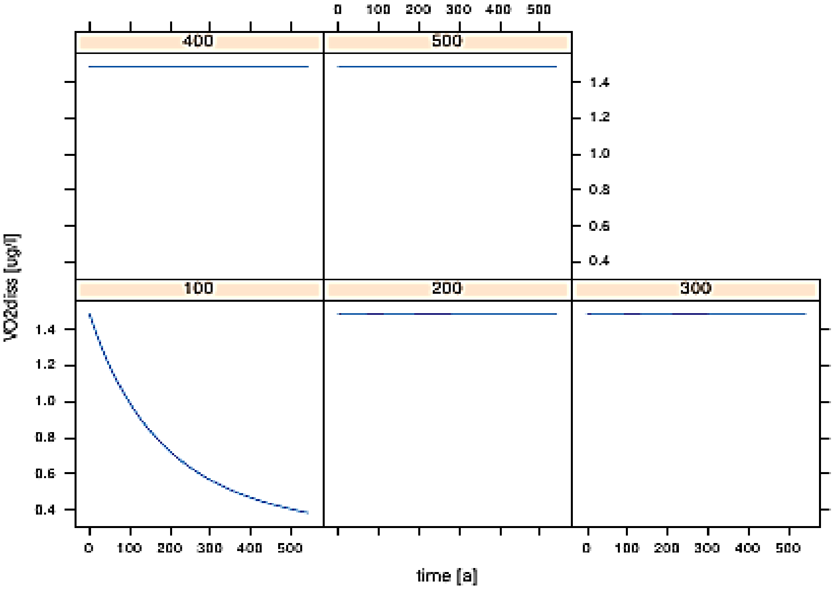


Figure B.13.1.2: Breakthrough curve for dissolved V (VO2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

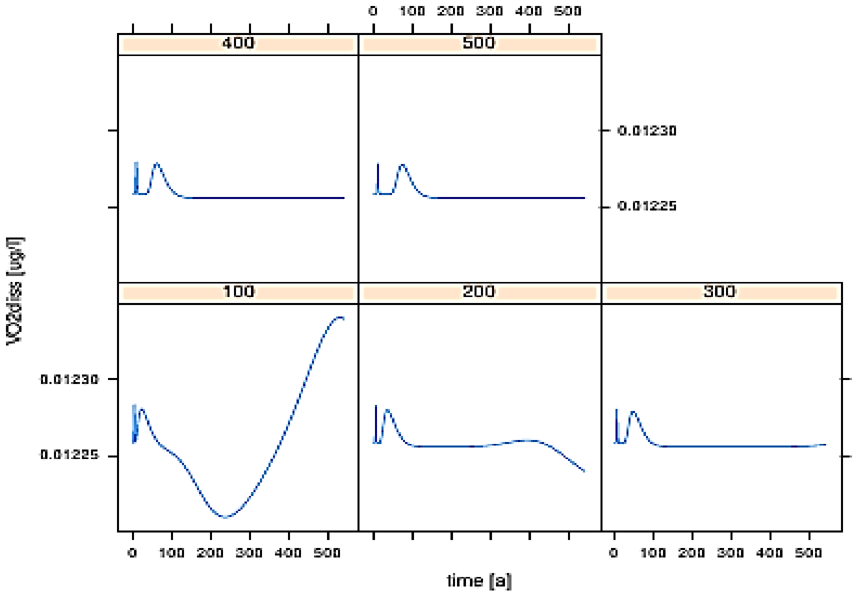


Figure B.13.1.3: Breakthrough curve for dissolved V (VO2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.13.2 *Soil profile*

Figures B.13.2.1 to B.13.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles.

