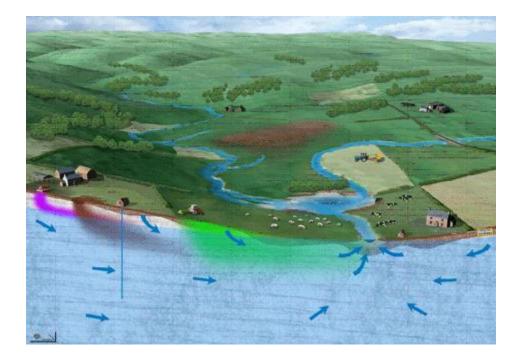




The influence of the land use on the groundwater quality in Achterhoek



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May 2010





The influence of the land use on the groundwater quality in Achterhoek

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Feng Miao and Sun Yaxin

May, 2010

Summary

In the Netherlands, both ground and surface water are used as drinking water sources. On a yearly basis, some 750 million cubic meters of groundwater is extracted from the soil for public water supply (data from: Water Information Net Work). In order to ensure the quality of water sources for both current and future needs, this project is going to clarify the influence of land use on groundwater quality in Achterhoek, a region in the province of Gelderland, the Netherlands.

It is important to understand the process of groundwater quality evolution before relating it to the influence of land use. To be more specific, the first step is to study the hydrogeochemical process of the groundwater and then relate it with the local situation. Groundwater forms from the portion of rainfall which is able to percolate through the subsoil (Herschy, 1998) and into the underground. The rainwater, and its dissolved substances in the subsoil, provides different elements in groundwater. This rainwater filtration process results from the use of surface land that influences the chemical formation of groundwater and its quality. For example, fertilizers might be applied on agricultural land where all the remaining chemical substances will eventually be filtered from rainwater to groundwater, which affects groundwater quality.

As for this project, groundwater quality data of the last 25 years (1985-2009) will be analyzed in order to discover the trend of groundwater quality and types of contamination substances. In addition, by researching the local circumstances, it will be possible to identify the main sources of contaminating elements in relation to regional land use. The nitrate concentration is a good example: high nitrate concentration in groundwater at Van Heek (marine sandy soil), caused by the use of agricultural land.

The standard applied for comparisons is the drinking water quality index. This research suggests that the element concentration in groundwater are not just affected by land use, but also are affected by other factors like soil composition where water seeps through.

The introduction information is specifically associated with the background of the research, which contains an explanation of the reasons for doing this research, the aim of this project, the research objective, and the methods. Also included is an introduction of the data used for analyzing in this research. In Chapter 2 the physical environment of the project area is examined, considering in particular land form, soil components, precipitation, geohydrological characteristics and major land use coverage. The findings of this chapter are of importance as they contribute towards the background information supporting the contaminants trend analysis which is the subject of Chapter 3. Chapter 3 is of crucial importance as the results will illustrate the outcome of the literature study, the products of the data analysis, and the results of potential risk analysis. After the results come out, finally, Chapter 4 is divided into two sections. Firstly, the main conclusion of this thesis is made, and then a discussion of the literature study and potential future work is undertaken.

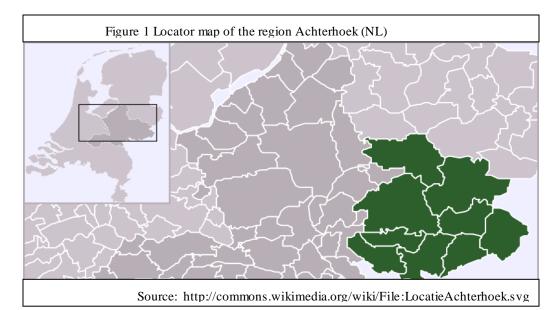
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1 Introduction

1.1 Background

Groundwater is a key natural resource for present and future generations, and the preservation of its quality is a crucial step towards the overall sustainability of resources (Custodio 2006)¹. The Netherlands is a country with 38,000 km² area and more than 16.5 million people. Groundwater is the major source of drinking water. Because of the intensive use of land near groundwater pumping stations, there are great problems with groundwater pollution over large areas, especially in the sandy regions, which cover about 42% of the whole country (EEA, 1997). In order to ensure that there is enough reliable water sources for the current and future needs, an impact assessment of the land use on the groundwater quality is necessary. For this reason, Vitens assigned Feng Miao and Sun Yaxin to do this research.



