RIVM report 703717011/2003

Determination of denitrification parameters in deep groundwater

A pilot study for several pumping stations in the Netherlands

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This research has been carried out by order of the Directoraat-Generaal voor Milieubeheer, Directie Bodem, Water en Landelijk gebied, as part of project 703717.

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Abstract

Groundwater nitrate measurements in the central and eastern parts of the Netherlands showed that denitrification occurs in many locations. This is why models used for analysis of management decisions for drinking-water production need to take denitrification into account. Little information is available on the denitrification rate and its spatial distribution. In this report a model concept is proposed to simulate denitrification and a pilot study is carried out for nine groundwater pumping stations in the central and eastern part of the Netherlands. The unknown parameters were determined using a calibration procedure with the optimisation program PEST. Nitrate measurements from monitoring networks were used for the calibration, along with nitrate data from the water abstracted at a number of public drinking-water pumping stations. In zones where the presence of organic substances is likely, denitrification is described as an exponential decay with a half-life of about 500 days. In zones where organic material is absent, the half-life is much higher (2750 days). Instantaneous nitrate reduction is assumed at or near the phreatic surface. Here, an average reduction of 50% is found. However, this figure may also represent a compensation for an over- or underestimation of the nitrate input at the water table. The parameter values were found to contain a large measure of uncertainty, for which several explanations are suggested and discussed. One factor that affects the parameter uncertainty is related to the simplifications in the model set-up. A second source of ‘uncertainty’ is due to parameters in the model that provided input data, such as groundwater velocities (LGM) and nitrate fluxes (STONE). Finally, a certain amount of uncertainty is inherent in the stochastic technique used for the solute transport simulation (Random Walk technique).

Contents

Samenvatting

Bij de modellering van nitraattransport in grondwater moet men zowel in ondiepe als in diepe aquifers rekening houden met denitrificatie (Kovar et al., 1998, RIVM rapport 730717002). In dit rapport wordt voor het denitrificatieproces een modelconcept voorgesteld dat bestaat uit drie afzonderlijke processen die zich met verschillende snelheid manifesteren:

i) een instantane nitraatreductie die zich afspeelt aan of in de buurt van het freatisch vlak;
ii) een betrekkelijk snel verlopend exponentieel verval dat optreedt in een zone waar zich voldoende organisch materiaal bevindt;
iii) een betrekkelijk langzaam verlopend exponentieel verval in de zone waar organisch materiaal nagenoeg afwezig is.

Om de parameters van de hierboven genoemde processen te bepalen, is in deze pilotstudy een kalibratie-procedure opgezet. Voor de eigenlijke kalibratie is het model onafhankelijke optimalisatieprogramma PEST gebruikt. Gedurende het kalibratie-proces worden modeluitkomsten vergeleken met meetgegevens. Als meetgegevens zijn nitraatmetingen gebruikt van waarnemingsputten die behoren tot het Landelijk en/of Provinciaal Meetnet Grondwater, (LMG en/of PMG). Daarnaast zijn nitraatmetingen gebruikt van het water dat op verschillende grondwaterwinplaatsen voor de openbare drinkwatervoorziening wordt gewonnen en als reinwater wordt afgeleverd, veelal na zuivering. De negen geselecteerde pompstations zijn gelegen in het centrale en oostelijke deel van Nederland, waar goed doorlatende freatische watervoerende pakketten voorkomen. Nitraatmetingen in waarnemingsputten kunnen worden beschouwd als puntwaarnemingen, zowel ruimtelijk als in de tijd. Zij vertegenwoordigen slechts een klein ruimtelijk gebied en een korte tijdsperiode. De gegevens van het in de pompstations onttrokken water zijn representatief voor een veel groter gebied. In horizontale zin komt dat gebied overeen met het intrekgebied van het pompstation. Nitraatgegevens van het onttrokken water en het afgeleverde drinkwater worden sinds 1992 verzameld in het kader van het REWAB meetprogramma (**RE**gistratie opgaven van **WA**terleiding**B**edrijven). Van voor 1992 zijn metingen beschikbaar van het Landelijk Meetnet Drinkwaterkwaliteit (LMD). De LMD metingen hebben alleen betrekking op het water na de zuiveringsstap (te weten reinwater metingen). In geen van de pompstations wordt overigens een specifieke nitraatzuivering toegepast. In een aantal gevallen zijn de nitraatgehalten voor en na de zuiveringsbehandeling vrijwel identiek. In andere gevallen (bijvoorbeeld bij Pompstation Herikerberg) is dat echter niet het geval.

Modellering van nitraattransport is niet mogelijk zonder informatie over de hoeveelheid nitraat die aan het freatisch oppervlak het grondwatersysteem binnen gaat. De daadwerkelijke waarden voor deze nitraatflux zijn niet beschikbaar op de schaal van in dit rapport gebruikte model. In deze studie worden waarden gebruikt die zijn gegenereerd met het uitspoelingsmodel STONE. Het modelconcept van STONE wijkt echter sterk af van dat van het grondwater

model, zowel in ruimtelijke als temporele zin. Verschillende vereenvoudigingen waren noodzakelijk om de STONE-gegevens om te werken naar het 'format' dat was gewenst voor het grondwatertransportmodel. Een andere vereenvoudiging betreft het grondwaterstromingsmodel zelf. De grondwaterstroming is hier opgevat als een stationair probleem. Het is echter bekend dat met name de onttrekkingshoeveelheden van de pompstations gedurende de gesimuleerde periode (1950-2000) niet constant is geweest. De aangebrachte vereenvoudigingen waren noodzakelijk om het rekenwerk mogelijk te maken, maar zij bemoeilijken wel de uiteindelijke vergelijking van modelresultaten met de waarnemingen.

Voor de 'instantane' denitrificatie nabij het freatisch oppervlak is een gemiddelde reductie factor gevonden van 47%. Deze factor wordt echter sterk beïnvloed door onzekerheden in de door STONE gegenereerde nitraat-input. Voor droge zandgronden zijn deze waarden een factor van 30% te hoog (Overbeek et al, 2001b). De gevonden denitrificatie-factor kan, onbedoeld, tevens dienst doen als een compensatie voor mogelijke overschattingen van de nitraatinput. Het is niet mogelijk om het aandeel van een daadwerkelijke denitrificatie en dat van het compensatie-effect nader te preciseren. De gevonden parameters voor de exponentieel verlopende denitrificatie worden in dit rapport uitgedrukt als halfwaardetijden. Voor de zone waar organische materiaal aanwezig wordt verondersteld – dwz onder beek- en rivierdalen en in de omgeving van kleilagen – is een gemiddelde halfwaardetijd gevonden van ongeveer 500 dagen, variërend van 165 tot 1485 dagen. Uffink en Römkens (2001) vonden hier een soortgelijke waarde (1½ jaar). Voor de zone met langzaam exponentieel verval is een halfwaardetijd van rond 2750 dagen gevonden, variërend van 1680 tot 4450 dagen. Deze waarden liggen hoger dan die uit de rapportage van Uffink en Römkens (3 tot 5 jaar). Deze laatste studie had betrekking op een klein deelgebied van het studiegebied dat in het huidige rapport wordt beschouwd, terwijl een handmatige kalibratie werd toegepast en uitsluitend nitraatmetingen werden gebruikt van de meetnetputten.

De onzekerheid van de gevonden parameters is tamelijk groot. Dit is het gevolg van een aantal factoren. Allereerst zijn er verschillende vereenvoudigingen in de model-opzet aangebracht. Omdat de grondwaterstroming stationair wordt verondersteld en de nitraatinvoer is omgewerkt naar langjarige gemiddelden, zullen seizoensschommelingen in de modeluitkomsten niet zichtbaar zijn. In de ondiepe waarnemingsputten zijn seizoensvariaties wel aanwezig. Ook de geleidelijke toename van de door de pompstations onttrokken hoeveelheid water wordt in het model niet in rekening gebracht. Een tweede belangrijke bron van onzekerheid loopt via de modellen die invoergegevens leveren voor de transportsimulatie, zoals de grondwatersnelheden (LGM) en de nitraatfluxen (STONE). Aangezien onzekerheden van deze gegevens niet bij de kalibratie zijn betrokken, komen deze uiteindelijk terecht bij de geschatte transportparameters. Tenslotte bestaat er een vorm van onzekerheid die inherent is aan de gebruikte oplossingstechniek in het transportmodel. De stochastische component in de 'particle-tracking' methode veroorzaakt een 'ruis' die alleen kan volledig worden geëlimineerd

door een oneindig aantal deeltjes toe te passen. In praktijk zal daarom altijd een zekere mate van ruis in de modelresultaten worden geaccepteerd. Een meer algemeen probleem dat eveneens met het bovenstaande te maken heeft, is het volgende. Bij lange-termijn voorspellingen en beleidsanalyses op regionale schaal worden meestal sterk opgeschaalde modellen gebruikt. In het algemeen zijn voor kalibratie van deze modellen alleen gegevens beschikbaar die afkomstig zijn van kleinschalige en kort lopende processen. Deze inconsistentie tussen de schaal van de waarnemingen en de resolutie van de modelberekeningen staat een zinvolle vergelijking tussen modelresultaten en waarnemingen vaak in de weg. Zolang middelen of technieken om de parameteronzekerheid te reduceren niet voorhanden zijn, lijkt een landsdekkende toepassing van de beschreven kalibratieprocedure nog niet zinvol.

Kalibratie leidt niet altijd tot een unieke verzameling parameterwaarden. Moeilijkheden bij dit ‘niet uniek zijn’ kunnen worden opgelost door een stapsgewijze kalibratie-procedure. Bij iedere afzonderlijke stap laat men slechts één of enkele parameters variëren, waarbij slechts de meetgegevens worden geselecteerd die het meest gevoelig zijn voor de vrije parameter(s). De selectie van de meest gevoelige waarnemingen kan het best gebeuren aan de hand van een gevoeligheidsanalyse. Dit is echter met de hier gebruikte versie van PEST niet mogelijk. Bij toekomstige kalibratieberekeningen wordt een gevoeligheidsanalyse echter sterk aanbevolen.

1 Problem description

In the Netherlands the situation concerning nitrates in groundwater is a matter at issue, especially in the sandy areas where the leachate from manure easily reaches the phreatic groundwater. Traditionally, these aquifers contain good and reliable groundwater that often is used as a source for the production of drinking water. During the last few decades, however, the nitrate levels here have risen significantly, mainly due to intensified animal farming. According to the EC Nitrate Directive groundwater with nitrate concentration above 50 mg l^{-1} are classified as polluted. Measures have been taken to decrease the load of nitrate entering the groundwater, but due to the large residence times the effects of these measures will be visible only at some time in the future, several decades of years from now. Solute transport models have been applied to prepare prognostications as support for management decisions. However, the predictive capacity of these models is still limited due to several problems. A common modelling problem is the lack of information on system parameters. For the subject of this report, this holds in particular for the parameters describing the transport of nitrate trough the groundwater system. A useful technique to test parameters values in a model is calibration. It involves a procedure of modifying model parameters until the model output matches a set of observed data.

For model calibration the availability of field data (measurements) is crucial. In the Netherlands groundwater heads are being monitored systematically. Leijnse and Pastoors (1996) have used the monitored groundwater head to calibrate the Netherlands Groundwater flow Model (LGM). However, when solute concentrations such as nitrates are being studied, simulation of the groundwater flow forms only a first modelling step, to be followed by a solute transport simulation. The transport model needs to be provided with additional transport specific parameters. It is recognised that denitrification plays a key role and therefore, parameters describing the denitrification process are required. However, little information is available on the values of the denitrification parameter in specific field situations. An appropriate way to assess these parameters is by model calibration, especially since many groundwater nitrates measurements are available from the national groundwater monitoring system. The present report presents a pilot study in which an automated calibration procedure is tested on a number of pumping stations abstraction water for the public water supply. These pumping stations are all located in the central and eastern part of the Netherlands, where the hydrological system consists of phreatic, high permeable sandy aquifers.

In previous studies (Kovar et al., 1996, 1998; Uffink and Römkens, 2001; Uffink and Mülschlegel, 2002) attempts have been made to estimate denitrification parameters in a Dutch phreatic aquifer system. Since the results of these studies are relevant for the present study,

the report starts with an overview of this work (Chapter 2). In Chapter 3 some topographical and geohydrological features of the present model area are described, while Chapter 4 gives information with respect to the groundwater abstraction sites in the area. The data and models that have been used in this study are briefly described in Chapter 5. Since denitrification is the main point of interest in the present study, a separate chapter is devoted denitrification. It also specifies the implementation of this process in the transport module. The calibration procedure itself is described in more detail in Chapter 7. Finally, the calibration results are presented and discussed in Chapter 8.

2 Former investigations

In the subarea 'Lochem', which is located in the present study area, an application of the Netherlands Groundwater Model (LGM) was carried out by Kovar et al. (1996). Kovar et al. determined traveltimes and concentration breakthrough curves for an ideal tracer using various grid densities, i.e. 1×1 km, 500×500 m and 200×200 m. The results of the study indicated that a grid density of 1×1 km would be too coarse. For phreatic abstraction sites a density of 250×250 was recommended. In a follow-up study 15 refined models have been set up with a grid density of 250×250 m^2 (Kovar et al., 1998). Again, the breakthrough of nitrates has been modelled for several groundwater-pumping stations. The model areas considered in the present report originate from Kovar's '1998'-study. In Kovar's study, however, denitrification was not considered. Therefore, most calculated nitrate values were overestimated, especially in anaerobic waters where denitrification is likely to occur. Accordingly, Uffink and Römkens (2001) made a first attempt to include denitrification using a first order (exponential) decay concept (see also Uffink, 2001). Uffink and Römkens applied their model on a small sub-area (40×30 km^2) of the present study area. The decay parameters were calibrated by hand using nitrate measurements from 28 monitoring wells with screens at several depths up to 30 metre beneath the phreatic surface. The observed nitrate levels indicated that nitrate concentrations are decreasing rapidly with depth. This implies that in the solute transport model a high vertical resolution is required. Although the head distribution within a separate aquifer is in principle two-dimensional in horizontal direction, a vertical velocity may still be defined using the Dupuit-Forchheimer-Strack approach (Strack, 1984). Artificial vertical mixing of nitrate is prevented by use of a particle tracking technique, which does not introduce numerical dispersion. Uffink and Römkens found decay-parameters, expressed as half-life times, ranging from 200 days to 2000 days.

Obviously, nitrate transport in the aquifer cannot be modelled without information on the amount of nitrate leaching from the root zone into the groundwater. In general, these leaching rates are not known from measurements, certainly not for the time and space scale considered in the present report. Therefore, leaching data have been obtained from different sources. Recently, a leaching model STONE has been developed (Overbeek et al., 2001a). STONE generates leaching rates of nitrate and other nutrients under several field conditions. However, during all studies mentioned above data from STONE were not yet available. In both Kovar's and Uffink and Römkens' study leaching data were based partly on calculations by Van Drecht (Van Drecht et al., 1991; Van Drecht, 1993; Van Drecht and Schepers, 1998). Boumans and Van Drecht (1998) provided the data for forested and urban areas by using a statistical analysis.

Shortly after completion of the study by Uffink and Römkens leaching data from STONE became available and prognostications were set up for the 5th National Environmental Outlook (RIVM, 2000). These prognostications, based on the newly generated nitrate fluxes, were established still using decay parameters that were calibrated on older leaching data. This discrepancy was recognised and discussed in detail by Uffink and Mülschlegel (2002). The new nitrate leaching rates appeared a factor 2-4 times higher than the ones used for calibration in Uffink and Römkens. Several explanations have been suggested. The main discrepancy comes from the concepts that were used to link the unsaturated zone and the groundwater system. The concept for the top-system in the leaching model is substantially different from the approach used in the National Groundwater Model LGM. For a detailed discussion see Chapter 5.

Uffink and Mülschlegel proposed several modifications for the coupling problem and took an additional nitrate reduction into account. These proposals have been implemented in the present study. Instead of calibrating the decay parameters by hand, in the present study an automatic calibration has been performed with the programme PEST (Anonymous, 1994). For the calibration nitrate measurements from the National Groundwater Monitoring Network of RIVM are used, supplemented with data from local monitoring networks. These data cover a time interval from 1980 until today. In addition to monitoring well data also nitrate measurements at pumping stations are available. These are used as well (breakthrough curves) in the present study.

3 Study area

3.1 General

The study area is localised in the eastern and central part of the Netherlands (Figure 1). In this part of the country the underground consists of sandy layers of Pleistocene origin. The total thickness of the Pleistocene sand complex varies from 20 to 300 metres and more. In some parts semi-pervious clay layers occur that separate the Pleistocene formation into several interacting aquifers. Where the clay layers are absent the system reacts as a single phreatic aquifer. For the greater part the aquifer system is replenished by natural recharge, although in some areas seepage occurs. Mostly, the seepage is drained off by a system of ditches and drainage tiles. In lower lying infiltration areas also a drainage system may be present. In this case part (or all) of the natural recharge may be drained off (see Chapter 5).

A characteristic feature of the study area is the presence of several ice-pushed ridges (Veluwe, Montferland, Nijverdal and Ootmarsum). These ridges were formed during the Saale ice age, during which the northeast and central part of the Netherlands was covered with ice. Typically, the ice pushed areas can be identified as good infiltration areas. Seepage is more prevalent in the lower laying areas (IJssel-Valley).

The study area has been subdivided into several 'subareas', for each of which a separate groundwater model has been set up (Kovar et al., 1998). The subareas, named Achterhoek, Veluwe, Twente and Hoogeveen in the present report, coincide with the model areas '*a2*', '*v2*', '*t2*' and '*h2*' respectively from Kovar's study. The dimensions and coordinates of the model areas are presented in Table 1. The areas Veluwe, Achterhoek and Twente partly overlap (Figure 1), while the Hoogeveen model is not connected to any of the other three. In the following sections, where the spatial distribution of various geohydrological parameters is presented, the sub-areas are combined into one plot. Note that this results in two non-contiguous areas.

Table 1. Geometric Properties of the model areas.