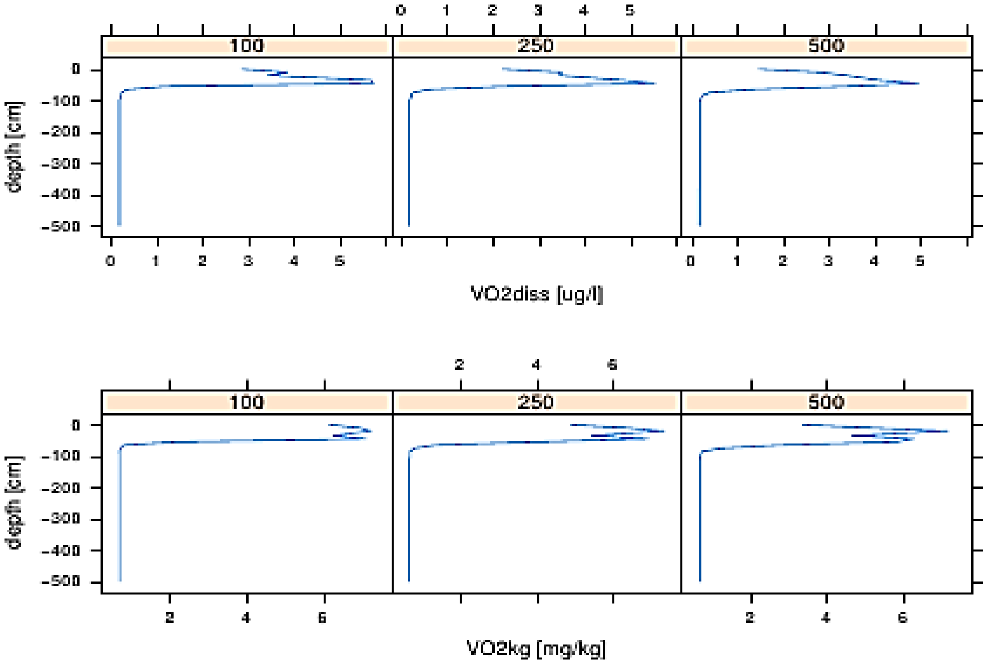


Figure B.13.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of *dissolved V (VO2diss) is given in the top figure; the lower figure gives V in the solid phase (VO2kg).*

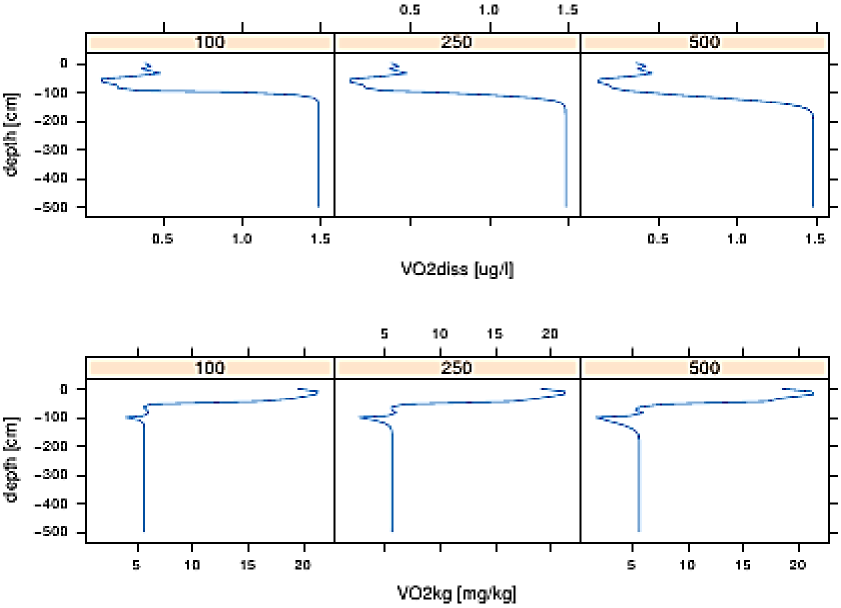


Figure B.13.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved V (VO2diss) is given in the top figure; the lower figure gives V in the solid phase (VO2kg).