Vitens is the biggest drinking water company of the Netherlands. Its services cover more than 2.3 million customers, with annual revenues of \in 475 million and with sales of 330 million cubic meter of water a year (data from a Vitens report: Innovative, cutting-edge water technology).



¹ M. T. Condesso De Melo and others, 2008, Monitoring and Characterisation of Natural Groundwater Quality, pp1. Introduction.

The project area is located on the eastern part of the Netherlands, namely Achterhoek. The river Ijssel and Load Ijssel are the south and north borders. It is one of the sandy areas where the land is mainly used for foresting, agriculture and residences. Vitens has 10 water harvest (pumping) stations in the Achterhoek region. In this research, three of them will be used: Klooster, Aalten and Van Heek.

1.2 Problem description

Previous groundwater research (David N. Lerner and Bob Harris, 2009^2 ; M. Balakrishnan and others, 2008^3 ; British Geological Survey⁴, 2009) had already indicated evidence that groundwater quality can be affected by the different land use. M. Balakrishnan, etc. (2008) found that comparing to other non-industrial areas, the groundwater samples collected from various parts of the dyeing industrial region has a much higher concentration of different contaminants like chloride, sulfate, iron and lead. The British Geological Survey (2009) also found that the intensive agricultural land use make the groundwater high with nitrate and pesticide ramification concentrations. Similar research in the Netherlands conducted by EEA (1997)⁵ discovered that, because of the intensive use of land, groundwater pollution becomes a vast problem over large areas, especially sandy regions.

The project area Achterhoek is one of many sandy regions in the Netherlands, where more than 60 % of the land is used for agriculture (data: consulting from M. Van Aken). Vitens Drinking Water Company has more than 10 pumping stations in this region which harvest groundwater and deliver it to its customers. In order to ensure the quality of drinking water, water sources from these pumping stations are evaluated every year by Vitens. According to the initial analysis by Vitens, the groundwater in Achterhoek has already been contaminated by certain substances which may affect drinking water quality in the future. A 25-year groundwater quality database has been established which contains the concentration of 25 main substances. The problem is that it is easy to discover contaminants and its trends, however, the causes of pollution are still unconfirmed which might be related to the regional land use.

During the period from 1985 to 2009, there have been no significant land use changes in the project area. For instance, based on the information provided by M.

² David N. Lerner and Bob Harris, 2009, *The relationship between land use and groundwater resources and quality*.

³ M. Balakrishnan and others, 2008, *Impact of dyeing industrial effluents on the groundwater quality in Kancheepuram (India)*. Indian Journal of Science and Technology.

⁴ British Geological Survey, 2009, Groundwater Information Sheet, *The Impact of Agriculture*.

⁵ EEA Topic Report, 14/1996, Groundwater Monitoring in Europe

Van Aken (2010), in the Van Heek area, 80% of the land was used for forestry and the rest of it for agriculture in the past 20 years. Currently 90% is still used for forestry. This brings the biggest problem in evaluating the influence of land use changes on groundwater quality. Nevertheless, these slight changes may still cause obvious changes in groundwater water quality. Referring to Van Heek again, 10% of its overall land use changed meaning that agricultural land decreased by 50%. It also means that the amount of certain chemical fertilizers may have also decreased.

Furthermore, agricultural activity might be the main cause of groundwater pollution in the past. Based on that, there is an assumption that the current groundwater quality should be better compared to 20 years ago. However, there are a lot of other limitations that will affect the groundwater quality, as for instance, the long time delay in land use effects and global climate change.

1.3 Research objective

The main goal of this research is to identify the major sources that may affect groundwater quality, and use this information to clarify the influence of land use on groundwater quality in Achterhoek.