Name of area	*Dimension* [km^2]	*coordinates* [km]			
		x_{min}	x_{max}	y_{min}	y_{max}
Achterhoek	50 × 50	200	250	425	475
Veluwe	50 × 50	160	210	425	475
Twente	55 × 42.5	215	217	462.5	505
Hoogeveen	98 × 25	170	268	512.5	537.5

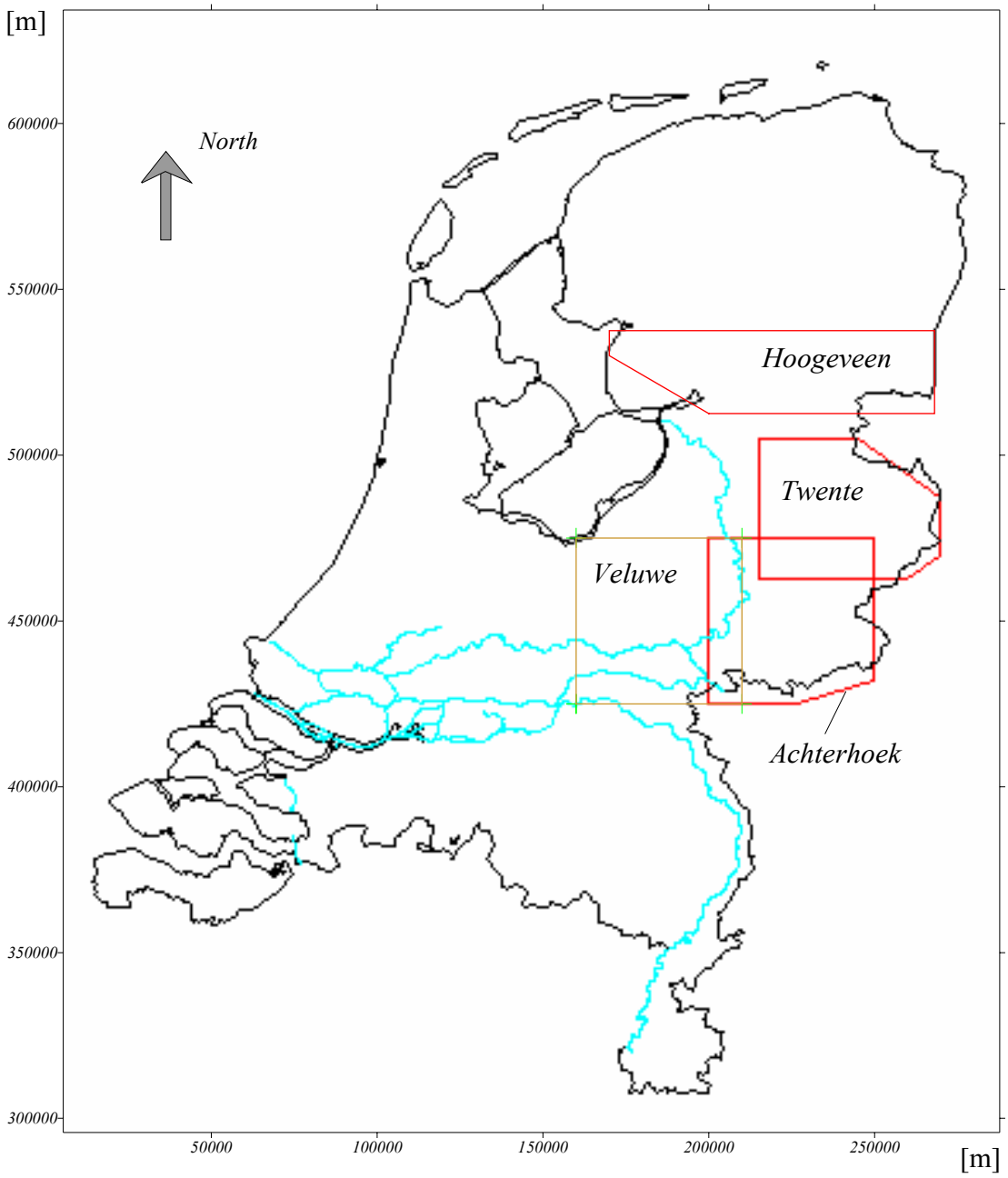

Figure 1. Location of model areas Veluwe, Achterhoek, Twente and Hoogeveen.

Figure 2 gives a three-dimensional view of the surface elevation with respect to Dutch datum level (NAP). The elevation varies between – 4 and 103 metres (NAP). Notice the presence of several ice-pushed ridges, where the elevation is higher than the direct surroundings.

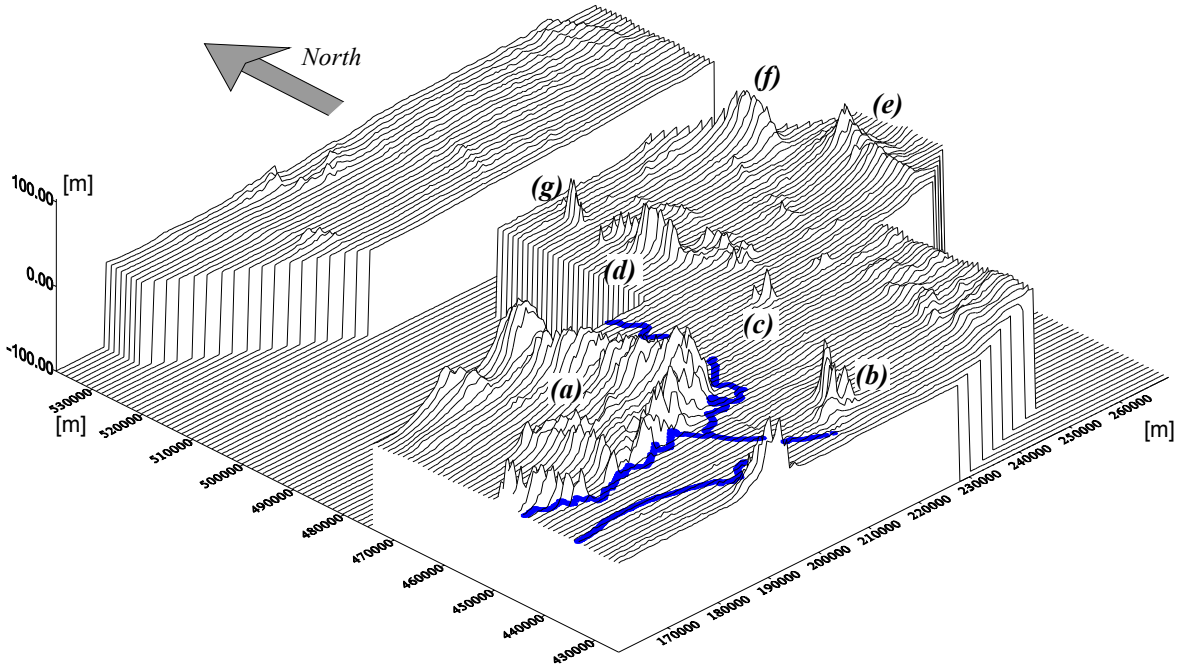

Figure 2. Three-dimensional view of the surface elevation.

(a) Veluwe
(b) Montferland
(c) Lochemerberg
(d) Holterberg (Nijverdal)
(e) Lonnekerberg (Oldenzaal)
(f) Ootmarsum
(g) Lemelerberg

3.2 Surface waters

The Rhine River, some of its branches (IJssel and Waal) and several smaller rivers are running through the southern part of the area. In the east several minor watercourses, such as the Slingebeek, Baakse Beek, Berkel, etc. follow the general descending inclination of the surface in eastwestern direction. All these streams finally discharge into the IJssel. This means that in fact the IJssel takes care of the drainage for most of the eastern section of the area. The part of Twente located north of the Schipbeek/Twente Canal discharges via De Regge and Dinkel into the Overijsselse Vecht along the northern edge of the area (see Figure 3).
The central part of the Veluwe/Achterhoek area consists of the IJssel Valley, where the IJssel River runs northward. The IJssel finally discharges in the lake IJsselmeer (not shown in the figure).

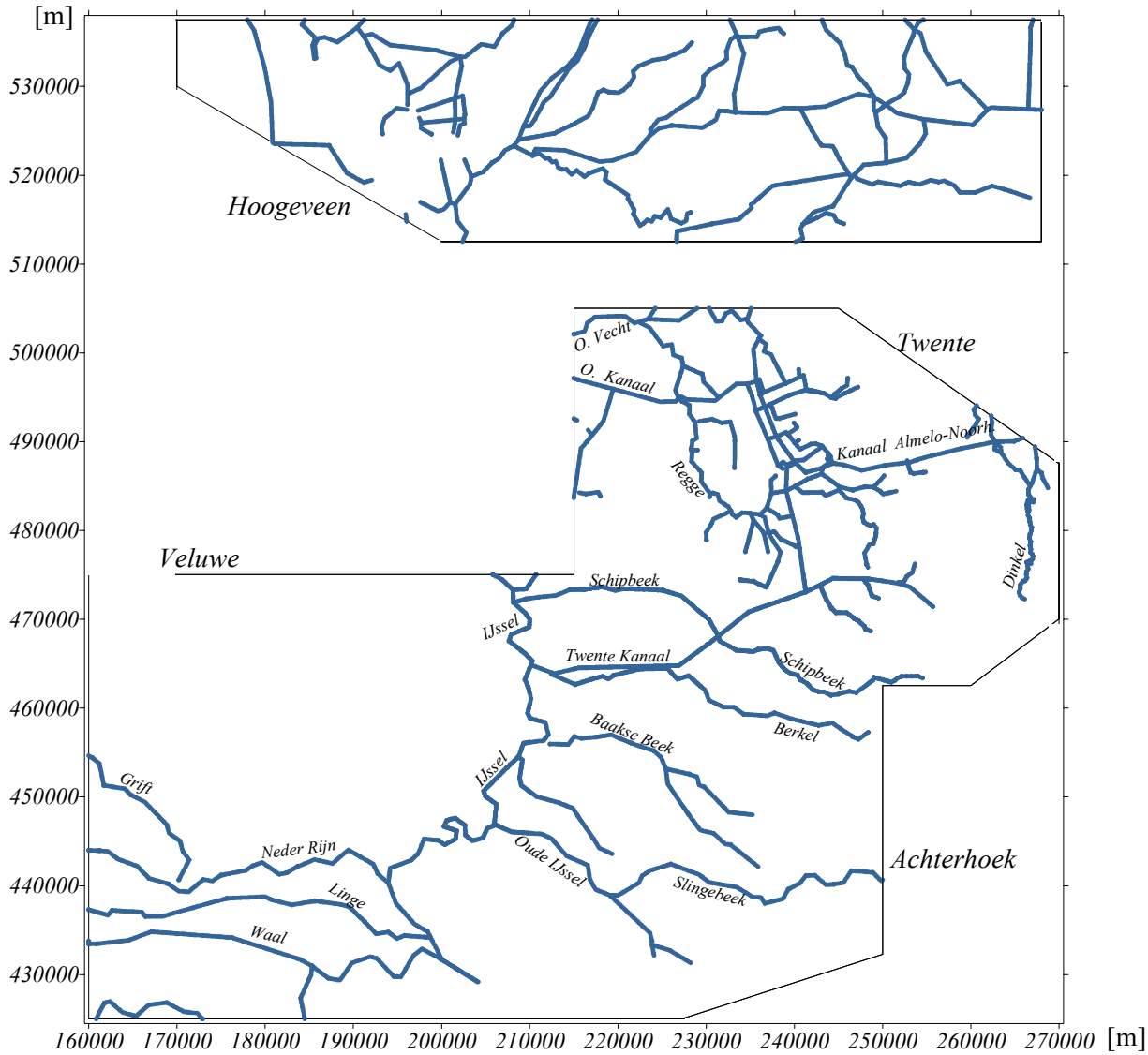

Figure 3. Surface-waters in the study area.

3.3 Aquifer system

The thickness of the Pleistocene complex that comprises the aquifer system varies considerably. At the southeastern side the thickness is between 10 and 30 metres. In the northwestern direction the thickness increases to 300 metres and more. This is due to the rapid decline of the low permeable Breda Formation, which is considered to be the base of the geohydrological system. Figure 4 presents a contourmap of the base elevation. Detailed geological descriptions of the area can be found in Grootjans (1984) and Vermeulen et al. (1996), as well as in the NAGROM/TNO report (Anonymous, 1993).

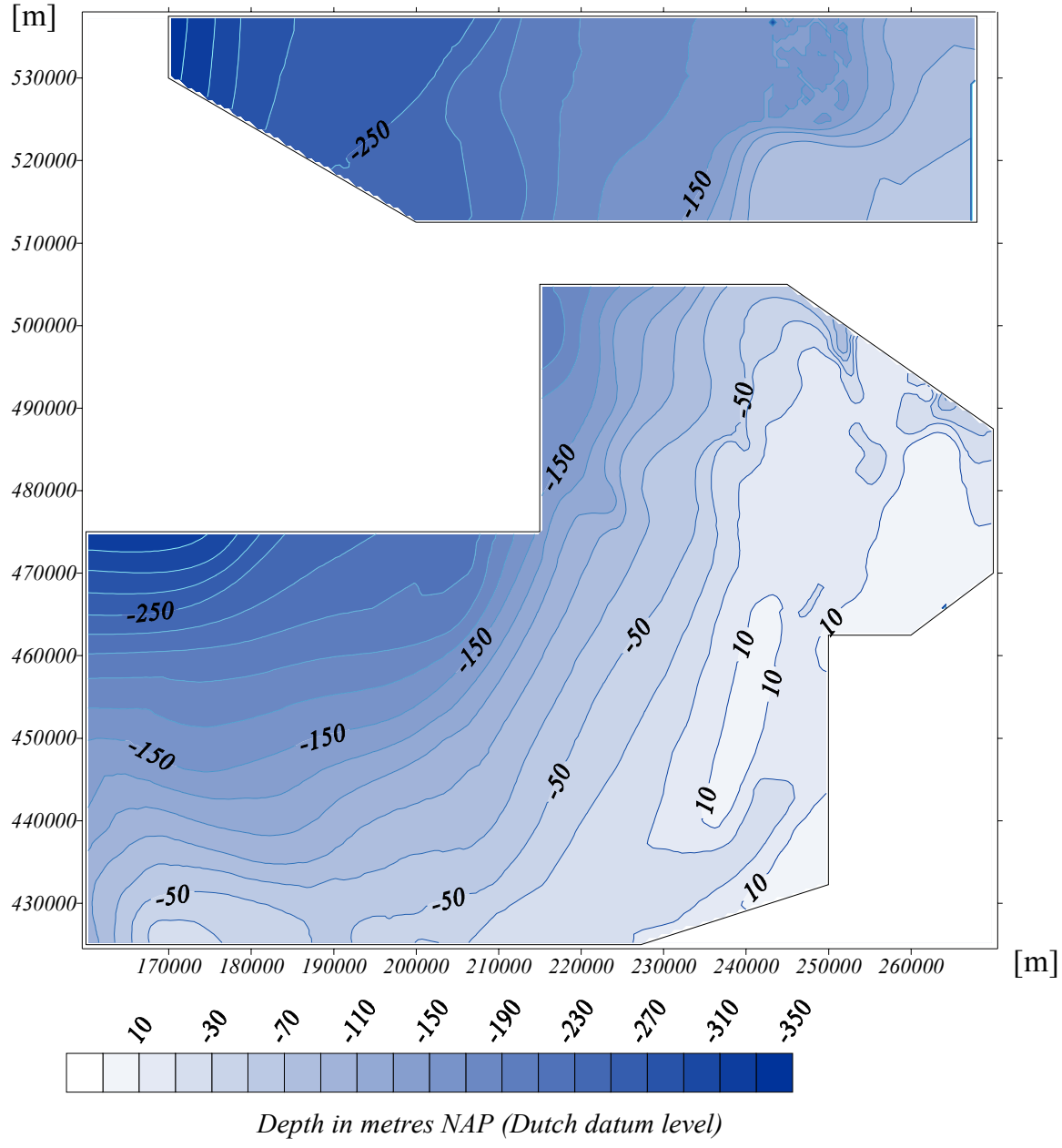

Figure 4. Contours of the base of the aquifer system.

Figures 5 and 6 show the presence and thickness of the first (Eemian-clay) and second aquitard (Drenthe/Tegelen-clay) as modelled in LGM.

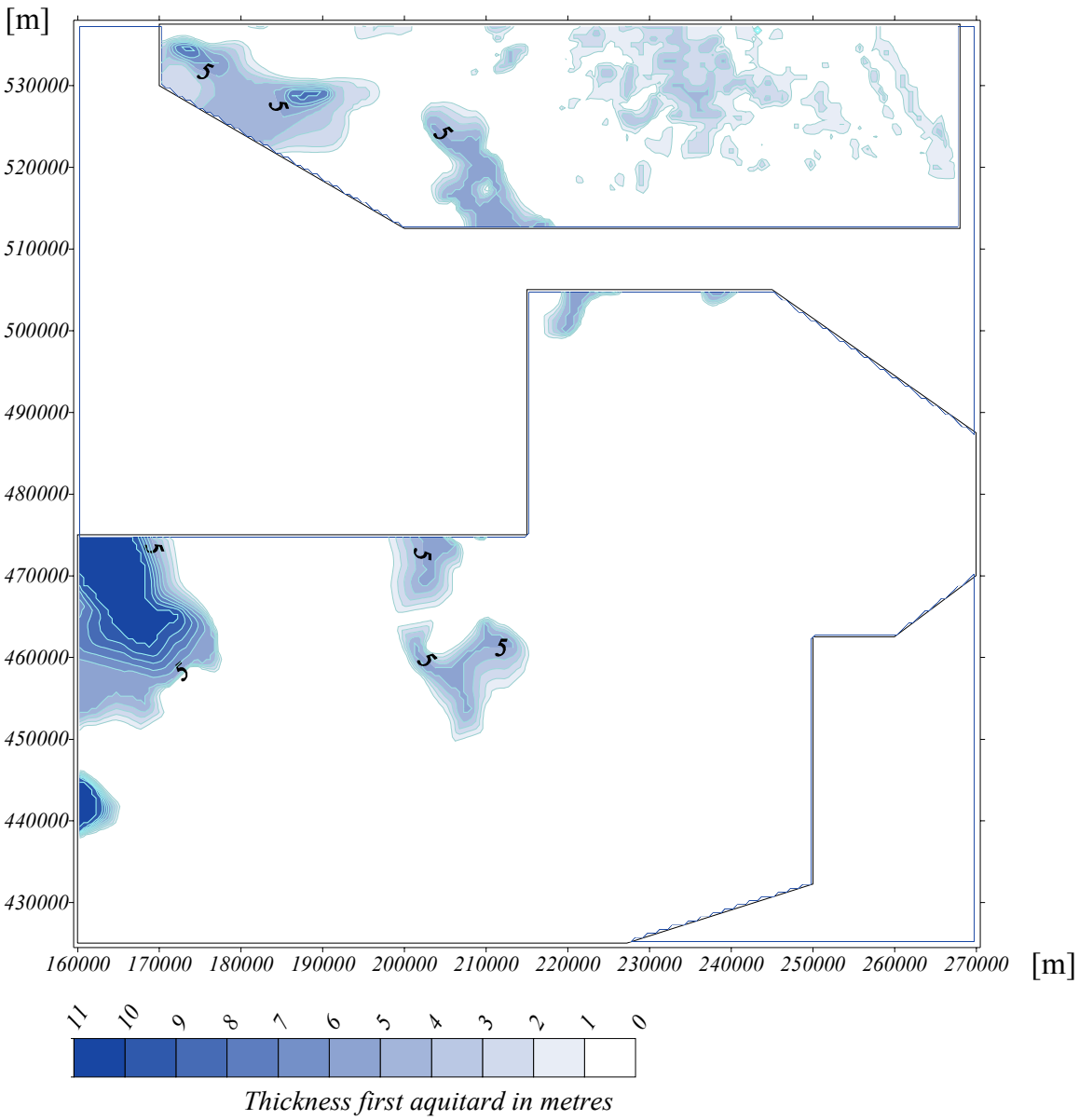

Figure 5. Presence and thickness of the first aquitard (Eem-clay).