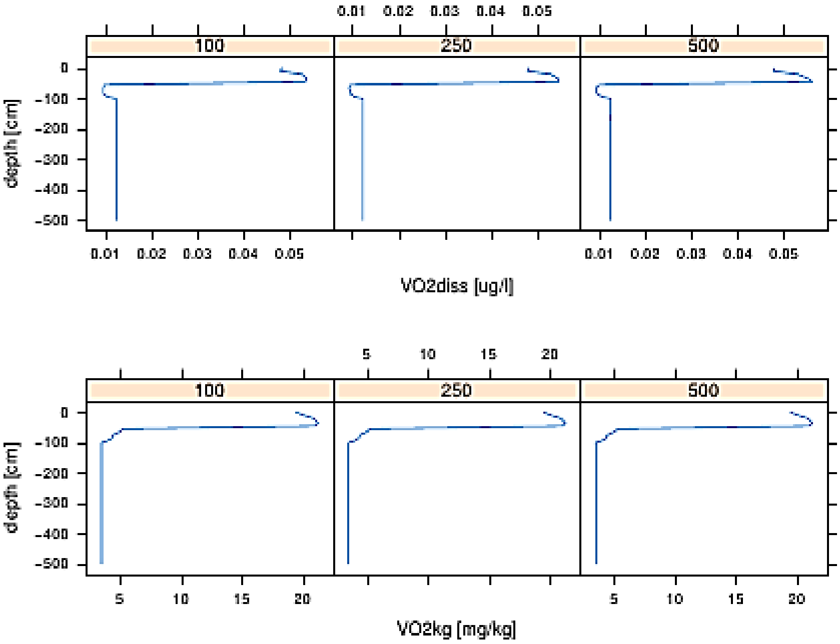


Figure B.13.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of *dissolved V (VO22diss) is given in the top figure; the lower figure gives V in the solid phase (VO2kg).*

12.13.3 Results standard scenario

Table B.13.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	0.03	-	3.5	-	0
	peat	1.245	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
residential	*sand*	0.05	-	3.5	-	0
	peat	1.317	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
industrial	*sand*	0.05	-	3.5	-	0
	peat	1.544	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
time: 500 yr, depth: 100 cm			-		-	
agricultural	*sand*	0.03	-	3.5	-	0
	peat	1.25	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
residential	*sand*	0.05	-	3.5	-	0
	peat	1.327	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
industrial	*sand*	0.05	-	3.5	-	0
	peat	11.779	-	3.5	-	3.4
	clay	0.02	-	3.5	-	0
time: 500 yr, depth: 500 cm			-		-	
agricultural	*sand*	0.03	-	3.5	-	0
	peat	1.245	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
residential	*sand*	0.04	-	3.5	-	0
	peat	1.318	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0
industrial	*sand*	0.05	-	3.5	-	0
	peat	1.463	-	3.5	-	0.4
	clay	0.02	-	3.5	-	0

12.14 Detailed results for zinc (Zn)

12.14.1 Breakthrough curves

Figures B.14.1.1 to B.14.1.3 show the breakthrough curves for Zn. In general, soil transport is predicted only in the sandy soil profiles. At each depth, from 100 cm to 500 cm, a clear curve is visible. For the peat and clay profiles only at the depth of 100 cm the concentration is increasing but the maximum concentration is not reached within 500 years.