So, the main research objective is to research *the influence of local land used on the groundwater quality in the Achterhoek region.*

To address this objective, the following research questions are formulated:

- What are the sources of major contaminants in groundwater?
- How do those elements appear in groundwater?
- What are the trends of contaminant concentrations of groundwater in the project area?
- What are the potential risks of groundwater quality in Achterhoek?
- What is the cause of those potential risks?
- Does current land use serve any good to groundwater quality at Achterhoek and why?

2 Methodology

Within the project area Achterhoek there are around 10 producing stations of Vitens. As mentioned before in this research, only three of them will be analyzed: Klooster, Van Heek and Aalten. The reasons for selecting these 3 locations are that Klooster has the most particular data and information compares with other stations; Van Heek has a similar land use set up but different soil structure and land form to Klooster; and Aalten has a similar soil structure and land form but different land use set compared to Klooster.

Their differences and similarities form the comparability of this research. The comparison and contrast method is the basic method used for analyzing data. Detailed information of how the comparison and contrast methods are used in this research will be illustrated in 2.3. Before that, 2.1 will first introduce the project set up, which is in order to give an overview of the whole project. Then the data information will be introduced in 2.2, where an introduction of different elements and the station wells will also be included.

2.1 Project set up

This project takes four months (from the middle of February to the end of June, 2010). Within these four months, the project was divided into four phases:

Phase 1: initial phase

The project plan was made and the background data (including groundwater data and land use data) was collected during this phase. The data was taken from the mentioned Vitens data base and transferred into a Microsoft Office Excel file. The literature studies also conclude this phase.

Phase 2: data analysis phase

In this phase the different excel line graphs of selected elements were made to explain each element's concentration situation of the past 25 years. Those graphs were also used for comparing the different groundwater situations among the three stations.

Phase 3: conclusion and discussion

Answers to the research questions were found during phase 3, by getting an overall look at all the results and analyzing it, combined with the physical environment of each station.

Phase 4: project end phase

During this phase, the project final report and presentation are finalized which will be delivered to both Larenstein and Vitens supervisors.

The detailed information of Phase 2 and 3 will be found in 2.3.

2.2 The data introduction

The wells of three different stations

The number of the wells in different pumping station is different (Figure 2). But all of them have both extraction well (blue points on the figure 2) and monitoring well (red points on the figure 2).

Pumping station Klooster: there are 13 extraction wells which have their filters in depths between 14 and 26 meters underground. It also has 15 monitoringmonitoring wells, each of them having around 40 filters. The distance between each filter is approximately 1 meter. As seen in Figure 6, the extraction wells concentrate around the pumping station in the forest area and the monitoring points are mainly located on the eastern side.



Van Heek: there are 10 extraction wells, and their filters are in depths between 27 and 31 meters underground. It has 5 monitoring wells, and each of them only has one filter. Figure 3 shows that the monitoring wells and extraction wells are concentrated in two locations.



<u>Aalten:</u> there are 4 extraction wells, and their filters are in depths between 47 and 50 meters under the ground. It has 5 monitoring wells, and each of them has 2 filters. From Figure 4, the monitoring wells surround the extraction well.



The Elements data of this research

As mentioned in the section 'problem description' (Chapter 1.2), Vitens evaluates its water sources on a yearly basis. It means water quality from each well should be evaluated at least once a year.

However, for the stations like Klooster, evaluations are carried out more frequently. Such high frequent evaluations may be due to conducted research programs or results from regular evaluations that indicate pollution risks. In these cases, the average value of each year will be applied in this research.

The other issue is caused by the operation time of each station. For some earlier established pumping stations, certain elements may have not been evaluated since 1985. Later, for these cases, the trend analysis will focus on shorter periods according to the data.

The data for evaluating is gathered and saved in Vitens database after the water samples have been analyzed in the Vitens laboratory. Each time, the lib will test more than a hundred elements their concentration level in the water sample, thus the database of Vitens contains more than one hundred element concentration readings. Considering the time limit and the project situation, Ir. M. Van Aken of Vitens, who is one of the supervisors of this thesis research, selected 25 elements for this research. The elements are listed in Table 1. For the introduction of those 25 elements can be found in the Appendix I. Within the table there are two standards for each element, one is 'limit value' and the other is 'target value'. The limit values are standards witch are legally required. The target values are Vitens policy. The target values sometimes are stricter for health or astatic (like color, taste and smell et.) reasons.