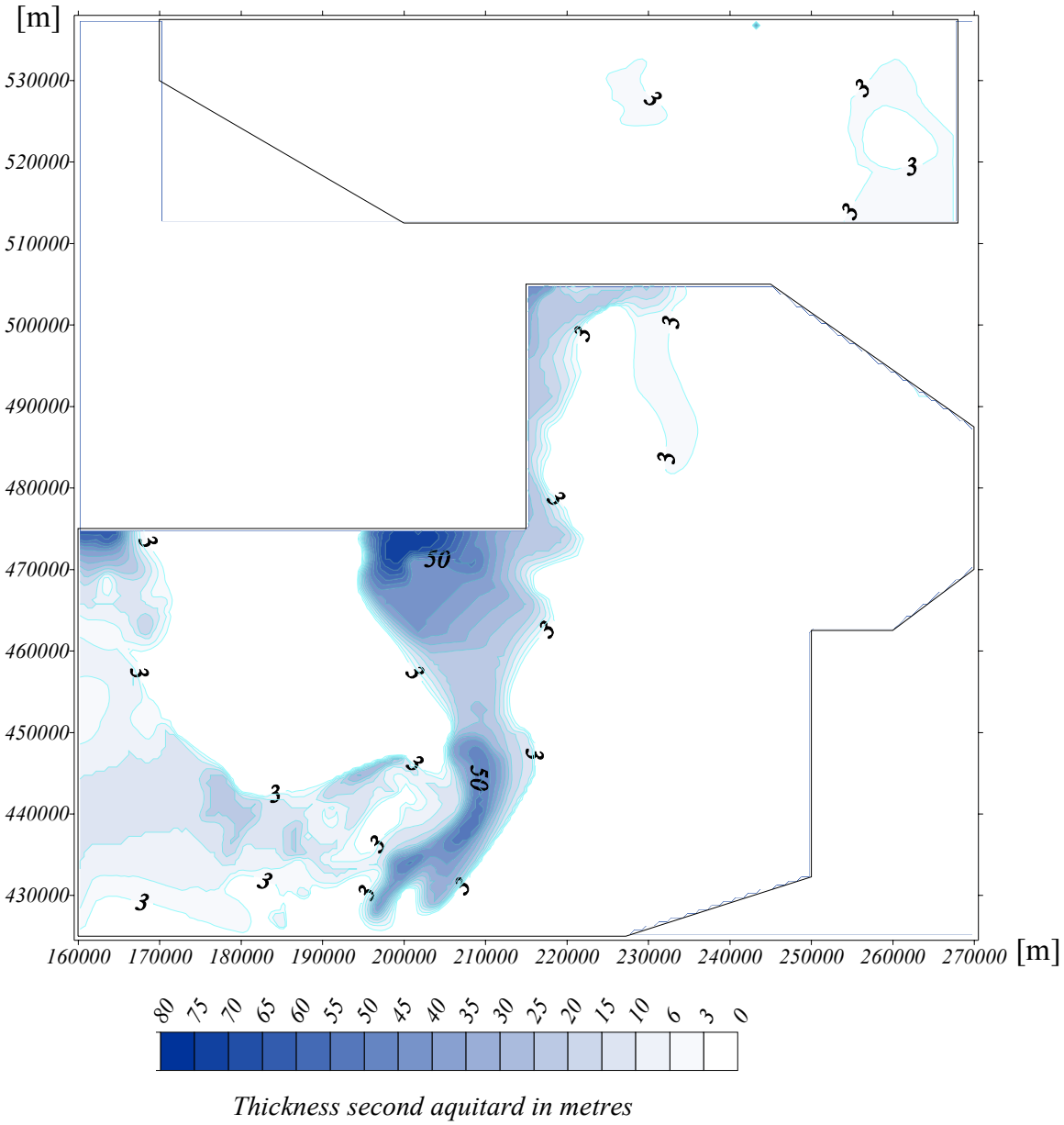

Figure 6. Presence and thickness of second aquitard (Drenthe-clay).

3.4 Groundwater heads and velocities

As mentioned in Chapter 2, the groundwater heads and velocities have been determined in a previous study (Kovar et al., 1998) by means of the National Groundwater Model (LGM, see also Chapter 5). The groundwater flow model is applied as a stationary model. Hence, the heads and velocities presented here are considered to be representative for an average situation over a longer period of time (several years). Figure 7 shows the distribution of the groundwater head in the upper aquifer.

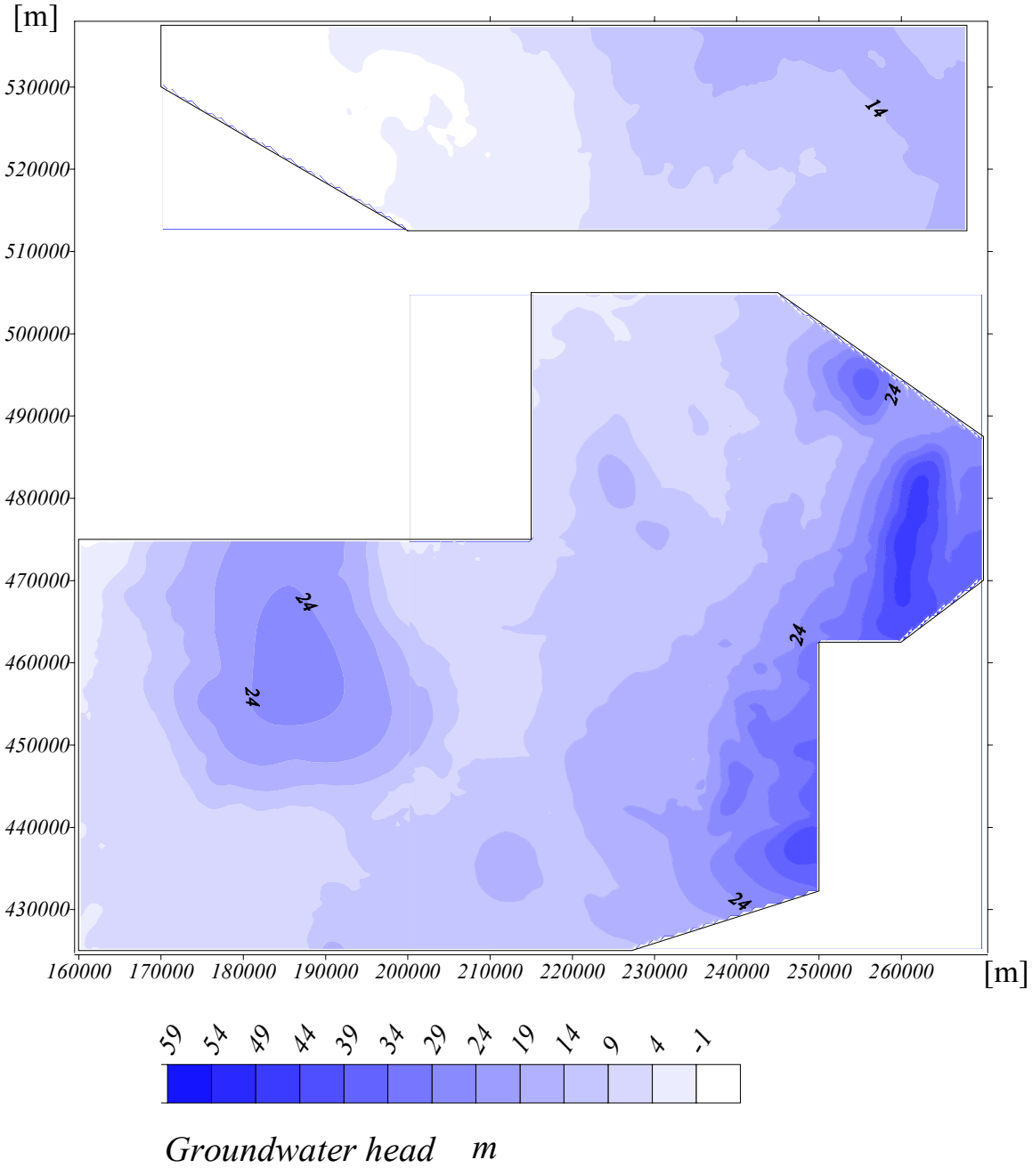

Figure 7. Groundwater heads in upper aquifer as determined by LGM in metres with respect to datum level (NAP).

This picture reflects the surface relief in a less pronounced manner. It shows a general decrease from the southeastern edge towards the IJssel valley in the central part. The higher heads under the ice-pushed Veluwe-hills in the southwest are clearly visible. Other ice-pushed ridges (Montferland, Nijverdal, Ootmarsum and Oldenzaal) can also be observed and associated with higher heads.

Figures 8 and 9 present the groundwater velocities at the depth of 0.1 m below the phreatic surface. The vertical component is displayed as a contourplot (Figure 8). Blue and blue-grey shades are indicative for an upward velocity (seepage), while yellow to red shades denote downward flow (i.e. infiltration). As it appears, the location of the ice-pushed ridges determines the pattern of infiltration for the greater part. Especially the Lemelerberg and Nijverdal emerge as dominant infiltration areas.

The horizontal velocity has been displayed in Figure 9 as a vector plot. The arrows indicate the direction of the flow, while the magnitude of the arrow indicates the magnitude of the velocity.

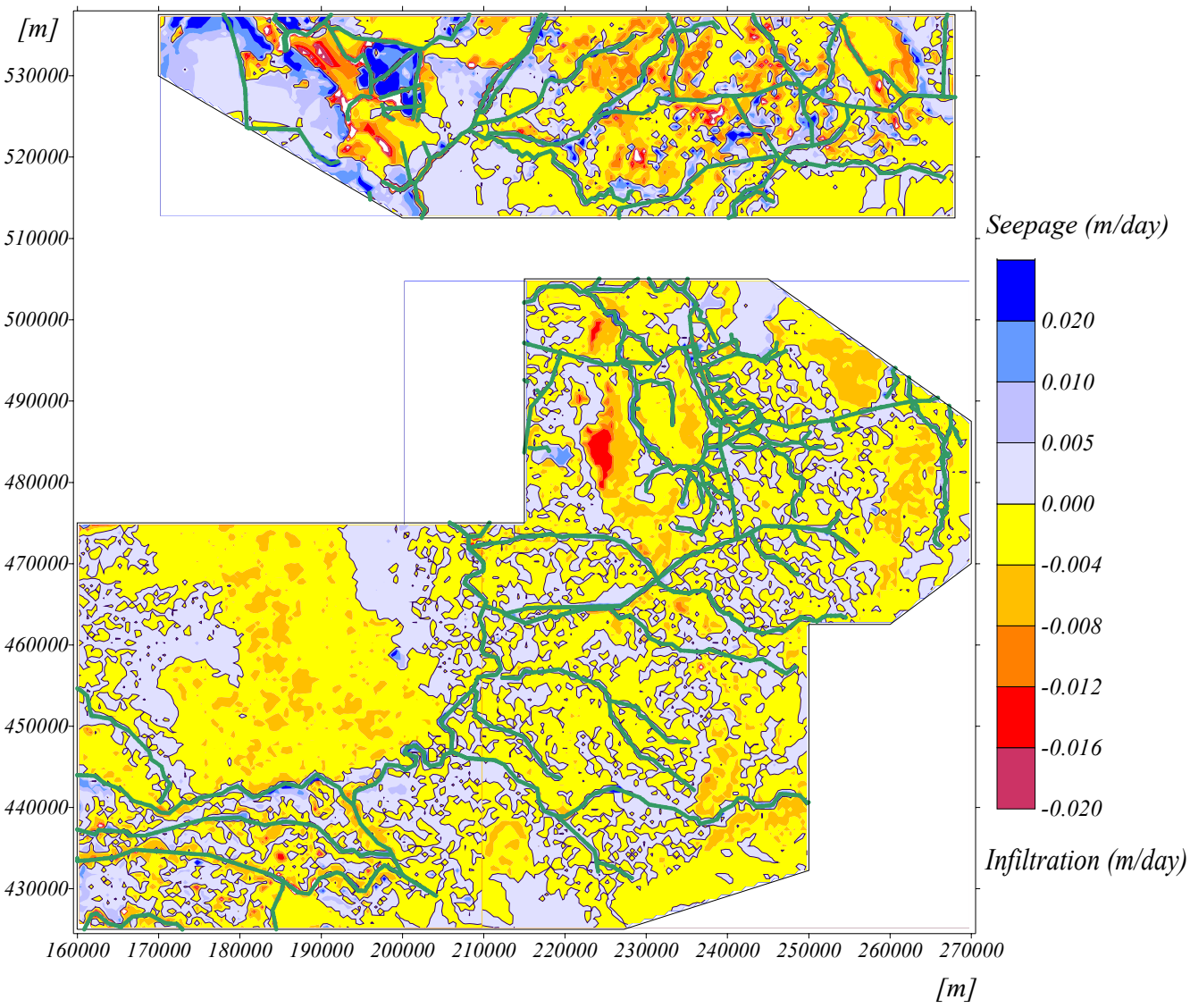

Figure 8. Vertical groundwater velocity at 0.1 m below phreatic surface.

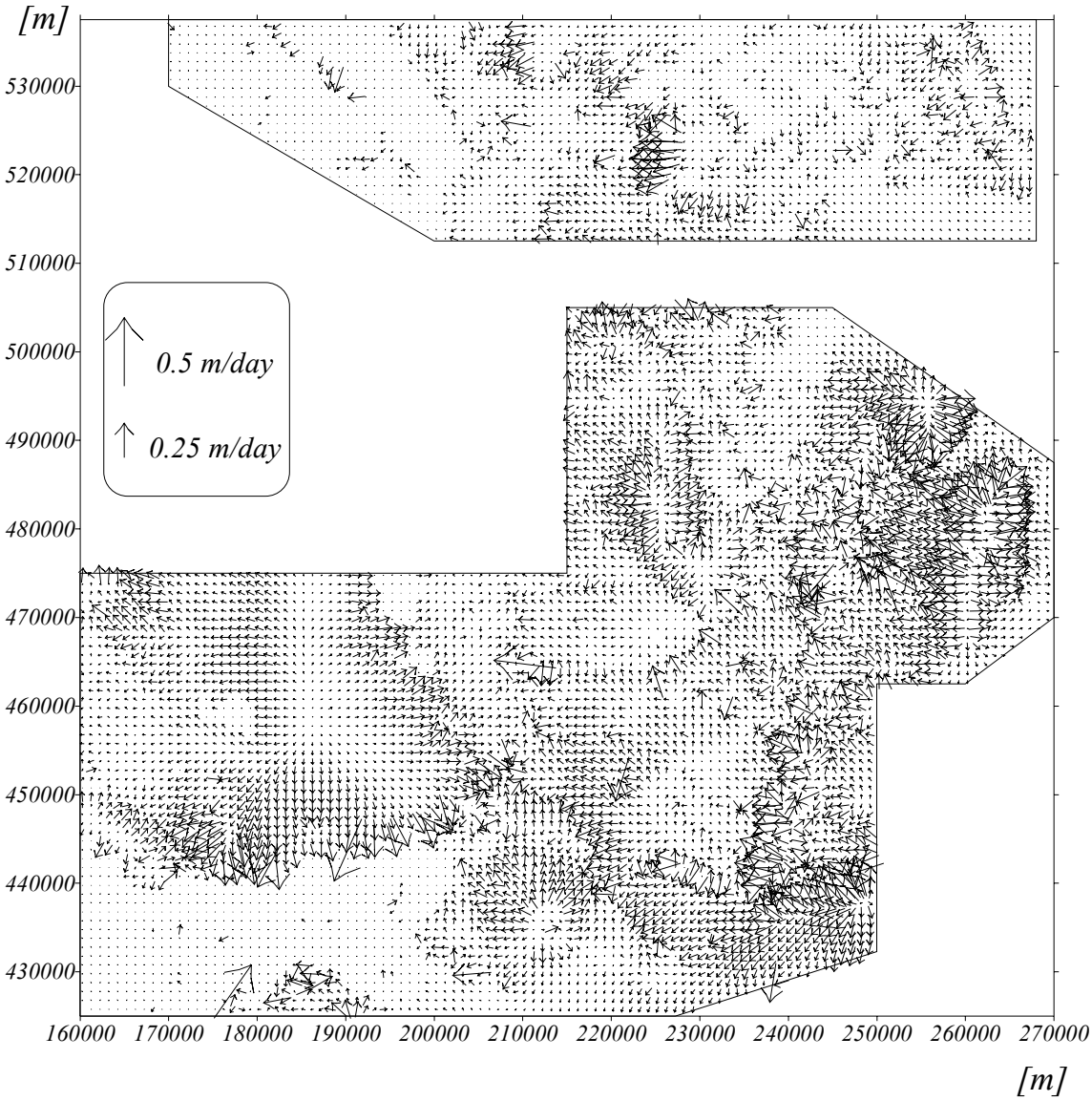

Figure 9. Direction and magnitude of horizontal groundwater velocities at 0.1 m below the phreatic surface.

4 Groundwater abstraction

4.1 Rates of discharge

In the study area a large number of industrial wells and private groundwater abstractions are present as well as a number of pumping stations abstracting water for public drinking water supply. The total groundwater abstraction for public water supply has increased substantially during the period 1960-'80. Since then, the level of abstraction more or less remained constant, while after 1990 a slightly decreasing trend can be observed. Examples are shown in the Figures 10 and 11. These graphs give the total amount of water (in million m^3 $year^{-1}$) abstracted for public water supply by the pumping stations in 2 of the 4 model areas. Industrial and private groundwater abstractions are not included in the graphs, but they are taken into account in the model. In both areas (Achterhoek and Twente) the industrial and private abstractions are approximately 50% of the total abstracted volume.