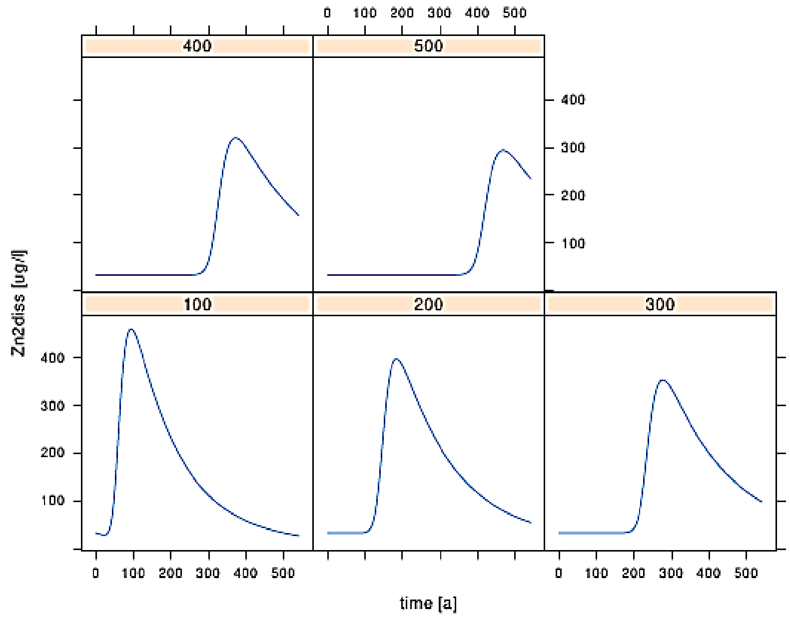


Figure B.14.1.1: Breakthrough curve for dissolved Zn (Zn2diss) in the sand profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

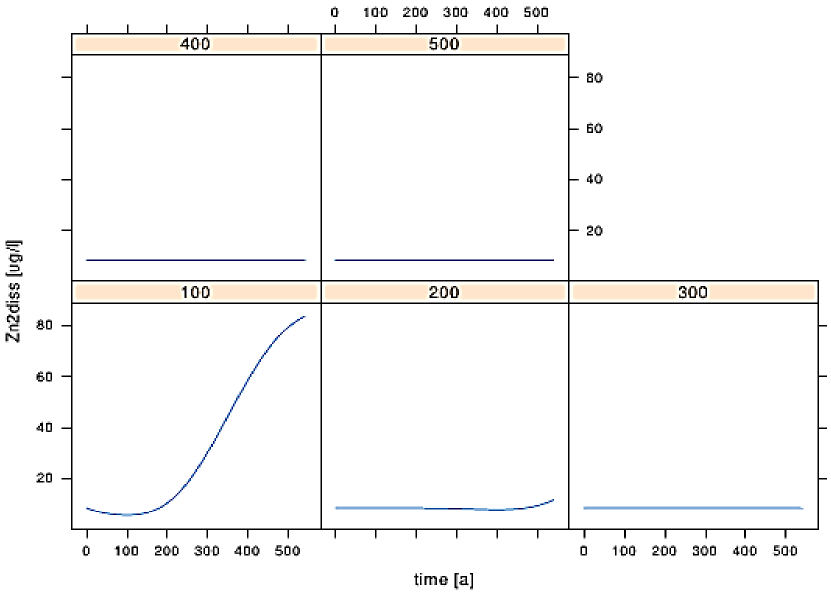


Figure B.14.1.2: Breakthrough curve for dissolved Zn (Zn2diss) in the peat profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

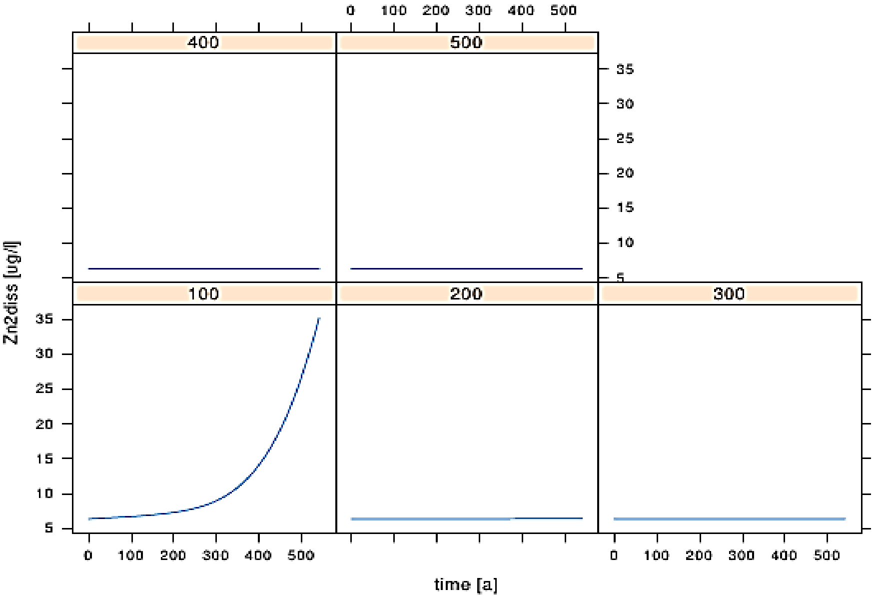


Figure B.14.1.3: Breakthrough curve for dissolved Zn (Zn2diss) in the clay profile. The figure gives the concentration over time at five different depths, cm below surface as indicated in the bars above the figure.