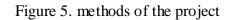
Parameter (Dutch)	Parameter(English)		Unit	Limit Vitens	Target Vitens
Aluminium	Aluminum	Al	ug/l	≤30	≤30
Ammonium	Ammonia	NH ₄	mg/l	≤0.2	≤0.05
Arseen	Arsenic	As	ug/l	≤10	≤10
BAM			ug/l	≤0.1	≤detectielimiet
Cad miu m	Cad miu m	Cd	ug/l	≤5	≤1
Chloride	Chloride	Cl	mg/l	≤150	≤100
Chroo m	Chro me	Cr	ug/l	≤50	≤10
Cyanide Totaal	Total Cyanide	CN	ug/l	≤50	≤10
	Dissolved organic				
DOC	carbon				
IJ zer	Iron	Fe	ug/l	≤100	≤50
koper	Copper	Cu	mg/l	≤2(tap)	≤2(tap)
Lood	Lead	Pb	ug/l	≤10	≤10
Mangaan	Manganese	Mn	ug/l	≤50	≤10
Natriu m	Sodium	Na	mg/l	≤150	≤120
Nikkel	Nic ke l	Ni	ug/l	≤20	≤10
Nitraat	Nitrate	NO ₃	mg/l	≤50	≤25
Nitriet	Nitrite	NO ₂	mg/l	≤0.05	≤0.03
рН				7≤pH≤9.5	7.8≤pH≤8.3
Si-index				≥-0.2	-0.2≤Si≤0.3
Sulfaat	Sulfate	SO_4	mg/l	≤150	≤100
TOC	Total organic carbon	с	mg/l	≪5	≤3
Totale hardheid	Total hardness		mmo l/1	1.0≤TH≤2.0	1.0≤TH≤1.2
Waterstofbicarbonaat	Bicarbonate	HCO ₃	mg/l	≥60	≥90
Pesticide					
МСРР			mg/l	≤0.1	
Bentazon			mg/l	≤0.1	

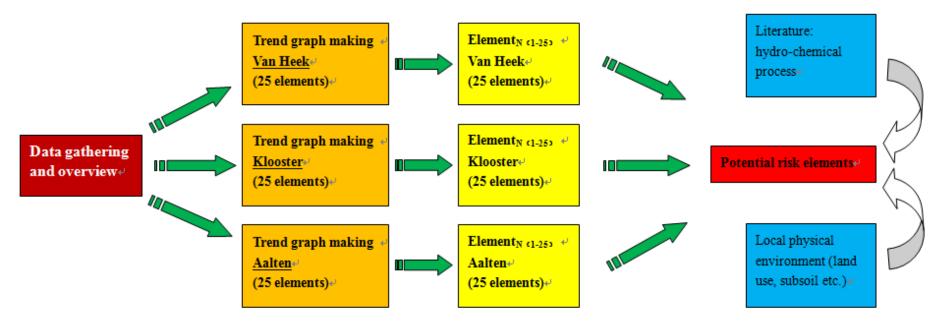
Table 1 the analyzed parameter and their standard.

2.3 Methods:

The flow chart (Figure 5) indicated the steps, methods and main outcomes of the research process.

- The first step is to make an overview of the database; the required water quality data was downloaded from the main database of Vitens and then transferred into Excel Sheets. It contains locations of sampling wells (X, Y coordinates); type of elements; depth of wells; time of sampling; and concentration of substances. The coordinates of the sampling wells were translated into geographical longitude and latitude by using the software *Google Earth* and *PCTrans423*; the water quality data was grouped into districts and separately presented in Excel files.
- The second step is to make trend graphs of each substance using *Microsoft Excel and Aquachem*; since the data consisted of three pumping stations, theoretically, three different trend graphs of each element should be established. However, due to some of the element concentrations being below its detection limit, only the data that are above detection limits were graphed (the detection limits of each substance changed from 1985 to 2009, which is determined by Vitens laboratory).
- The last step is to combine the established data analysis results and external information (for example local land use situations) results from literature study; to identify the sources of potential risk elements. This will be done by consulting experts and internal discussions. The final result will be applied as conclusions to this report.
- The next step is data comparison. The analyzing tools that were applied during the process were *Microsoft Excel and Aquachem*. The reference standard is the drinking water guideline which was developed by Vitens. The concentration of each element from the three pumping stations were compared with the reference standard in order to establish a holistic view of the concentration status (Table 3) and differences among pumping stations.