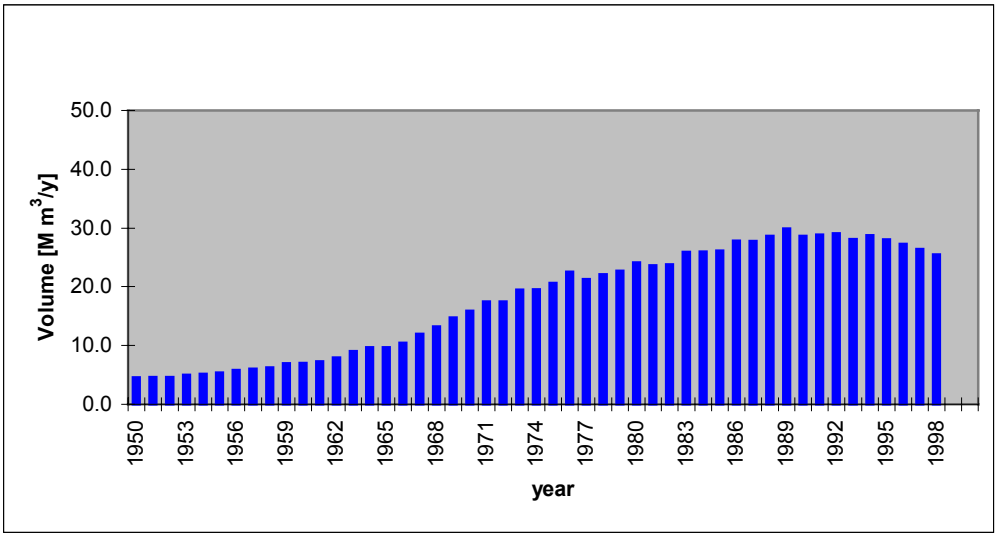

Figure 10. Yearly abstracted volume of groundwater by pumping stations in model area Achterhoek.

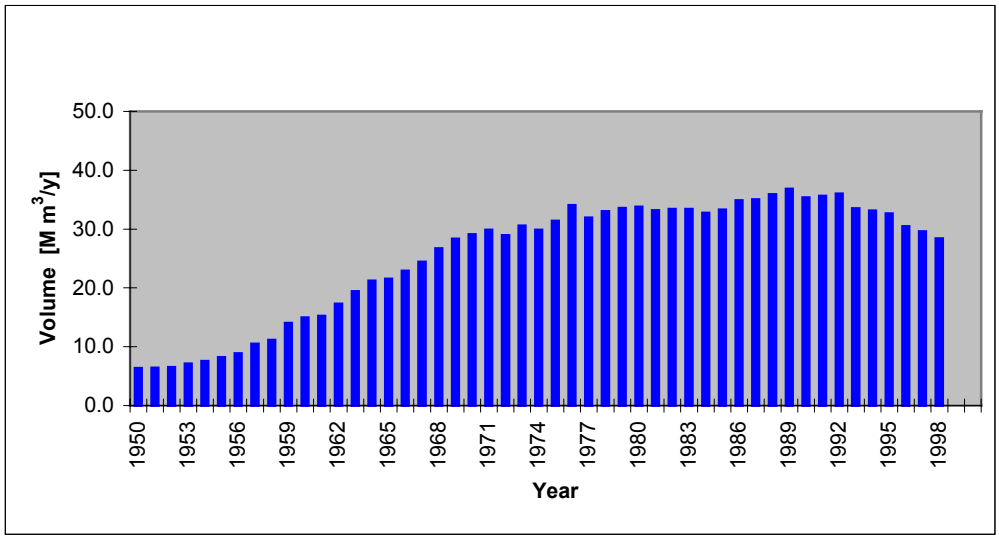

Figure 11. Yearly abstracted volume of groundwater by pumping stations in model area Twente.

4.2 Locations

The locations of all groundwater abstractions are displayed in Figure 12. Private and industrial abstraction wells (with a discharge larger than 50000 m^3 year $^{-1}$) are indicated as red circles, while the public water supply pumping stations are shown as black circles. The sizes of these circles are proportional to the amount of abstraction. In the present report attention is focused on 9 public water supply pumping stations, which were randomly selected throughout the central and eastern part of the Netherlands. In this part of the country the occurrence of nitrate in groundwater is a topical subject. For the selected pumping stations also the capture zone is given in green (Figure 12).

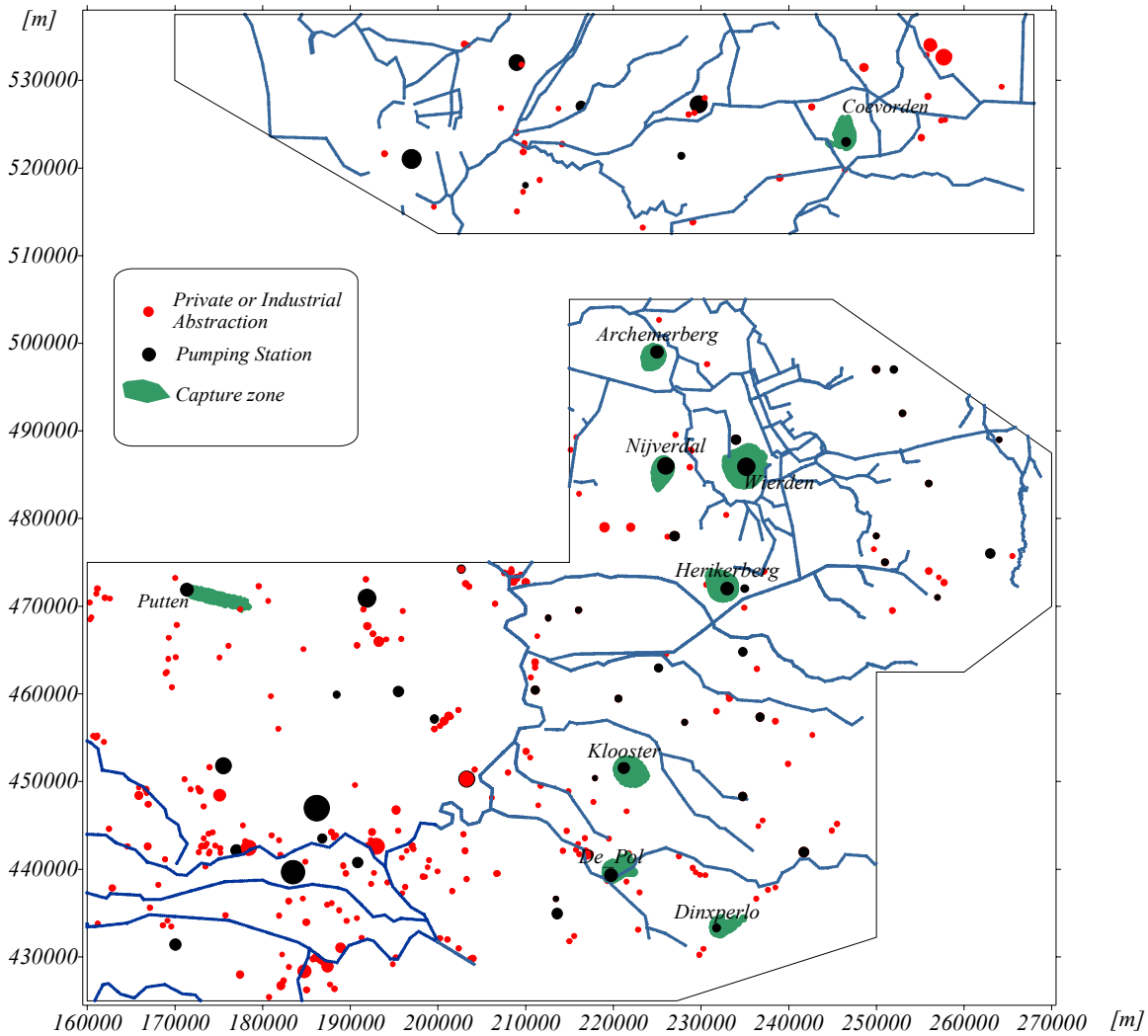

Figure 12. Location of the groundwater abstractions and the capture zones of selected pumping stations.

5 Data and models

5.1 Nitrate measurements

Parameter estimation or calibration is the process of fitting measured data with data generated by the model that includes the unknown parameter(s). The set of nitrate measurements used in this report may be divided into two categories. The first category consists of data from monitoring wells (Monitor Well Data). These data originate from the National Groundwater Monitoring Network, which has been installed during 1979-1984 (Snelting et al., 1990). Groundwater samples are collected at least annually at various filter depths (up to 30 metres below surface). The volume of the water samples is relatively small in comparison to the spatial resolution of the groundwater transport model. For, instance, a calculated concentration represents a volume $125 \times 125 \times 10$ m^3, while the measurements are based on a volume of several litres. Therefore, in practice, the measurements may be regarded as point measurements. From detailed local studies it is known that nitrate levels fluctuate during the year and vary considerably in space as well. The data used in this study are representative for four moments in time, respectively the years 1982, 1990, 1995 and 2000. In order to obtain the data in the right format, some pre-processing and averaging has been applied. For a certain moment t the measurements are averaged over an interval starting at t - 500 days until t + 500 days. In a few cases data from local monitoring networks have been added to the data set.

The second category of data (Breakthrough Data) consists of nitrate contents measured at the pumping stations. The main difference with the monitoring data is that breakthrough data refer to a mixture of waters that have infiltrated at different locations and at different times. Therefore, this is a mixture of waters with different ages and origins. Nitrate measurements at the pumping stations should preferably be taken from the water **before** the purification process. For most pumping stations nitrate contents have been collected since 1992 in the so-called REWAB programme (in Dutch: **RE**gistratie opgaven van **WA**terleiding**B**edrijven). These measurements refer to the untreated water as well as the water after purification. A longer series of data is available from the LMD measuring programme (in Dutch: Landelijk Meetnet Drinkwaterkwaliteit), which refers to the nitrates of the water **after** the purification. In the purification process no specific nitrate decontamination is applied and in a number of cases the measurements in the treated and untreated water hardly differ. However, this does not hold for all pumping stations.

5.2 Leachate model

At present STONE is being used as the standard tool in national scale nutrient leaching studies. STONE (Beusen et al., 2000; Overbeek et al., 2001a) calculates the flux of several

nutrients from the root zone into the groundwater system on a temporal basis of decades (10 days). The spatial differentiation of the model results is obtained by applying the model for a large number of unique combinations of soil type, land use and hydrological features. For the present study area nitrate leaching rates have been calculated by STONE within the framework of the fifth National Environmental Outlook. These are described in more detail by Overbeek et al. (2001b). The temporal resolution of 1 decade of days of the STONE data is too detailed for the solute transport model. Therefore, the data have been transformed into 15-year averages for the interval from 1950-2000.

5.3 Groundwater model

As mentioned before, Kovar et al. (1998) calculated the groundwater heads and velocities in the area with the groundwater flow model National Groundwater Model LGM (Pastoors, 1992; Kovar et al., 1992). LGM is based on finite elements and describes the groundwater flow in a multi-aquifer system separated by one or more aquitards. Within each aquifer the head distribution is treated two-dimensionally in horizontal direction, while through the aquitards purely vertical flow is assumed. In terms of groundwater velocities the model is quasi-three-dimensional. The horizontal flow components are derived from Darcy's low, while the vertical flow is obtained by an approximate procedure, known in the literature as Strack's interpretation of Dupuit-Forchheimer (Strack, 1984). In short, the approximation may be formulated as follows: within the aquifers vertical conductivity is assumed infinitely large, while in the aquitards the horizontal conductivity is assumed to be zero.

At the top of the upper aquifer, interaction occurs between the groundwater and the drainage system of ditches and drainage tiles. This zone is referred to as the top-system. In principle natural recharge infiltrates at the phreatic surface. This vertical groundwater flux is denoted by q_{re}. A portion of this recharge may leave the underground after a relatively short stay (e.g. several days) and discharge into the drainage system. The latter portion is referred to as the top system discharge, denoted by q_{ts}. The top system discharge plays a role in the determination of the nitrate flux that reaches the groundwater.

The top system discharge is taken into account in the groundwater model via the following expression:

$$q_{ts} = \frac{\varphi - h_0}{c} \tag{1}$$

where the coefficient c is the so-called drainage resistance (days), h_0 is the zero drainage level (drainage base) and $\varphi(x,y)$ is the groundwater head as calculated by LGM. The amount of water infiltrating into the aquifer system, q_{as}, is q_{re} - q_{ts} or:

$$q_{as} = q_{re} - \frac{\varphi - h_0}{c} \qquad (2)$$

Note that q_{re} , h_0 and c are all given input parameters, while both $\varphi(x,y)$ and also q_{as}, need to be calculated by the model. When φ is greater than h_0 , the aquifer system discharges water into the drainage system. Irrigation occurs when φ is less than h_0 , i.e. water infiltrates from the ditches and drains into the aquifer. Both h_0 and c may vary in space, so q_{ts} also is a function of the horizontal co-ordinates x and y. The parameters c, h_0 and q_{re} are all given as model input.

The drainage or irrigation that take place in the top-system is not only relevant for the mass balance of water, but also for the net amount of nitrate that finally enters the aquifer system. Together with the discharge q_{ts} an amount of nitrate is removed via the drainage system. This nitrate term must be taken into account. In case of infiltration/irrigation an additional amount of water enters the aquifer. The nitrate content of this term is unknown. In this study it is assumed to be zero.

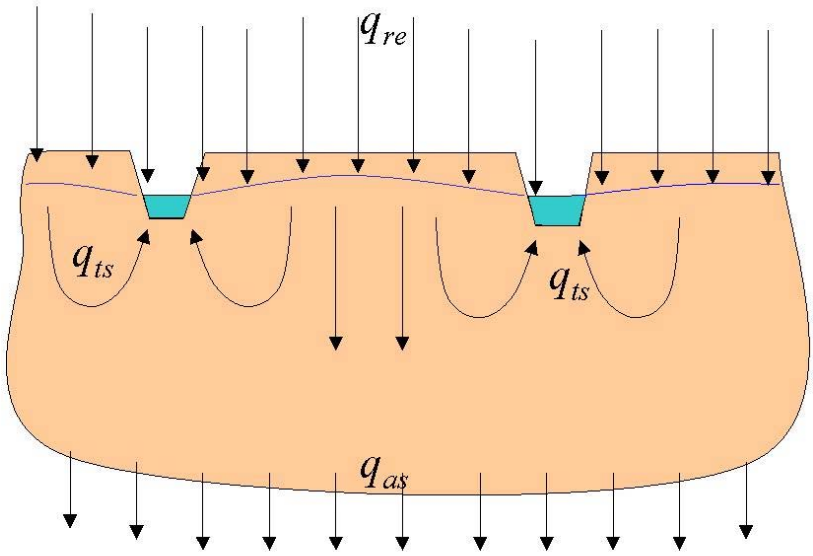

Figure 13. Scheme of the Top-system.

In principle, LGM can be applied for non-stationary flow situations, but in the present and previous studies steady conditions have been assumed. The recharge data represent recharge from the year 1988, which is considered to be a rather ‘wet’ year. Model parameters such as aquifer transmissivities and aquitard resistance have been calibrated on measured head data (Leijnse and Pastoors, 1996).

5.4 Solute transport model

The next modelling step concerns the nitrate transport. The LGM-package includes the solute transport module LGMCAD (Uffink, 1996, 1999). LGMCAD uses the particle tracking technique, which means that during the calculating process particles are introduced in the aquifer. The particles are characterised by several time dependent attributes, such as x, y and z co-ordinates and a (solute) mass m, here representing a certain amount of dissolved nitrate. The model calculates the displacement and mass changes for each particle separately. The particle displacement consists of a deterministic component that describes advective transport and a stochastic component that accounts for the dispersive transport. More information on this modelling technique and its application in LGMCAD is found in Uffink (1990) and Kinzelbach and Uffink (1991).

The main input data for the transport model are the (3D) groundwater velocity distribution for the aquifer and the nitrate fluxes at the upper boundary. The groundwater velocity distribution is provided the groundwater flow module (LGMFLOW). Nitrate fluxes at the phreatic surface have been generated with the leaching model STONE. Observations show that in the vertical direction steep nitrate concentration gradients occur. To retain such gradients in the simulation, special attention is required to the simulation of vertical mixing processes. Numerical dispersion should be avoided by all means, since it would destroy all vertical resolution. The random walk particle technique is an effective procedure in this respect, since numerical dispersion is absent. Small vertical dispersivity values are used.

As stated earlier, nitrate transport in the aquifer can only be simulated when information is available on the amount of nitrate entering the aquifer from the unsaturated zone. This information forms the upper boundary condition in terms of solute fluxes. The leaching data generated by STONE need to be pre-processed before an adequate upper boundary condition can be set up. This is due to the rather complicated situation at the upper boundary (top-system) and the fact that STONE and LGM are based on different modelling concepts for the top-system.

Schematically the situation is as follows. At the bottom of the unsaturated zone a hypothetical surface is considered, through which a downward groundwater flux $q_{re}(x, y)$ occurs. Since the groundwater flow model is stationary, this term does not depend on time. When the nitrate concentration is denoted by $c_N(x, y, t)$, the nitrate flux Φ_{re}, through this surface is the product $c_N \times q_{re}$. Note that contrary to the water flux, the nitrate flux does depend on time since the concentrations depend on time. In the absence of the drainage system the product $c_N \times q_{re}$ provides the upper boundary solute flux for the transport model. However, due to the drainage system, the actual water flux into the system, may be reduced to q_{as} , as given by eq. (2), and the solute flux becomes $c_N \times q_{as}$. In fact, this product represents the coupling of the leaching

and solute transport model, since c_N is produced by STONE, while q_{as} is determined by LGM. However, in the leaching model the situation is more complicated since it describes not only the unsaturated zone, but also part of the saturated zone and thus part of the drainage system. Further, instead of the (stationary) hypothetical surface considered in the groundwater we have a fluctuating phreatic surface. Since the model concepts that are used are essentially different, it is not directly clear what depth must be chosen to couple the two models. In the present study we use the STONE data at the so-called GHG-level (mean highest groundwater head). This level is a standard depth for the STONE output. Overestimated nitrate flux may be expected when these data are used, since nitrate concentrations demonstrate a rapid decrease with depth between GHG-level and GLG-level (mean lowest groundwater head). Even directly below GLG-level a rapid decrease of nitrates occurs. Overbeek et al. (2001b) have reported a nitrate reduction with 20-25% in the first 0,5 meter below GLG. The overestimation in the nitrate flux may be compensated when a reduction factor or zero-order denitrification concept is included in the denitrification module. This is described in more detail in Chapter 6.

6 Denitrification

6.1 General

Denitrification in the unsaturated zone and the upper zone of the aquifer is quite well documented (Mariotti, 1986; Hiscock et al., 1991; Korom, 1992). Also a substantial denitrification is known to occur in the deeper zones of the aquifers, although the latter has been less frequently reported (e.g. Lawrence and Foster, 1986). Nitrates are generally found to be relatively stable in aerobic groundwater. However, as oxygen is consumed, nitrate may become the source of energy for microbial life. Subsequently, the nitrate content is reduced. On many places where, based on conservative transport, nitrate is expected, it appears to be absent or the concentration has decreased to a level that can not be explained by dilution or dispersion only. Although at present the theoretical mechanism of denitrification is rather well understood, at field situations there is little information on where, when and at what rate denitrification can be expected.

Denitrification refers to the reduction of nitrate first to nitrite and finally into N_2. The process takes place through mediation of bacteria. Generally, the bacteria are assumed to be present always and everywhere in the aquifer. Normally the bacteria use oxygen for their energy supply, but in anaerobic conditions they switch to an anaerobic metabolism using nitrates. Besides anaerobic conditions the presence of an electron donor is required, which can be either organic or inorganic. Furthermore, the bacterial activity is dependent on temperature and pH. In practice, the presence of the electron donor appears to be the limiting factor for the occurrence of denitrification. Usually the electron source consists of organic material. Inorganic denitrification (e.g. by pyrite) also occurs, but is less common (Hiscock et al., 1991).