12.14.2 *Soil profile*

Figures B.14.2.1 to B.14.2.3 show the concentrations in the dissolved and solid phases in the three soil profiles. The downward migration, up to 5 m depth, is most obvious in the sand profile. The clay and peat profiles show minor migration, up to a depth of around 2 m in 500 years. The soil concentrations in the sand profile show several peaks. A minor fraction of Zn appears somewhat stationary while the major part migrates downwards.

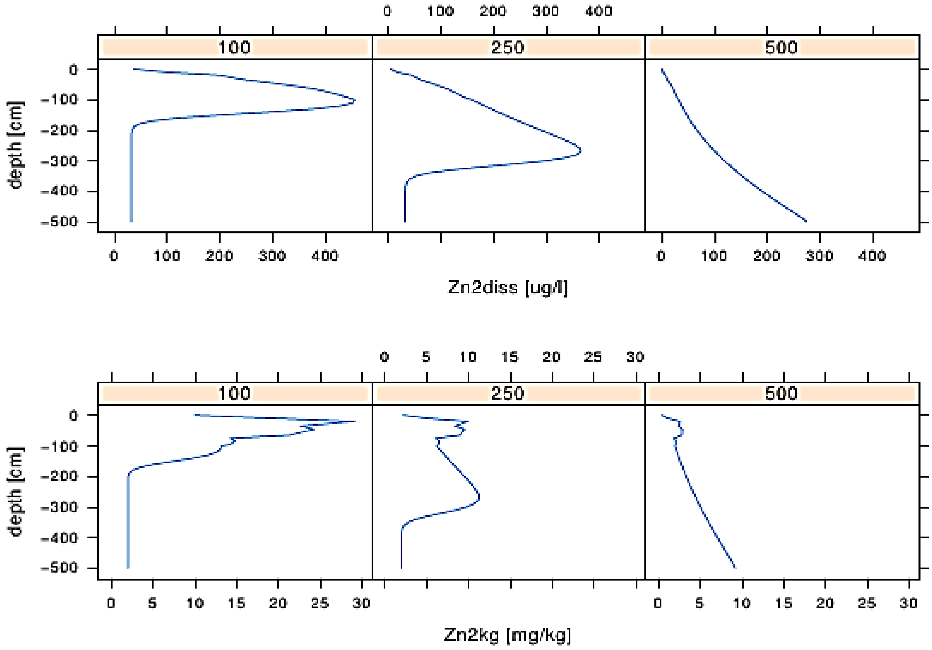


Figure B.14.2.1: Concentrations in the sandy soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Zn (Zn2diss) is given in the top figure; the lower figure gives Zn in the solid phase (Zn2kg).