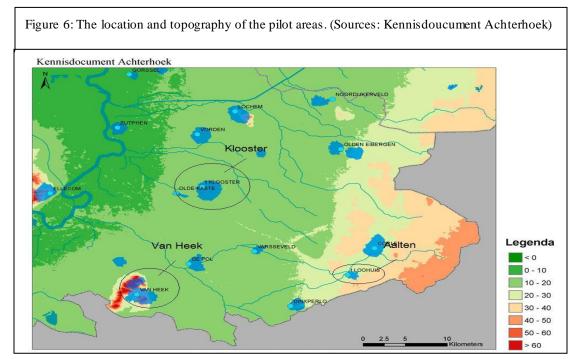




3 Site Description

3.1 Location

The Achterhoek region is part of the Gelderland province which is located in the eastern part of The Netherlands. The river Ijssel and Old Ijssel are the south and north border. For Achterhoek, there are around 10 pumping stations, but considering the limitation of time, 3 stations (Klooster, Aalten and Van Heek) were taken as the project areas for this thesis research. As Figure 6 shows, Klooster is in the middle part of Achterhoek. Aalten is in the southeast of Achterhoek. Van Heek is in the southwest of Achterhoek.



3.2 Topography

Achterhoek is part of the catchment basin from the North Sea, a drop zone where the hinge at the Achterhoek is approximately located near the line Neede-Groenlo-Lichtenvoorde-Aalten.

The height of the ground level of Achterhoek runs off regularly from the east to the west. In the eastern part the height of the ground level is approximately 50 meters above see level, in the western part along the river IJssel about 10 meters NAP(see Figure 6). The border between the eastern Netherlands terrace and the Pleistocene basin (the terrace border) shows between Aalten and Groenlo a well visible area crack. In the north of Groenlo, there is a terrace edge that is less clear due to erosion during the Pleistocene period. Remarkably, topographical features are the remains of lateral moraines (Montferland and Lochemerberg).

The surface drainage of the area takes place by multiple eastern and western narrow surface drainages (Berkel, Slinge, Baakse Beek, Veengoot, Oude IJssel). These streams walk more or less parallel and follow the decreasing trend of ground level in east-west direction and flows into the river IJssel. The IJssel provides drainage of the Achterhoek, through the earlier mentioned streams.

As we can see from figure 2, Klooster shows a light slope. The ground is located near the wells around 15.5 m + NAP. The Aalten also shows quite a slow slope. The ground of the wells is around 25 m + NAP. But in Van Heek it is less flat. The ground of the wells range from 15m + NAP to 25m + NAP.

3.3 Soil and Geology

Achterhoek can be divided into the Dutch East plateau or terrace, and the Pleistocene basin. The boundary between these two areas is between Aalten and Groenlo visible as a bend in the terrain. The soil structure of Achterhoek is relatively simple and consists mainly of fine sand, coarse sand and clay on the moraine along the IJssel and Oude IJssel. (KWR, 2006)

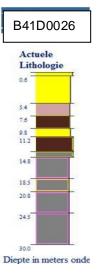
Because of the moraine, the Achterhoek area consists of young deposits with high levels of reactive components such as organic matter and lime, as well as locally pyrite and siderite. (KWR, 2006) The chemical composition of filtered (rain) water will interact with these reactive components in the soil layers.

B34C0102	Monitoring	Monitoring well B34C0102: soil and geology information in Klooster					
Actuele	Depth(m)	Main lithology	color	grain size	incorporation		
Lithologie	0-1	Sand	brown	moderately fine	silt, moderately humeus		
	1-5	Sand	brown-yellow	very fine	strong silt		
31.0	5-11	Sand	brown	medium fine	slightly silt,,		
41.0	11-31	Sand, Gravel	gray-brown	very coarse	gravel		
	31-41.0	Sand	gray	medium fine	slightly silt		
54.0	41.0-63	Sand	gray-green	moderately coarse	slightly silt		

The soil and geology in Klooster Figure 7.