Indicative for the occurrence of denitrification is, besides the low oxygen content, a high sulphate content in case of pyrite-oxidation (Kölle et al., 1985), while bi-carbonates contents are increased in case of organic denitrification (Trudell et al., 1986). In the case of reduction of pyrite usually sharp nitrate fronts are found. Therefore, it may be concluded that denitrification by pyrite occurs almost instantaneously. Denitrification based on reduction of organic material is a much slower process. According to Van Beek et al. (1994) this is due to the slow rate at which organic material becomes available to the bacteria. The greater organic molecules cannot be used directly by the bacteria and first must be transformed into smaller ones. According to Van Beek this so-called decomposition process may be described as a first-order decay process. In that case, it may be modelled by an exponential function of the travel time $\exp(-\lambda t)$. Strictly speaking the decay rate λ rather reflects the rate of decomposition than the denitrification itself. An alternative decay parameter is the half-life

time, $T_{½}$, which expresses the time needed to reduce the initial concentration by a factor ½. Half-life time and decay rate are related by

$$T_{½} = \frac{\ln 2}{\lambda} \approx \frac{0.7}{\lambda} \tag{3}$$

Especially in artificial denitrification projects the biodegradation process has been studied intensively. Artificial denitrification is a technique where on purpose nitrates are added to the groundwater in order to stimulate the bacteria in their degradation process. In those cases the final objective is to reduce the amount of organic contaminants. Often, in these studies the kinetics are described by the so-called Monod equation, which is of the following form:

$$\frac{dc}{dt} = -a\frac{c}{K+c} \tag{4}$$

where *K* and *a* are constants. Mathematically, this non-linear equation is difficult to model, but for low concentrations ($c \ll K$) it may be approximated by a first-order (exponential) equation (Bekins et al., 1998):

$$\frac{dc}{dt} = -\frac{a}{K}c \tag{5}$$

For higher concentrations, however, the first order approximation leads to an overestimated nitrate reduction.

6.2 Implementation

A first order decay process is easy to implement in a solute transport code that applies particle tracking. Uffink and Römkens (2001) have obtained experience with the exponential denitrification model. It appeared that results obtained with a single decay parameter (no zones) were not satisfactory. Therefore a spatial (zonal) distribution of the parameter was proposed. At first a constant ‘background’ value is assigned everywhere in the aquifer system. This value is changed in a zone of 5 metre directly above and beneath the major clay-layers (aquitards) and in the direct vicinity of local streams and rivers. The reasoning behind this approach is that in these zones more organic material is present and therefore a higher denitrification capacity may be expected. For instance Meinardi (1999) has observed in a study area in the Achterhoek (Hupsel) that denitrification occurs when the deep groundwater is in contact with the clay inclusions at the base of the aquifer. The decay-parameters found by Uffink and Römkens, expressed as half-life times, are ranging from 200 to 2000 days.

In the present transport model, besides a first order decay, an additional type of denitrification has been implemented. Directly after the groundwater (and nitrate) has entered the aquifer an

instantaneous nitrate reduction is considered to occur. This is referred to as the zero-order nitrate reduction. As the groundwater continues its path into the deeper zones, nitrates further decrease according to the exponential first-order equation.

An example of nitrate reduction in time is given in Figure 14. The graph presents the mass change from the moment a particle infiltrates into the aquifer. The moment of infiltration is taken as *t=0* , while the initial mass is M_0 . Further, we assume that the aquifer consists of two zones A en B with decay-rates λ_A and λ_B , respectively. During simulation, the actual moment of infiltration and particle mass is determined from the leaching data. After time *t* the particle has travelled through zone A during an interval τ_A, and through zone B during τ_B, where $t = \tau_A + \tau_B$. Then, we may write for the particle mass at time *t:*

$$M(t) = M_0 \, \varepsilon \exp(-\lambda_A \tau_A - \lambda_B \tau_B) \tag{6}$$

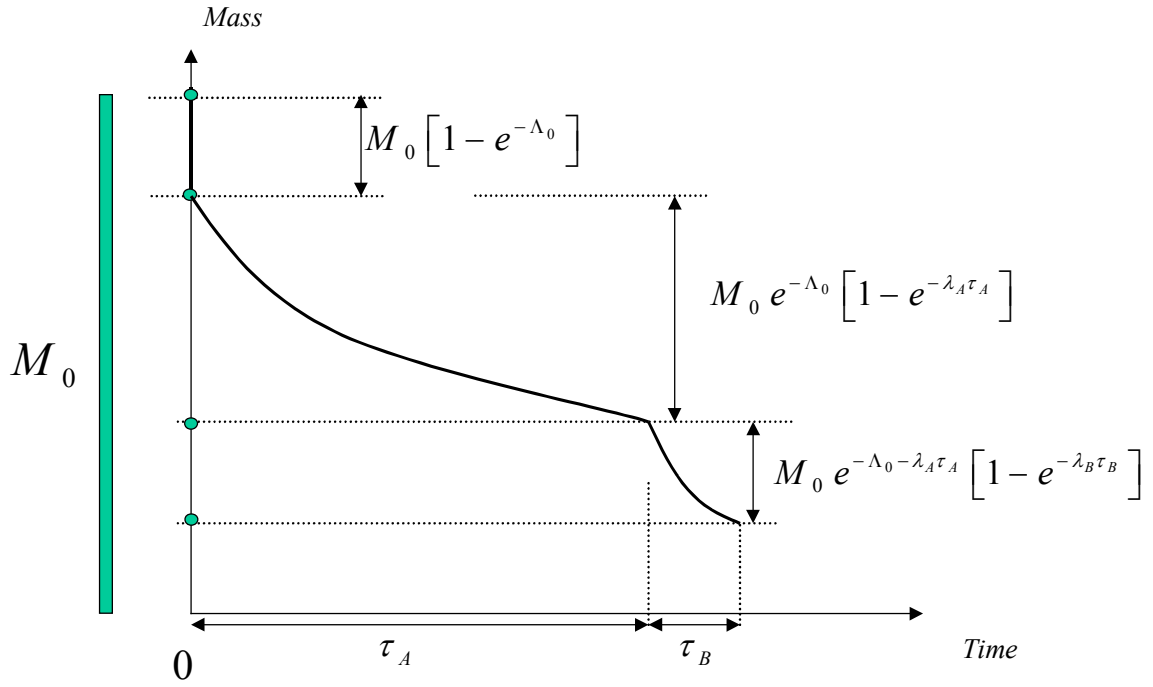

Figure 14. Changes of particle mass, during transport.

The reduction coefficient ε ($\varepsilon < 1$) represents a rapid nitrate reduction right before the particle enters the saturated groundwater. To stay in line with the first-order notation we may write this as:

$$\varepsilon = \exp(-\lambda_0 \tau_0) \tag{7}$$

where λ_0 is a (high) denitrification rate that is supposed to occur in a very short time τ_0. The concept of a zero order denitrification implies that the product $\tau_0\lambda_0$ remains constant when $\tau_0 \to 0, \lambda_0 \to \infty$. So, with $\Lambda_0 = \tau_0\lambda_0$ this leads to:

$$M(t) = M_0 \exp(-\Lambda_0 - \lambda_A\tau_A - \lambda_B\tau_B) \tag{8}$$

The concept of exponential decay has also been applied by Wendland (1992) to describe denitrification in similar aquifer types in Germany. However, the decay parameter λ should not be associated too closely with the actual denitrification processes. According to Van Beek et al. (1984) it also reflects the decomposition process of the organic material. This also means that its value may not be derived directly from soil-parameters. So far, values can best be guessed or, when data from measurements are available, determined by calibration techniques, as is done in the present report. Obermann (1982) has applied a reduction factor, similar to the zero order term proposed here. For the lower Rhine region in Germany factors are reported of 0.16, 0.63 and 0.70 (Haag and Kaupenjohann, 2001).

For the spatial distribution of the exponential decay rates a zonal approach is applied, which means that in the model area two zones are defined. One zone covers a default or background zone, where the decay rate is considered to be low. Then, in the aquifer system a second zone is identified, where the decay rate is expected to be higher, e.g. because it may be expected that in this zone more organic material is present. For the present study the high decay rate is applied in a layer of 5-metre thickness above and underneath the claylayer (first aquitard) and in all gridcells adjacent to rivers and minor courses of surface water. The same distribution scheme has been used in Uffink and Römkens (2001) as well as in Uffink and Mülschlegel (2002). The location of the surface water and rivers has been displayed in section 3.2, while the occurrence of the claylayers has been presented in section 3.3.

Finally, a spatial pattern emerges that in vertical direction is composed of three layers. Within each layer a regular grid with 500 x 500 m cells is defined. In each gridcell the decay rate is either equal to λ_A or λ_B. The allocation of the decay rate depends on whether a claylayer is present or not, or whether the cell is underneath a river or stream. The elevation and thickness of the middle zonal layer is directly related to the Drenthe-clay-layer. In case clay is present, the layer is defined between 5 metres above the top of the clay until 5 metres underneath the bottom. At those location where the clay is absent the actual elevation of the layer is not relevant since here no distinction between the layers exists. The upper zonal layer extends vertically from the surface to the top of the middle layer, while the lower zonal layer runs from the bottom of the middle layer to the base of the aquifer system.

Figure 15 shows schematically the vertical set-put of the layers. The distribution of the decay rate in the upper and middle zonal layer is given in Figure 16 and 17. The horizontal distribution in the lower zonal layer is identical to the upper layer.

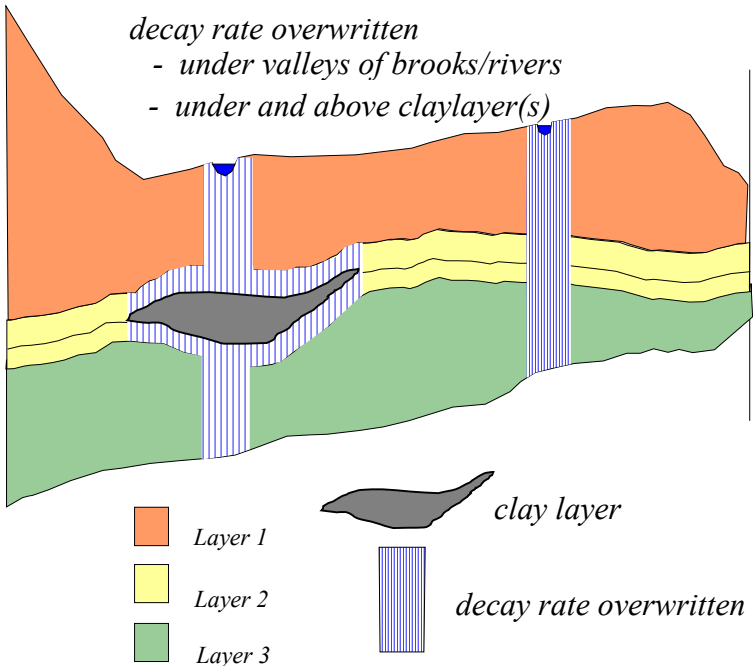

Figure 15. Schematic vertical cross-section with zonal layers.

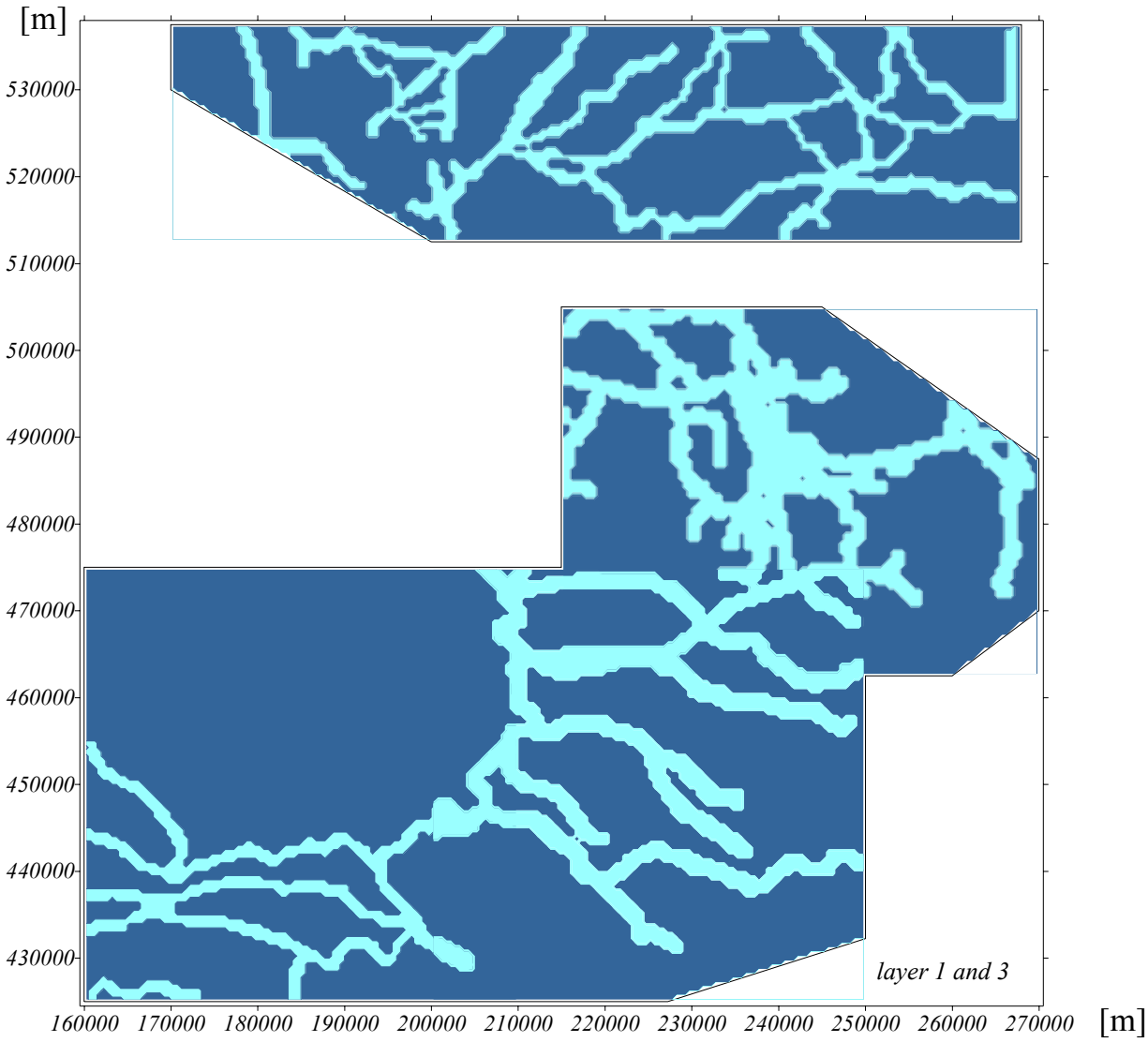

Figure 16. Zonation for calibration of decay rate in layer 1 and 3.

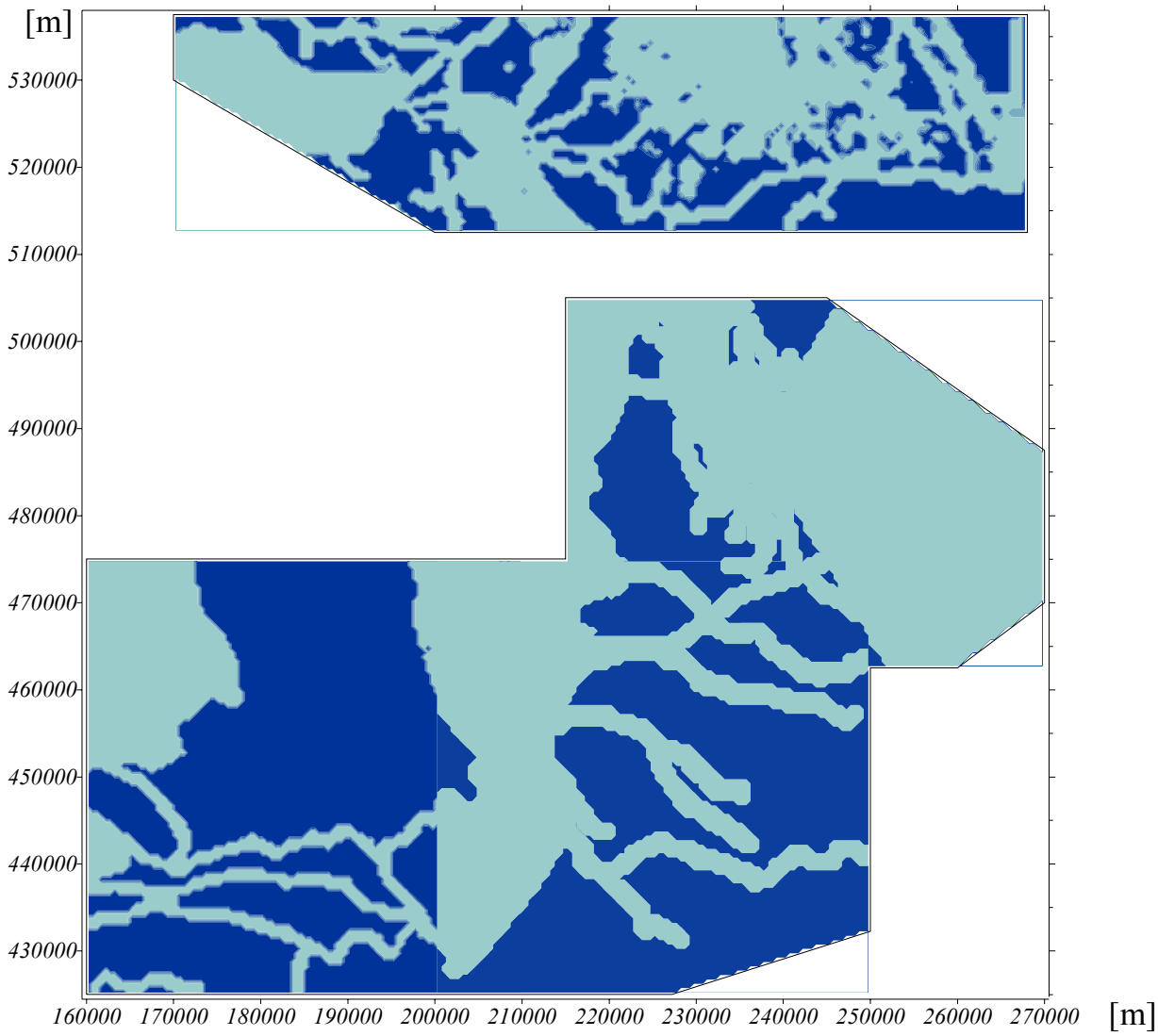

Figure 17. Zonation for calibration of decay rate in layer 2.