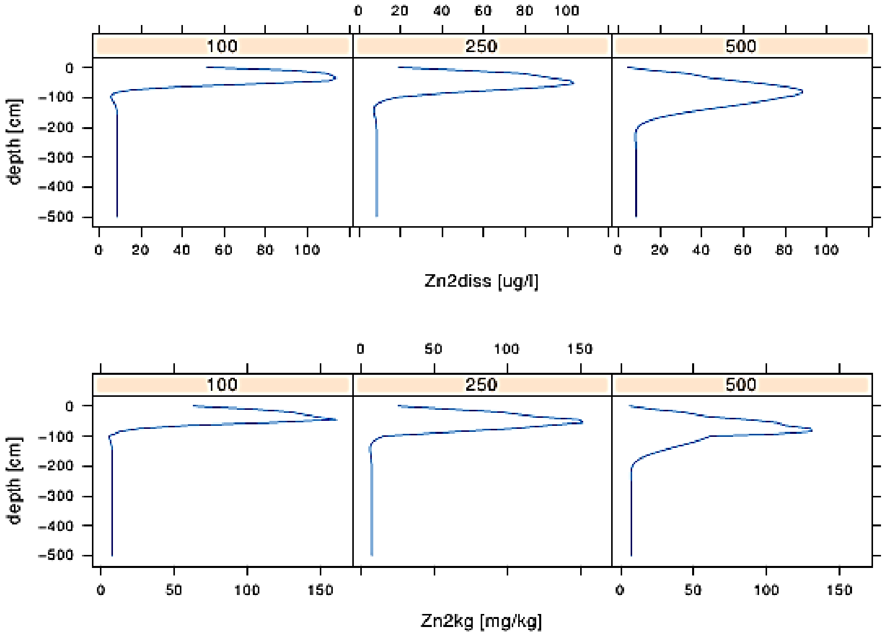


Figure B.14.2.2: Concentrations in the peat soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Zn (Zn2diss) is given in the top figure; the lower figure gives Zn in the solid phase (Zn2kg).

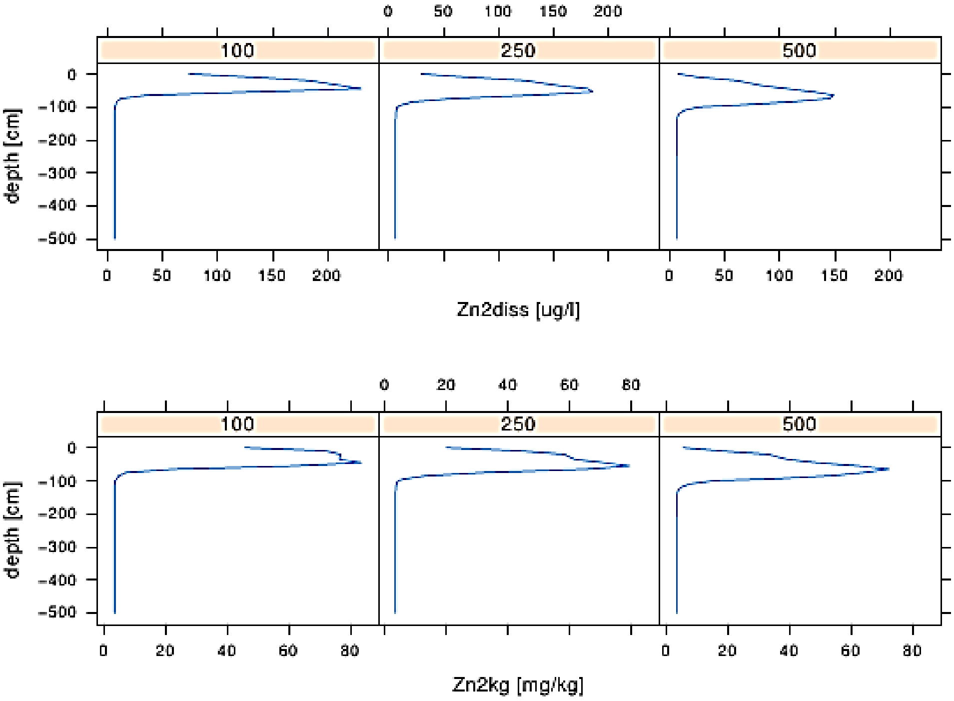


Figure B.14.2.3: Concentrations in the clay soil profile at three moments in time. The bar above the figure indicates the time in years. The concentration of dissolved Zn (Zn2diss) is given in the top figure; the lower figure gives Zn in the solid phase (Zn2kg).

12.14.3 Results standard scenario

Table B.14.3.1: Peak concentrations (peak) compared with the soil type-specific MC and MPA criteria for the three usage scenarios (agricultural, residential and industrial area) and the three standard soil profiles, concentrations in ug/l. The concentrations are given at 100 cm and 500 cm depth and after 100 year and 500 year. The >MC and >MTT columns denote the ratio of peak concentration divided by the criteria. Please note that the concentrations are given for a single soil profile.