63.0

Diepte in meters ond



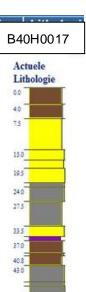


Figure 8. The soil and geology in Aalten

Monitoring well : soil and geology information in Aalten					
Depth(m)	Main lithology	color	grain size	incorporation	
0-0.6	Sand				
0.6-5.4	Sand	yellow	medium fine	gravel	
5.4-7.6	Sand	red-gray	very fine	weak slit ,strong	
				gravel,	
7.6-9.8	Sand	red-brown	very fine	weak slit,	
9.8-11.2	Sand	yellow	medium fine	strong silt	
11.2-13.7	Sand	red-brown	moderately coarse		
14.3-30.0	Loam	gray		Strong sand	
				gravel,humeus	

Figure 9. The soil and geology in Van Heek

Monitoring well B40H0017: soil and geology information in Van Heek					
Depth(m)	Main lithology	color	grain size	incorporation	
0-7.5	Sand	brown	fine	silt	
7.5-19.5	Sand	Unknown	coarse	gravel	
19.5-33.5	Sand	gray	moderately coarse	gravel	
33.5-36	Sand	Unknown	moderately coarse,	gravel	
36-37	Clay	Unknown			
37-43	Sand	brown	fine	silty	
43-50	Sand	gray	coarse	gravel	

in meters onder maaivel

50.0

Figure 7, 8, 9 shows the soil information in 3 stations. Sandy soil is the main soil for three stations. (More detail information can be found in website <u>www.dinoloket.nl</u>

As indicated in Figure, sandy soil is most common soil in all 3 stations. The soil particles in klooster and Aalten at depths of 10-30 meters are fine, but in Van Heek the soil is coarse or moderately coarse.

3.4 Climate

The Netherlands has a temperate maritime climate influenced by the North Sea and Atlantic Ocean, with cool summers and moderate winters. Since the country is small, there is little variation in climate from region to region, although the marine influences are less inland. Compared to coastal areas, the inland area has bigger temperature amplitude. The detail climate information of Achterhoek collected from the FAO website can be found in the Appendix II

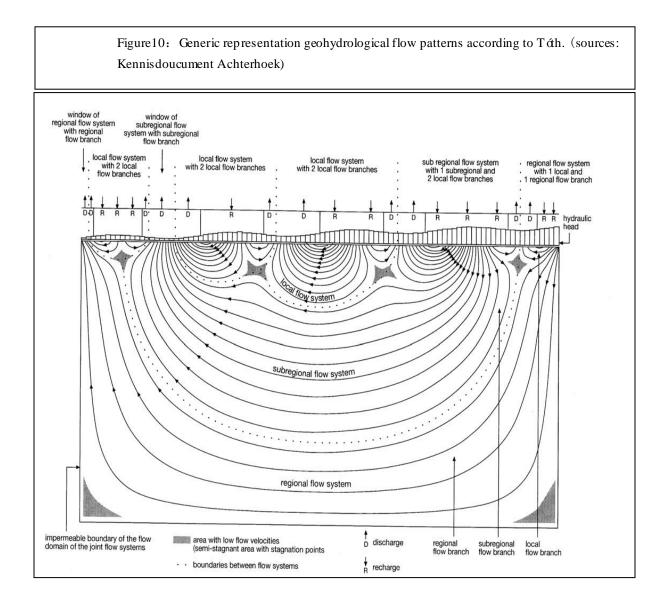
According to the data (FAO), the annual rainfall is 749 mm. It was well distributed throughout the year, ranging from 45 mm/m to 74mm. The temperature ranges from 1.9 C to 20.1 C.