7 Calibration

7.1 Parameters

The parameters to be estimated during the calibration procedure are the denitrification constants Λ_0, λ_A and λ_B, as given in equation (6). In the simulation programme, however, these parameters are given in an alternative notation [see eq. (3) and (5)]:

- ε : zero order reduction term [-]
- $T_{½}^{A}$ first order decay-rate, zone A [T]:
- $T_{½}^{B}$ first order decay-rate, zone B [T]

In this pilot study nine pumping stations have been selected (sect 4.2, Figure 12). For each selected pumping station a separate calibration exercise is performed using nitrate measurements from the monitoring wells located in a 20×20 km^2 area around the pumping-station and the breakthrough data from the pumping well itself. Hence, for each pumping station a separate set of the parameters given above is obtained. These parameter values are representative only for the area around the pumping station. Note that the monitoring wells do not exclusively lie inside the capture zone and, consequently, the representative area is not restricted to the capture zone.

7.2 Log transform of concentrations

During a calibration procedure the unknown model parameters are varied, while for each set of values the match between measured data and model outcomes is examined. The parameters that yield the 'best' match between model results and measurements are considered as the best estimates. Calibration has been applied successfully to estimate the aquifer transmissivities and hydraulic resistances of aquitards for the groundwater flow model (LGM) for the Netherlands (Leijnse and Pastoors, 1996). Leijnse and Pastoors used observed groundwater heads for their calibration. For the present problem observed groundwater heads are useless, since the unknown denitrification parameters do not affect groundwater heads. For the present calibration exercise the most adequate data consist of measurements of groundwater nitrate concentrations. The user still is still free to choose in what way measured and observed data are expressed, e.g. linear or logarithmic.

The magnitude of the measured nitrated values varies within a wide range. Therefore, a calibration based on the ratios between predicted and measured concentration (or differences of the logarithms of the concentrations) makes more sense than using the concentration

differences directly. The effect of the log-transform is best illustrated by the simple example. Consider two monitoring wells A and B. In well A measured and calculated concentrations are, respectively 102 and 103, while in well B measured and calculated concentrations are 2 and 3. When the difference between measurements and model values to determine the goodness of the match, it appears that the match is equally well for both wells. However, when we want to expressed that at well A the calculated value is less than 1% off, while at well B the model outcome is 50% larger than the measured value, we need to consider logarithms of measured and calculated values. In general, if one is interested in relative errors rather than absolute errors it is more natural to consider the logarithm of the model outcomes and measurements. In this study we consider the log-transformed concentrations, since we are dealing with a wide range of concentration values and a relative error seems more relevant than an absolute error:

$$Y_i^m = \ln c_i^m \tag{9}$$

$$Y_i^c = \ln c_i^c \tag{10}$$

Superscript *m* (measured) and *c* are used for observations and calculated values, respectively. The index *i* denotes an individual measurement, while c_i^c represents the calculated concentration at the place and time of the i^{th} measurement. The difference between measured value and model outcome at location *i* is known as the residual. During the calibration procedure an objective function *E* is optimised, which is defined as the sum of the weighted (squared) residuals:

$$E = \sum_{i=1}^{N} \gamma_i \left(Y_i^m - Y_i^c \right)^2 , \tag{11}$$

where γ_i denotes a weight factor and *N* is the total number of observations. Weights may be used to express the importance of an observation with respect to the rest of the measurements. Weights may be used in various ways to control and manipulate the calibration process. For instance if one wants to exclude a particular observation from it calibration process, either temporarily or permanently, this can be achieved by a weight factor of zero. The objective function *E* may be optimised by techniques such as Gauss-Marquardt-Levenberg method. For further details see e.g. Cooley (1983) or Hill (1992).

7.3 Software

Calibration is performed with the programme PEST (Parameter Estimation). PEST is a model independent parameter optimisation programme developed by Doherty of Watermark Computing (Doherty and Johnston, 2003). It is widely used in several fields including the

field of groundwater flow. It uses a non-linear optimisation technique, based on the Gauss-Marquardt-Levenberg method. Various versions of PEST exist, both commercial and free (but limited) versions. In this study a freeware version has been used that runs on a DOS platform. (Anonymous, 1994). The groundwater nitrate transport simulations, however, are running on UNIX machines. Several tools and scripts have been written to handle command switches between the PC and UNIX machines. The advantage of the use of PEST is that the simulation programme itself does not have to be modified to perform the calibration. A disadvantage is that the programme PEST is used as a 'black box'. For instance, intermediate results of the calibration process, such as the sensitivity matrix, are not given as output and remain inaccessible. In the present study e.g., the sensitivities would have provided useful information to obtain a stable calibration procedure (see 7.4).

7.4 Procedure

Preliminary runs showed that calibration based on breakthrough data alone did not lead to a unique set of decay-parameters. When only the breakthrough data are used a so-called ill-posed problem arises. The system becomes better defined, when –in addition to the breakthrough data– measurements from the monitoring wells are included. Problems due to the 'ill-posed-ness' may be circumvented by using a step-wise calibration procedure. At each step only a single parameter is free to be varied, while the other are kept constant. Only observations are used with a high sensitivity to the free parameter. For this approach information on the sensitivity matrix would be helpful. As mentioned above, PEST does not provide this information. As an alternative, observations have been selected based on a more intuitive argument. This has led to the following step-wise procedure.

- Step 1. First, a calibration run is performed without the breakthrough data using only monitor well measurements from the shallow filters. Switching off the breakthrough data can be realised easily by setting the weights equal to zero. The purpose of the first run is to calibrate the zero-order decay term. The nitrate levels measured at shallow depth are the most affected by the zero-order parameter, since the residence times are still relatively short and the first-order decay has not been active very long. In this step, only the zero-order and one of the first-order (the fast one) are allowed to vary. The slow exponential decay is set at a constant value ($T_{½}^{A}$ is 5000 days).
- Step 2. Accordingly, the zero-order reduction parameter is frozen at the level found in step 1. Both shallow and deep monitoring data are included, while we calibrate only the two exponential decay parameters. The results of this run are given in the appendix.
- Step 3. All observations are included. In the final step all parameters are allowed to vary, but the ratio between $T_{½}^{A}$ and $T_{½}^{B}$ is kept constant at the value found in step 2.

8 Results

8.1 Calibration results

The transport model LGMCAD combined with PEST has been applied for a 20×20 km^2 area around each selected pumping station. The Figures 18 to 26 give the location of the monitoring wells and capture zone of the pumping station projected on a map of the zonal distribution of the decay parameter. The figures at the left-hand side give the zonal distribution of the layers 1 and 3 (upper and bottom layer), while at the right-hand side figures show the zonation in layer 2 (middle layer). Note that the middle layer encloses the clay-layer (aquitard). The zonal distribution in this layer only differs from the one in the top layer at the places where the clay layer indeed exists. For each pumping station a set of parameter values has been obtained. The final results are given in Table 2. For the pumping station **Putten** the final denitrification values could not be obtained. In principle it may be concluded that at **Putten** no denitrification occurs. The model residuals for the pumping well data remain positive, even for extremely high values of the half-life time (very slow denitrification) and a zero-order reduction factor equal to 1.0. In terms of nitrates a positive residual says that model result shows less nitrate than is observed in the real system. In fact, when the zero-order reduction factor is not bounded by an upper limit of 1.0, a value of 1.4 is obtained. This may be an indication that nitrate fluxes are underestimated, while it also demonstrates that the instantaneous (zero-order) reduction does not occur here. At pumping station **Klooster** the values for the two zones appear to be essentially the same. For an explanation refer to Figure 21. In this figure it is seen that most of the shallow monitoring filters and the entire capture zone of the pumping wells are located in one and the same zone (zone *A*). Only a few monitoring wells are located in zone *B*, but very near to the border between the two zones. Note that the exact borders are drawn somewhat arbitrarily. Therefore, for this particular part of zone *B* a really faster decay parameter is not likely. It may be concluded that this area in fact belongs to zone *A*. At the pumping station **Coevorden** the breakthrough data for nitrate are extremely low. Almost all nitrate appears to be removed by denitrification (see also sect. 8.4). The calibration procedure results in a zero order reduction rate of 5%. However, it is doubtful whether this is a realistic, physical value. A final set of half-life times could not be obtained here.

Table 2. Final Calibration Results.

	Slow-zone ($T_{½}^{A}$) [days]	Fast-zone ($T_{½}^{B}$) [days]	Zero-order (ε)
De Pol	**4468**	**3017**	**0.37**
Archemerberg	**4063**	**2804**	**0.71**
Herikerberg	**1801**	**421**	**0.59**
Klooster	**2612**	**2487**	**0.17**
Dinxperlo	**2492**	**843**	**0.22**
Nijverdal	**2207**	**64**	**0.41**
Wierden	**5075**	**634**	**0.29**
Putten	*(>20000)*	*(>20000)*	*(>1.00* **)**
Coevorden			< 0.05

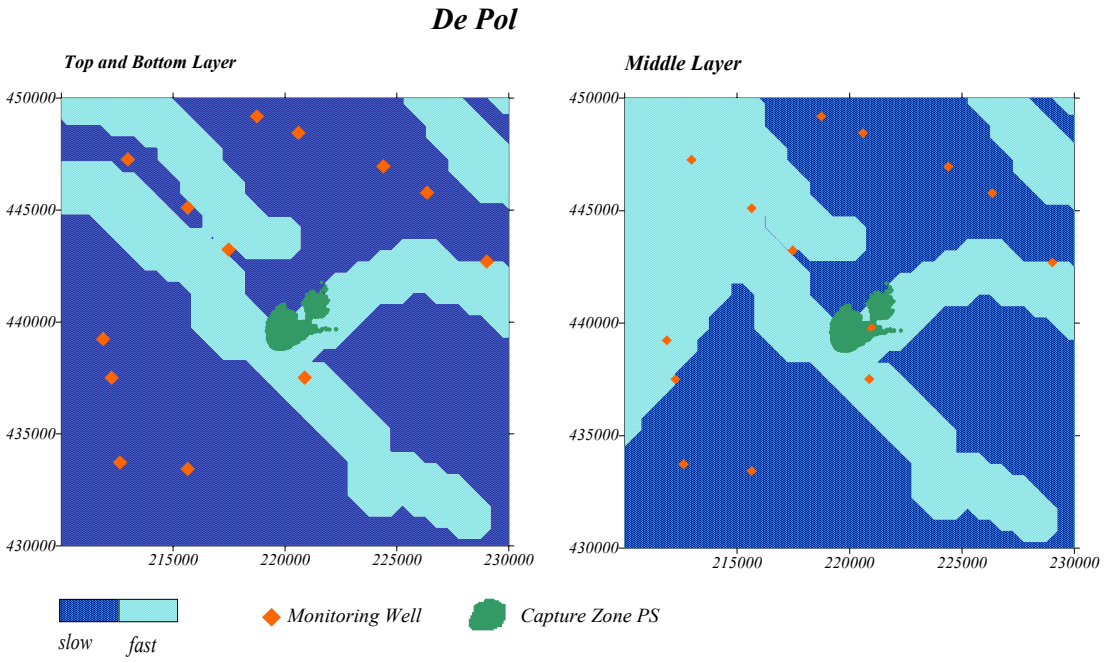

*Figure 18. Location of monitoring wells and capture zone for pumping station **De Pol** with zonation of denitrification parameter as background.*

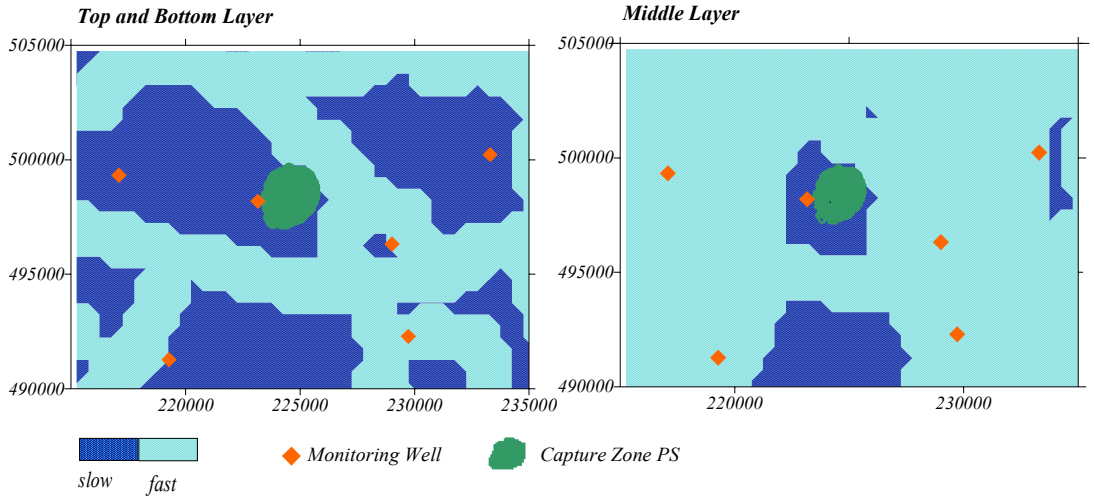

*Figure 19. Location of monitoring wells and capture zone for pumping station **Archemerberg** with zonation of denitrification parameter as background.*

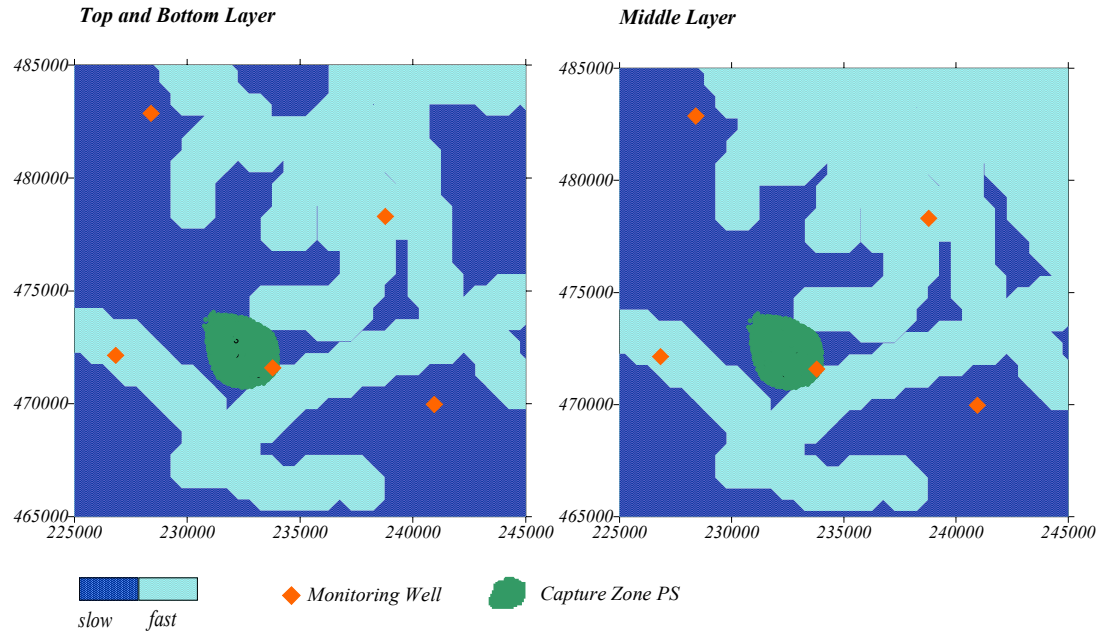

*Figure 20. Location of monitoring wells and capture zone for pumping station **Herikerberg** with zonation of denitrification parameter as background.*

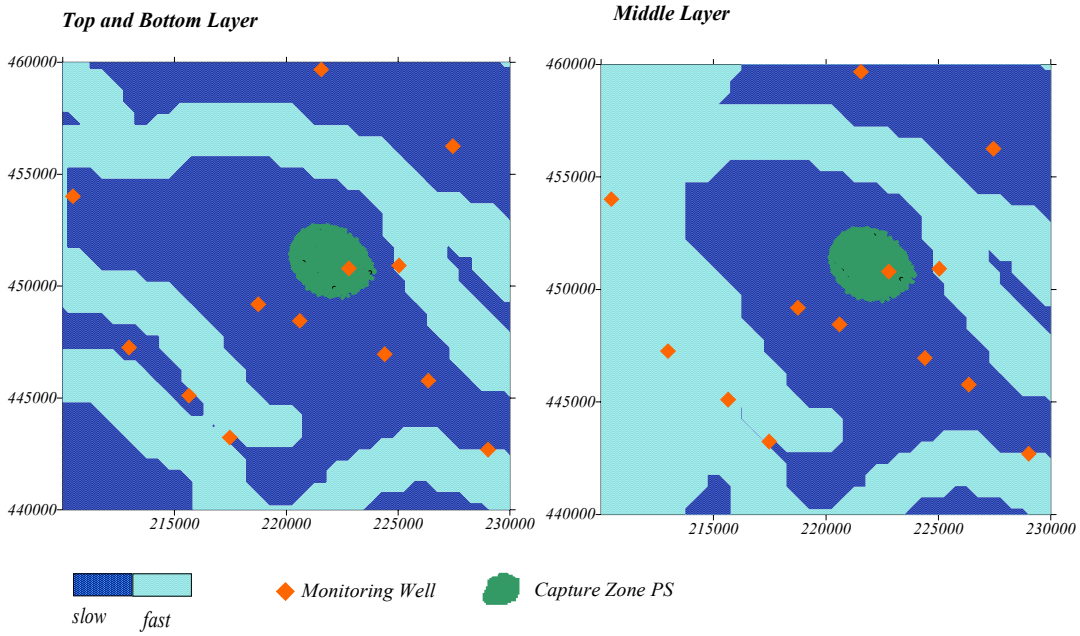

*Figure 21. Location of monitoring wells and capture zone for pumping station **Klooster** with zonation of denitrification parameter.*