Scenario		**Peak**	**MC**	**MPA**	**>MC**	**>MPA**
time: 100 yr, depth: 100 cm						
agricultural	*sand*	225.1	159.9	7.3	1.4	30.8
	peat	4.5	44.4	7.3	0.1	0.6
	clay	9.1	2.8	7.3	3.2	1.2
residential	*sand*	718.9	159.9	7.3	4.5	98.5
	peat	4.5	44.4	7.3	0.1	0.6
	clay	9.1	2.8	7.3	3.2	1.2
industrial	*sand*	8994.8	159.9	7.3	56.3	1232.2
	peat	5.2	44.4	7.3	0.11	0.7
	clay	55.4	2.8	7.3	19.7	7.6
time: 500 yr, depth: 100 cm						
agricultural	*sand*	392.1	159.9	7.3	2.5	53.7
	peat	44.7	44.4	7.3	1	6.1
	clay	26.7	2.8	7.3	9.5	3.7
residential	*sand*	789.2	159.9	7.3	4.9	108.1
	peat	77.4	44.4	7.3	1.7	10.6
	clay	96.8	2.8	7.3	34.3	13.3
industrial	*sand*	8994.8	159.9	7.3	56.3	1232.2
	peat	581.9	44.4	7.3	13.1	79.7
	clay	1576.9	2.8	7.3	559.4	216
time: 500 yr, depth: 500 cm						
agricultural	*sand*	17.8	159.9	7.3	0.11	2.4
	peat	4.4	44.4	7.3	0.01	0.6
	clay	9.0	2.8	7.3	3.2	1.2
residential	*sand*	94.9	159.9	7.3	0.59	13
	peat	4.4	44.4	7.3	0.1	0.6
	clay	90	2.8	7.3	3.2	1.2
industrial	*sand*	2361.4	159.9	7.3	14.8	323.5
	peat	4.4	44.4	7.3	0.1	0.6
	clay	9.0	2.8	7.3	3.2	1.2

13 Appendix C: Results of scenarios with 10^{-4} M SO_4^{2-}/Ca^{2+}

For the modelling a concentration for Ca^{2+} and the counterbalancing SO_4^{2-} is set at 10^{-3} M, according to the data of Dijkstra et al. (2004). This concentration is also used in Verschoor et al. (2006) and Spijker et al. (2008).

Based on a different dataset from Groot et al. (1998) and Groenenberg et al. (2010) the median SO_4^{2-} concentrations are around 10^{-4} M, ten times lower than Dijkstra et al. (2004).

SO_4^{2-} is important for the mobility of Sb and Ba. The results of this study show almost no retention of Sb and immobile Ba. To see how the mobility of these elements is affected by a lower SO_4^{2-} concentration, according to the alternative dataset, a separate model run was performed for the three standard soil profiles with soil concentration at the level of the Maximum Value Agricultural. In this separate model run the SO_4^{2-} concentration was set at 10^{-4} M.

Because Ca^{2+} counterbalances the charge of SO_4^{2-}, the Ca^{2+} input concentration was also lowered to 10^{-4} M. This will affect the cation exchange and the competition of Ca^{2+} with other cations like metals.

Mol (2002) presents data of centrifuged soil pore water in which he determined Ca concentrations. His soil samples were taken from Pleistocene sandy soils in the Netherlands. He found Ca concentrations within the same order of magnitude as the 10^{-4} Ca^{2+} concentration. This confirms that lowerering the Ca^{2+} concentration by a factor of 10 does not lead to unrealistic input values.

Figure C.1 shows the results of this exercise. The regular model run (10^{-3} M Ca^{2+}/SO_4^{2-}) is compared with the custom model run (10^{-4} M Ca^{2+}/SO_4^{2-}). This figure shows that Ba does indeed get more soluble, resulting in a higher maximum average concentration, while lowering the Sb concentration. However, the effect of these changes is regarded as limited.