3.5 Geo-hydrology

Achterhoek slopes from east to west, which determines the direction of both surface and underground flows. Within past 60 years, the dewatering of Achterhoek improved, resulting in a greater drain during the winter season and smaller during the summer season, and a lowering of groundwater. This deeper dewatering in the Veengoot, near extraction station Klooster, led to a large variation in the quality of surface water. During winter, the surface water is largely fed by shallow groundwater, which is affected by agricultural activities and wastewater discharges. During summer, it is mostly fed through the deep seepage of old groundwater which is considered good quality. This phenomenon will most certainly also occur with other streams in Achterhoek. (KWR, 2006)

Superimposed on this basic system of groundwater flow are other systems: regional flow systems powered by the moraine, and local systems powered by small increments, as dekzandruggen (dutch) and enken (dutch). In order to describe the geohydrology of areas, a distinction is made between regional, sub-regional, and local flow patterns. This is shown schematically by Tóth (Figure 10)

The report named *Kennisdocument Achterhoek* (2006) mentioned that, at multiple extraction sites, some of the extracted groundwater originated from the filtered surface water. In some extraction sites, the surface water filtered a short distance before reaching the extraction well. Thus in some extraction wells the water quality was highly affected by the quality of filtered surface water, including current contaminants.



3.6 Land Use

There are three main land use types in the Achterhoek region: forests and nature, agricultural land, and residential land. As the Table 2 shows, for stations K looster and Aalten, land is mainly used for agriculture which occupies around 70 percent of land. But K looster however has more forests and nature than urban areas, whilst Aalten has more urban land than forests and nature areas. Because of the limitation of data, we can only get data from 2000. Considering that there is no major change about land use in those stations, we will use this data as the basic information for land use in these three project stations. For the station Van Heek, we also have some data about its land use. But according to M. Van Aken's (2010) estimations, the forests and nature occupy around 80 percent of the total land, whilst the rest are agricultural.

Name	Urban	Agriculture	Forests and Nature	water
Olde Kaste	5	94	1	0
't Klooster	4	70	26	0
De Pol	10	72	17	0
Vorden	4	59	36	0
Lochem	0	100	0	0
Noordijkerveld	4	86	11	0
Haarlo	16	76	8	0
Olden Eibergen	12	83	4	1
Varsseveld	6	81	10	4
Dinxperlo	3	93	4	0
't Loohuis /	19	67	12	0
Aalten				
Corle	6	86	7	0

Table1 2. Landuse of the 100-year zone of the wells in Achterhoek (source: Kennisdocument Achterhoek.)

4 Results

4.1 Both humans and nature bring Groundwater impurities

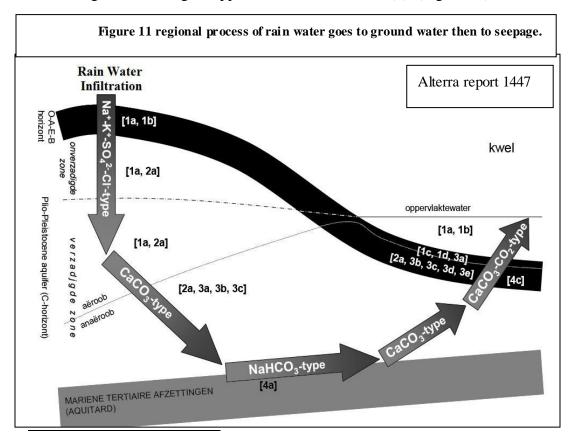
Ground water is water that goes through the rocks and soil under our feet, which can be found almost everywhere. It is formed from the portion of rainfall that is able to percolate through the subsoil, and accounts for about 99 percent of freshwater in the world, excluding snow and ice (Herschy, 1998). Rainwater is slightly acidic, which means its pH should be lower than 7, therefore it tends to dissolve solid minerals in the soil and in the aquifer. Also, as different rocks are found in the soil (such as sandstone, limestone, and basalt), it provides minerals to the ground water whichwill have different compositions (D. Nelson, 2002). Rainwater dissolved minerals mixed with different compositions of rocks cause the ground water to become impure water (H_2O). Thus, natural ground water quality may evolve due to water–rock interactions over time, ranging from a few months to many thousands of years (M. T. Condesso De Melo and others, 2008). However, the ground water quality evolution process is not only related to natural conditions, but also is affected by human activity (especially land use changes).