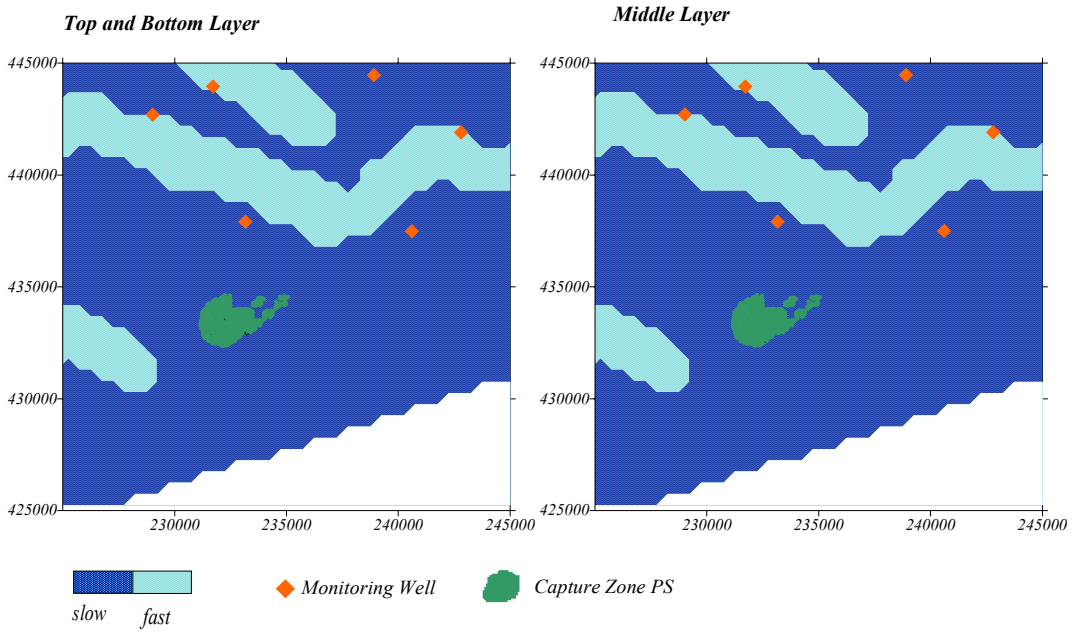

*Figure 22. Location of monitoring wells and capture zone for pumping station **Dinxperlo** with zonation of denitrification parameter.*

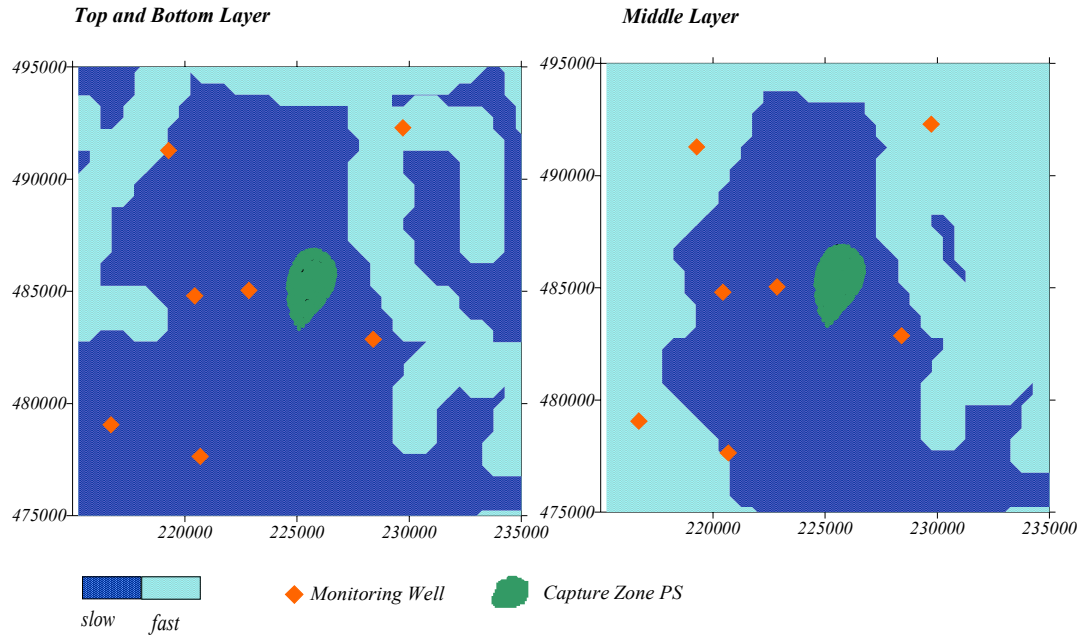

*Figure 23. Location of monitoring wells and capture zone for pumping station **Nijverdal** with zonation of denitrification parameter.*

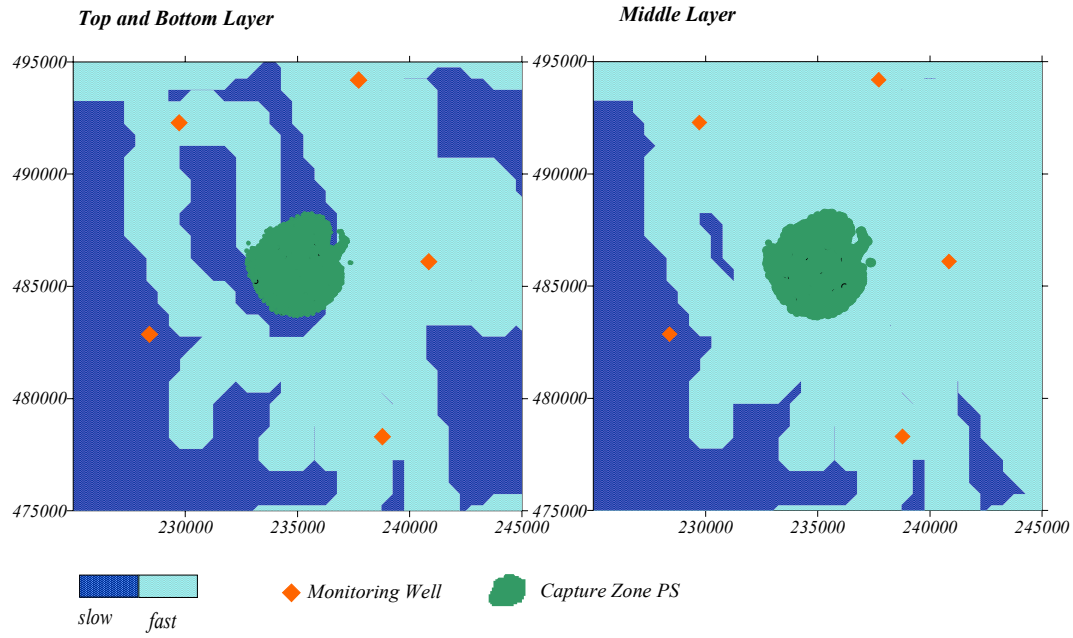

*Figure 24. Location of monitoring wells and capture zone for pumping station **Wierden** with zonation of denitrification parameter.*

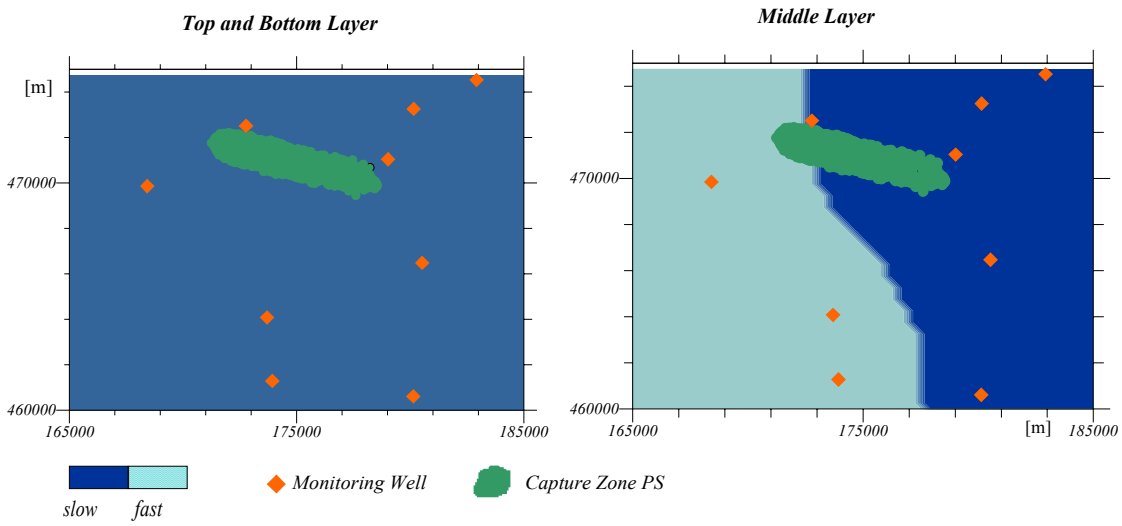

*Figure 25. Location of monitoring wells and capture zone for pumping station **Putten** with zonation of denitrification parameter.*

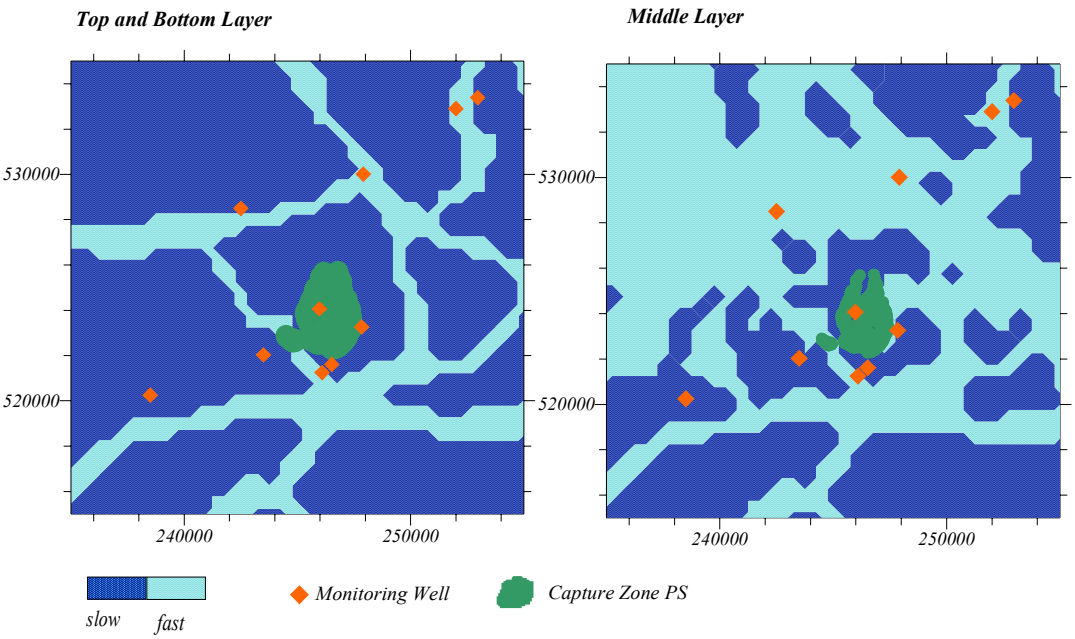

*Figure 26. Location of monitoring wells and capture zone for pumping station **Coevorden** with zonation of denitrification parameter.*

8.2 Uncertainty

An indication for the parameter uncertainty can be obtained from the confidence limits. The 95% confidence limits, as calculated by PEST, are given in Table 3. Note that these limits are based on the assumption that the probability distribution of the parameters is normal and the model is linear. Clearly, this assumption is not satisfied and consequently, at several cases the limits have physically impossible values (negative half-life times and negative reduction factors). Nevertheless, as a rough indication for the measure of uncertainty one may take the ratio between the bandwidth (difference between upper and lower limit) and the parameter value. For most cases shown in Table 3 the bandwidth is approximately two times the parameter itself.

At pumping station **Dinxperlo** the uncertainty appears to be much higher than average for the half-life time in zone B ($T_{½}^{B}$), while at the same time the uncertainty for $T_{½}^{A}$ is considerably lower. An explanation may be obtained by examining Figure 22. It appears that most of the monitoring wells and the entire capture zone are located in zone *A*. Therefore, the value of $T_{½}^{B}$ is not likely to affect the model results. This lack of sensitivity translates to a wide bandwidth for this parameter. A similar argument holds for the situation around pumping station **De Pol**.

In general the uncertainty in the parameters is quite large. In this respect it must be mentioned that the parameter uncertainty not only reflects the reliability of the observations. It also leads back to the incompleteness of the model concept and to the uncertainty of other model parameters and input data. For instance, the groundwater model has been treated as a steady state system. However, over the simulation period (from 1950 to 2000) the actual hydrological situation around the pumping stations has not been constant. This is best seen from the development of the abstraction rates of the pumping stations in the Figure 10 and 11. Further, nitrate fluxes that enter the aquifer represent long time averages. Therefore, seasonal variations, –still present in the shallow monitoring data– are absent in the model results. Another source of uncertainty is related to the transmissivities and hydraulic resistances used in the flow model. These parameters have been calibrated with head measurements. It has been mentioned earlier that groundwater heads do not depend on the denitrification parameters. Conversely, the nitrate concentrations **do** depend on the transmissivities and hydraulic resistances. An integrated calibration procedure to obtain hydraulic parameters and denitrification constants simultaneously should be preferred, but this is still quite an ambitious exercise. A similar argument hold for the nitrate leaching data as provided by the model STONE. Finally, a source of uncertainty exists that is inherent to the technique used for the solute transport simulation. The simulation is done by the random walk method, which introduces particles that are tracked through the system. The particle motion equations consist of a deterministic and a stochastic component. Due to this stochastic component, always some ‘noise’ exists in the model outcomes. Using a large number of particles can reduce the level of

noise, but this increases computational time. Therefore, in general a certain amount of 'noise' is always accepted.

Table 3. The 95 % Confidence Limits

De Pol	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε)
lower limit	2310 days	1560 days	0.08
value	**4468** days	**3017** days	**0.37**
upper limit	6626 days	4474 days	0.66

Archemerberg	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε)
lower limit	2713 days	1872 days	0.15
value	**4063** days	**2804** days	**0.77**
upper limit	5413 days	3735 days	1.4

Herikerberg	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε)
lower limit	646 days	199 days	0.40
value	**1802** days	**421** days	**0.59**
upper limit	2952 days	642 days	0.79

Klooster	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	1769 days	1687 days	-0.37
value	**2612** days	**2487** days	**0.17**
upper limit	3454 days	3287 days	0.72

Dinxperlo	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	2028 days	-2623 days	-
value	**2492** days	**843** days	**0.22**
upper limit	2956 days	4309 days	-

Nijverdal	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	-2377 days	-69 days	-0.07
value	**2207** days	**64** days	**0.41**
upper limit	6791 days	197 days	0.89

Wierden	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	494 days	62 days	-0.18
value	**5075** days	**634** days	**0.29**
upper limit	9655 days	1206 days	0.75

Putten	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	- days	- days	-
value	- days	- days	-
upper limit	- days	- days	-

Coevorden	Slow-zone ($T_{½}^{A}$)	Fast-zone ($T_{½}^{B}$)	Zero-order (ε_0)
lower limit	- days	days	-0.18
value	- days	- days	**0.05**
upper limit	- days	days	0.75

8.3 Spatial distribution

With respect to the spatial variation the logarithm of the half-life time $T_{½}$ is considered rather than the parameter itself. The logarithm of the parameter is a more natural quantity to examine, since $T_{½}$ should be a non-negative quantity. For the so-called slow-zone (zone *A*) an average half-life time ($T_{½}^{A}$) of 2745 days is found with a 65% interval ranging from 1680 to 4450 days. This is slightly higher than the range from 3 to 5 years as reported by Uffink and Römkens (2001). The difference may be due to the fact that Uffink and Römkens did not include a separate zero-order denitrification concept.

The decay zone *B* (fast decay-zone) yields a mean value for $T_{½}^{B}$ of 745 days and a 65% interval ranging from 225 to 2470 days. When pumping stations De Pol and Klooster are excluded – at these locations the fast zone is not essentially different from the slow-zone - one obtains a mean value of 495 days and a range between 165 and 1485 days. Uffink and Römkens reported for this zone a value ranging from 1 to 2 years.

The ‘instantaneous’ denitrification, which is supposed to occur in the region near the phreatic surface, is a complicated factor. Besides a real physical process the factor represent also a compensation for a potential overestimation of the nitrate-input rates at the phreatic surface. Overbeek et al. (2001b) already pointed out that for dry sandy areas the leaching model STONE gives a 30% higher nitrate flux than similar models. One must be aware that all potential errors in the nitrate fluxes eventually end up in the zero order reduction term. Therefore, a direct physical interpretation of the reduction factor must be avoided. The average value for ε amounts to 0.47 with a 65% range between 0.14 and 0.80. With respect to the average figure of 0.47 it is remarkable that Uffink and Mülschlegel (2002) mention a reduction factor of 0.4 to be applied when nitrate fluxes generated by STONE are compared to fluxes obtained by Van Drecht (1993) and Boumans and Van Drecht (1998).

8.4 Match of observed and calculated breakthrough curves

For a few pumping stations the final simulated breakthrough curves are given together with the measured data (Figures 27 to 31). Several comments can be made on these graphs.

- ***Herikerberg.***
  The graph in Figure 27 gives both the raw water data (untreated water) and purified water data. Since the year 1992 data from both measuring programmes are available. For Herikerberg, the nitrate contents of the treated and untreated water are clearly substantially different. Apparently during the purification process nitrates are removed. For the calibration process the LMD data have been discarded and only the data on untreated water have been used

- ***Dinxperlo.***
  The breakthrough curve for Dinxperlo is given in Figure 28. With respect to the measured data there seems to be no systematic difference between the data for raw water and purified water. Therefore, there is no reason to discard the data on treated water. A considerable increase of the nitrate concentration is observed after 1993 in both data sets. However, this sudden rise is not visible in the simulation data. The final set of calibrated parameter values is clearly a compromise. The calibrated model overestimates the early measurements and underestimates later time measurements.

- ***Archemerberg.***
  As can be seen on Figure 29, the curve of the measured nitrates is growing more rapidly than the calculated one. This may be the effect of the variation of the well discharge. From Figure 29 can be seen that before the year 1970 the overall rate of abstracted water in the area Twente was considerably less than the present level. Although it is not certain whether this is the right explanation, the earlier time measurements (i.e. before 1985) have been given a lesser weight that the more recent ones.

- ***De Pol.***
  Over the period where measurements on both treated and untreated water are available no systematic difference between the data is observed (Figure 30). When the data on treated water are considered it appears that the nitrate content suddenly rises in the late seventies, while they continue to drop after 1988. This fluctuating behaviour is not found in the simulation data. Again, the optimised values are compromises. When e.g. the measured values before 1978 are discarded higher denitrification rates (or lower half-life times) would be found.

– ***Putten.***
Model results and measured data for the pumping station Putten are given in Figure 31. At this pumping station no purification treatment is applied and all measured data refer to the untreated water. Even when all denitrification processes are switched off, the model results remain below the measurements, as can be seen from the graph. As mentioned earlier in section 8.1, a possible explanation for the mismatch may be an underestimation of the nitrate fluxes. Additional information about the fit between all measured and calculated data may be obtained by considering the model residuals. In Figure 32 all measurements, including the monitor data, are plotted versus the calculated data. The solid grey line indicates a perfect fit. If a data point is above the line, the model residual is positive, which means that the model result is below the observed value. It is seen that although for all breakthrough data the residual is positive, quite high negative values are found for a number of monitoring data. This suggests that denitrification may still occur, at least outside the capture zone of the pumping station.

– ***Coevorden.***
At the pumping station Coevorden very little nitrate is found both by in treated and untreated water, see (Figure 33). In fact, there is too little information in the measurements to obtain reliable denitrification parameters.