More important is the effect of Ca^{2+} on the competition with other cations. For sand and peat the maximum average concentrations of elements like As, Cd, Co, Mo, Ni, V and Zn are also lower by an order of magnitude. In clayey soils this effect is still present but to a smaller extent.

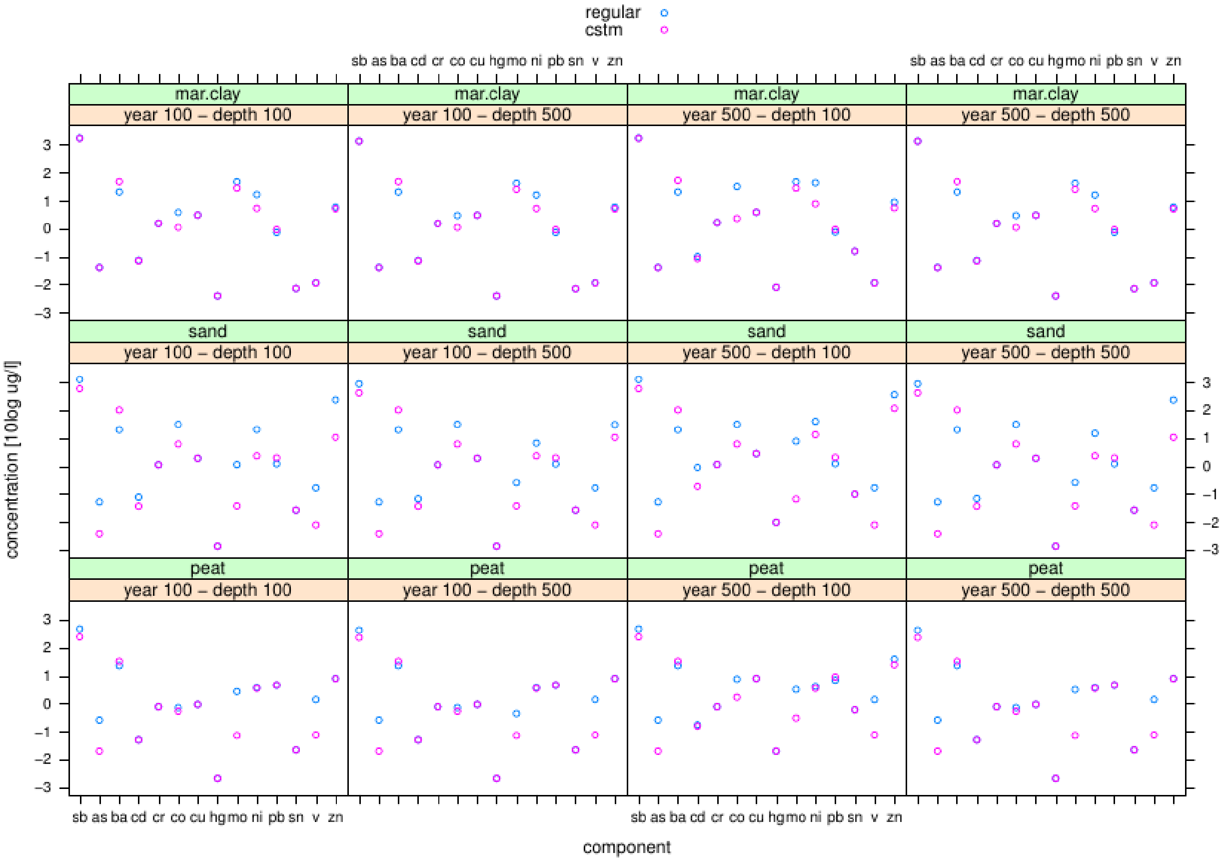


Figure C.1: Results of modelling of the three standard soil profiles for the scenarios with concentrations at the level of the Maximum Value Agricultural. The regular calculation (blue) is based on the standard SO_4^{2-} and Ca^{2+} of 10^{-3} M. The custom calculation (purple) is based on input concentrations for SO_4^{2-} and Ca^{2+} of 10^{-4} M.

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