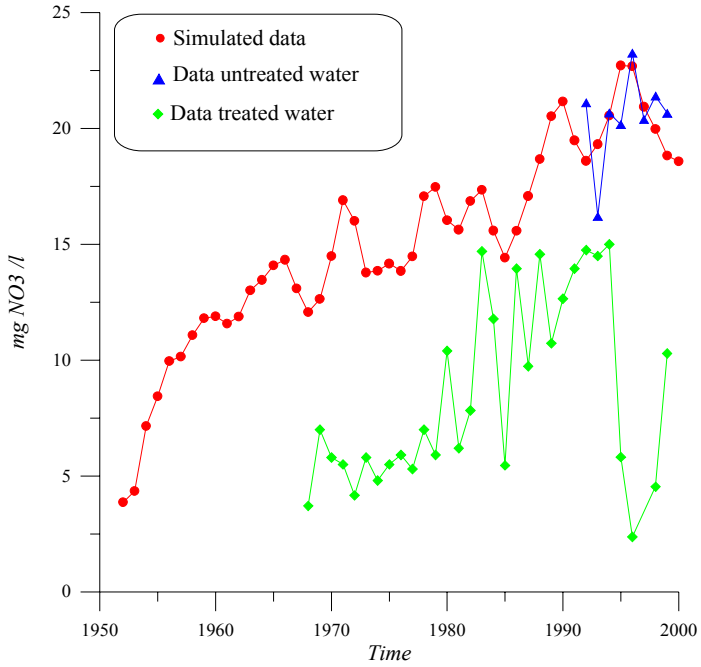

*Figure 27. Comparison of simulated breakthrough curve with measured data for the pumping station **Herikerberg**.*

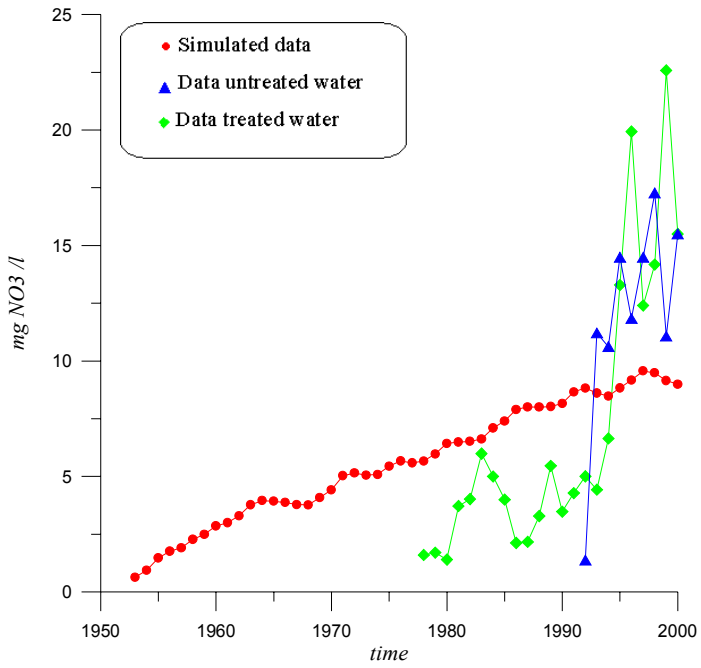

*Figure 28. Comparison of simulated breakthrough curve with measured data for the pumping station **Dinxperlo**.*

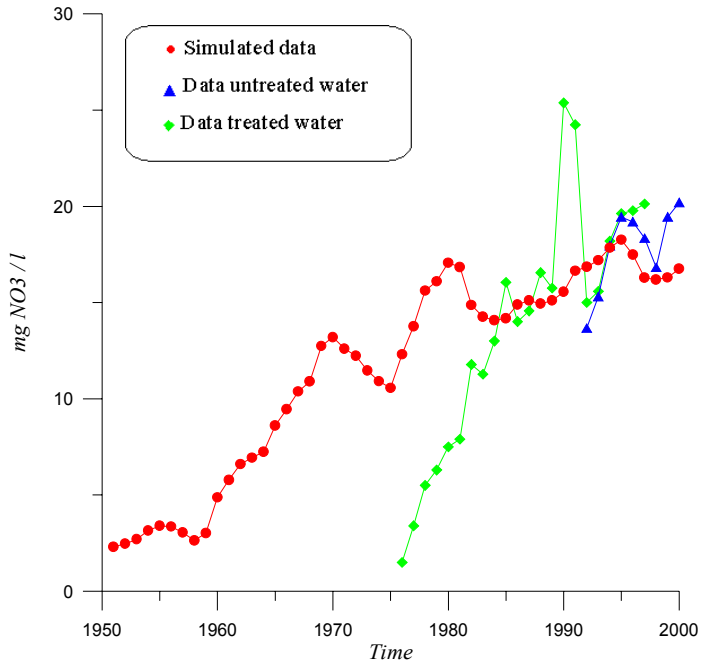

*Figure 29. Comparison of simulated breakthrough curve with measured data for the pumping station **Archemerberg**.*

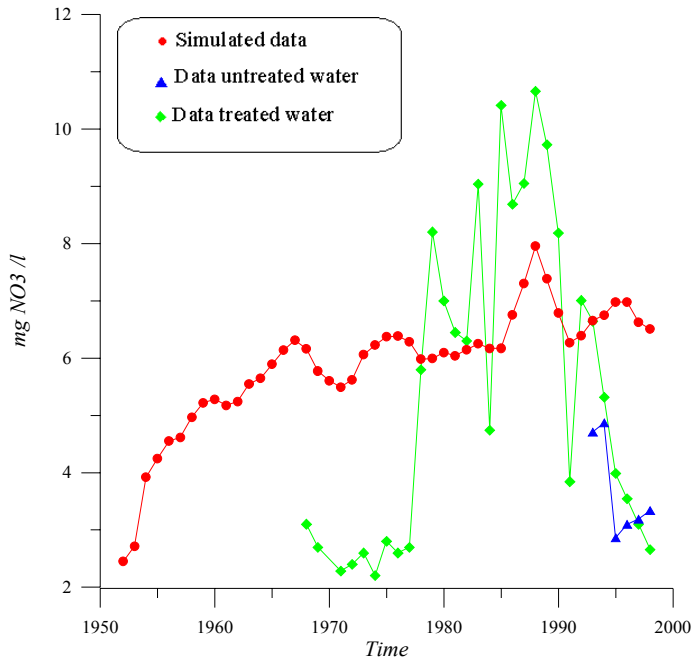

*Figure 30. Comparison of simulated breakthrough curve with measured data for the pumping station **De Pol**.*

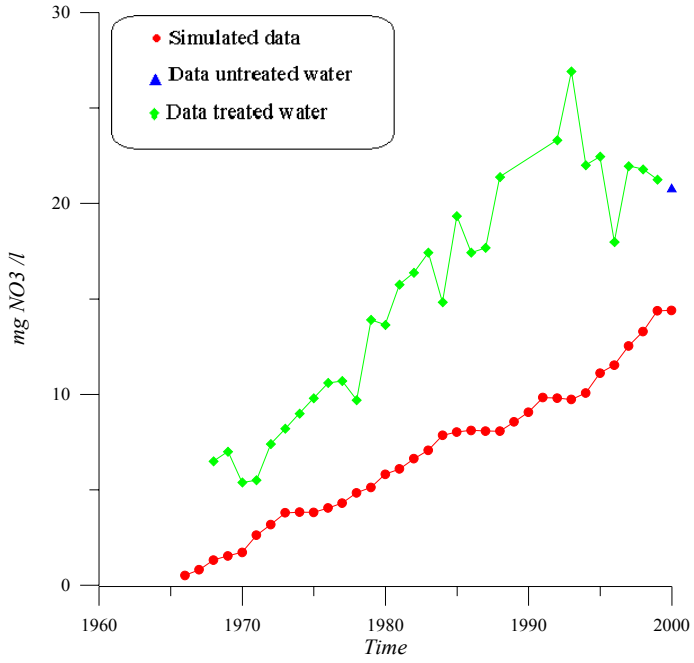

*Figure 31. Comparison of simulated breakthrough curve with measured data for the pumping station **Putten**.*

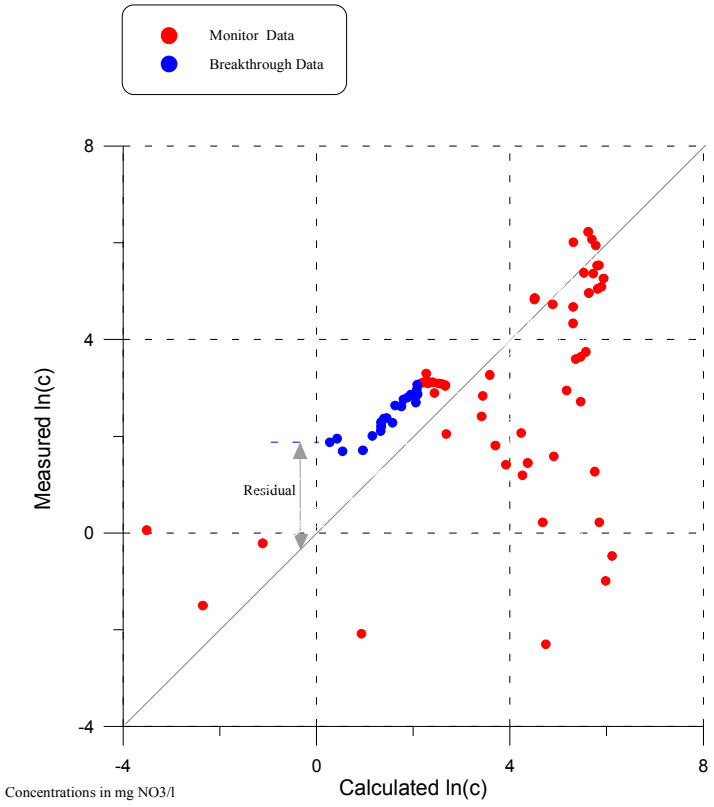

*Figure 32. Measured data versus model results for the pumping station **Putten**.*

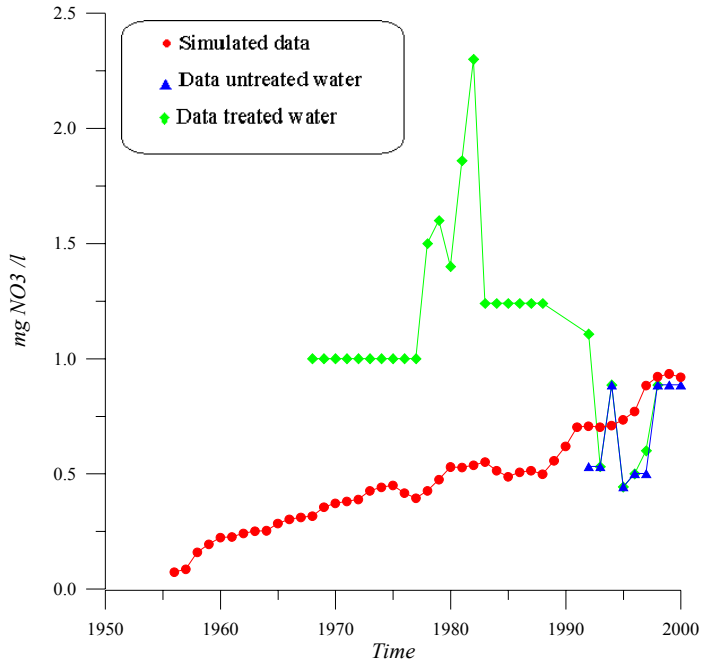

Figure 33. Comparison of simulated breakthrough curve with measured data for the pumping station ***Coevorden****.*

9 Summary and conclusions

In modelling groundwater nitrate transport, denitrification has to be taken into account. For the simulation of denitrification the proposed model concept consists of three separate processes acting at different time rates:
i) an instantaneous denitrification acting at or near the phreatic surface,
ii) a relatively fast exponential decay that takes place in a zone where organic matter is likely to be present,
iii)a relative slow exponential decay in zones where organic material is absent.

The pilot study described in this report concerns the development and testing of a calibration procedure to estimate and optimise the parameter values of these three types of denitrification. The calibration itself has been carried out with a model-independent programme PEST. During calibration, model outcomes are matched with measured data. The data used for matching are nitrate concentrations observed in monitoring wells (LMG and PMG Monitoring Networks), nitrate concentrations measured in the raw abstracted water as well as in the treated water of several public water supply pumping stations. The nine selected pumping stations are located in the central and eastern part of the Netherlands where highly permeable phreatic aquifers exist.

Nitrate measurements from the monitoring wells are representative for a small spatial area and a small time period. In practice these data can be considered as point measurements. Data taken from the water abstracted at the pumping stations represent a much larger area. In horizontal direction it corresponds to the capture zone of the pumping station. Nitrate measurements of the abstracted water (breakthrough data) are collected since 1992 by the REWAB measuring programme. The REWAB data refer to water samples taken before the purification process (untreated water) as well to samples from the purified water. Earlier data exist from water samples taken after treatment (LMD measurement programme). During the purification process no specific treatment is used for denitrification. In some cases nitrate contents before and after treatment are essentially the same. However, in other cases (e.g. at Herikerberg) a considerable difference is observed.

Nitrate transport modelling can not be carried out without information on the amount of nitrate entering the aquifer system at the phreatic surface. Actual values for this nitrate flux are not available. The present study uses nitrate fluxes that have been generated by the leaching model STONE. However, the STONE model concept differs from that of the groundwater model, both temporally and in space. Therefore, several simplifying assumptions were needed to transform nitrate fluxes from STONE to the format required for the groundwater transport model. Another important simplification is related to the groundwater flow. The groundwater flow has been treated as a steady state system. However, it is known,

for instance, that the pumping rates at the pumping stations in the model area have not been constant during the simulated period (1950-2000). These simplifications increase the difficulty of fitting model results and observations.

For the ‘instantaneous’ denitrification at or near the phreatic water table an average reduction factor of 47% has been found. This factor however, is strongly influenced by uncertainties in the generated nitrate input by STONE. For dry sandy areas for instance, these rates are reported to be 30% too high. The value found for the ‘instantaneous’ denitrification also acts as a compensation for a possible overestimation in the nitrate input. It is not possible to specify more precisely the individual contribution of an actual denitrification process and the compensation effect. For the exponential decay the parameters are expressed as half-life times. For the zones where organic matter is likely to be present – i.e. underneath courses of surface water and in the vicinity of clay layers – a mean half-life time of 495 days has been found with a range between 165 and 1485. Uffink and Römkens (2001) found a similar value for this zone (1½ year). For the slow exponential decay an average value of 2745 days is found with a range between 1680 to 4450 days. These values are higher than reported earlier (3 tot 5 years). With respect to the distribution of the slow and fast decay zone it may be mentioned that different procedure may be adopted leading to a different arrangement (layer thickness etc,) of the zones and consequently to different values for the decay parameters.

The uncertainty of the calibrated parameter values is rather high. In essence, the parameter uncertainty derived from a calibration process is a measure for the scatter of observation points with respect to the ‘optimised’ simulation results. Several factors affect the uncertainty. One factor is related to the simplifications in the model set-up. Seasonal variations are absent in the model results, since the groundwater flow system is treated stationary and the nitrate fluxes entering the aquifer have been converted to long time averages. However, seasonal variations are present especially in the shallow monitoring data. Further, the gradual increase since 1970 of the groundwater abstraction rates of the pumping stations has not been taken into account in the (stationary) groundwater model. A second source of ‘uncertainty’ stems from parameter uncertainty in the models that provided input data for the solute transport module, such as groundwater flow velocities (LGM) and nitrate fluxes (STONE). Since the uncertainty of these data is not included in the calibration process, it ends up in the final estimated transport parameters. Finally, a certain amount of uncertainty is inherent to the technique used in the transport simulation. The ‘noise’ induced by the stochastic component of the particle tracking routine can only be reduced completely by using an infinite number of particles. In practice, some statistical ‘noise’ in the simulation results has to be accepted.

Uncertainties are high, but on the other hand it is unknown what level of uncertainty is tolerable or realistic. The mismatch between observations and model results is highly related to the difference in scale that decision-makers, modellers and field-data collectors are interested in. Decision-makers are working on higher levels of abstraction and need answers from regional and national-scale models, while the majority of these models are up-scaled

models that have been designed originally for the local scale. The up-scaling procedure requires simplifications of the physical reality of the spatial and temporal variability. Obviously, we may not expect that these models produce accurate predictions for a certain time at a certain location in 3D space. Nevertheless, this is exactly what is expected when results from larger scale models are compared with local scale measurements. At present a framework that allows us to transform raw measured data into figures that are more in line with the model scale is not available. A future parameterisation and calibration of the model must rely on data derived from a statistical analysis that gives information on the representativeness of the measured data with respect to the model scale.

A more general aspect which is related to the above is the following. For long term predictions and management evaluations on a regional scale usually highly up-scaled models are applied. Generally, however, for calibration of these models only data from small scale and short term processes are available. This inconsistency between the scale of observations and the resolution of the simulated data often prohibits a meaningful comparison of model outcomes and observations.

Calibration does not always lead to a unique set of parameter values. Difficulties with this non-uniqueness can be solved by application of a step-wise calibration procedure. In each separate step only one or a few selected parameter(s) are allowed to vary, while only those measurements are selected that are the most sensitive to the ‘free’ parameter(s). The selection can be carried out at best by a sensitivity analysis. However, sensitivity analysis was not possible with the version of PEST used in this study. A sensitivity analysis is highly recommended for future calibration exercises.

Finally a general remark must be made. From a groundwater quality point of view the occurrence of denitrification is always regarded as a blessing. Indeed, it helps to remove an excess of nitrate in groundwater. So far however, little attention is paid to the adverse effects of denitrification. For instance, it is unknown whether the denitrification capacity of the underground is unlimited or not. If the denitrification capacity gradually diminishes and the process is irreversible, it is a serious concern from the point of sustainable groundwater management, especially as it is not known how fast this damage may develop. In the case of denitrification by pyrite-oxidation, trace elements (e.g. nickel, arsenic, zinc, and cadmium) dissolve in the groundwater, while it leads oxidation of sulphides to sulphates and may increase the water hardness. Another harmful aspect is the production of N_2O as one of the final products of the denitrification process (Ronen et al., 1988). This gas is known as a potential destructor of the ozone layer and as a contributor to the ‘greenhouse’ effect.

The study described in this report demonstrates that for a stable groundwater transport model can be set-up for nitrates using a mixed zero and first order process to describe denitrification. Spatial variation of the denitrification parameters is possible by application of a zonation

approach. Calibration of the model parameter is possible using nitrate measurements at monitor wells and nitrate breakthrough curves at groundwater abstraction wells.

Acknowledgements

Hereby, I would like to acknowledge my colleagues Karel Kovar and Jan Mülschlegel. Their comments and fruitful suggestions have been of high value. Further, I would like to thank my colleagues Rien Pastoors for providing the groundwater flow data (LGM), and Kees Schotten for preparation of the data from the leaching model (STONE).

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