In this chapter the major chemical reactions during the ground water formation process will be discussed in the first part. This is followed by a discussion on potential factors which may affect the ground water quality.

The major chemical process of impurities goes into ground water

The chemical components of water change during the process of water going through soil particles from the surface to the ground. This part will focus on the major chemical process. The applied information is mainly from the report 1447 of Alterra⁶ and report Kennisdocument Achterhoek of KWR⁷.

Rainwater contains a lot of atmospheric acid deposits that consist of sulfur and nitrogen oxides and ammonia. The pH of rain water in the Netherlands is around 5.0 (H. van den Dool, 2010), although there are slight differences among regions. As the rain water filters through different soil layers, the deposition concentrated in will be neutralized by the lime in the soil, leading to a high hardness in the extracted ground water (evidence shows the result of Total Hardness). In other words, the acidic condition provides the possibility of dissolving soiled minerals like Mg, Ca into the water. The chemical formula (2a) explains this process. In the mean time, the soil layers, where water gets filtered, is full of oxygen, named the aerobic zone, so the reaction is mainly oxidation. The oxidation process is calculated through the formulas (1a) to (1d). After this stage, the water goes into the anaerobic layer, where the reductive reaction begins to happen (formula 3). When the water touches hard sediments, depending on the pH situation, some weathering reactions might happen as shown in formula (4). (Figure 11)



⁶ Altarra report 1447: MP.C.P. Pailissen, R.C. Nijboer, P.F.M. 2007, Verdonschot, Ground water in perspectief, Een overzicht van hydrochemische watertypen in Netherland. Alterra, Wageningen, The Netherlands.

⁷ Report Kennisdocument Achterhoek of KWR: K. van Beek, G. van den Berg, M. Jalink, 2006, Kennisdocument Achterhoek: winningen 't Klooster en Olde Kaste. Vitens, The Netherland.

Major process happens underground (Figure 9)

Process

(1) Reactions in oxidative environment

(1a) (Aerobic) mineralization:

CHO~N~P~S(s) + O2 $(aq/g) \rightarrow H2O(1)+CO2(aq/g)+NH4++PO43-(aq)+SO42-(aq)$ ---soil in inzijggebied ---aerobic zone in Plio-Pleistocene aquifer

(1b) Nitrification:

NH4+ (aq) +2O2 (aq/g) →NO3-(aq)+2H+(aq)+H2O(l)

(1c) Iron oxidation:

 $4Fe2+(aq) + O2(aq/g) + 10 H2O(l) \rightarrow 4Fe(OH)3(s) + 8H+(aq)$

---Seepage zone where ground water O2 step down (in this case PO43- may precipitate with Fe3+)

---Contact zone relative O2 -rich in ground water and in deeper ground water,

(1d) Sulphide Oxidation :(including whether pyrite oxidation troiliet)

 $4\text{FeS2(s)} + 15 \text{ O2} (aq/g) + 14 \text{ H2O} (l) \rightarrow 4\text{Fe(OH)3 (s)} + 8\text{SO42-(aq)} + 16\text{H} + (aq)$ ---pyrite oxidation is usually the result of desiccation of the wet area, where FeSx O2 deposit can reach.

Impact on ground water compositions

-O2 Drop, -CO2 rise, -PH drop because of CO2 drop

-PH drop because of release of H+ -O2 Drop.

-PH drop because of release of H+,
-O2 Drop,
-PO₄³⁻ may precipitate with Fe(OH)₃

-PH drop because of release of H+, -O2 Drop, -PO₄³⁻ may precipitate with Fe(OH)₃

(2) Weathering reactions

(2a) CaCO3 solution and CaMg(CO3)2

 $\begin{array}{l} CaCO3(s) + H2O \ (l) + CO2(aq/g) \ \Rightarrow Ca2+ (aq) + 2HCO3-(aq). \\ CaMg(CO3)2 + 2 \ H2O \ (l) + 2CO2(aq/g) \ \Rightarrow \ Mg2+ (aq) + Ca2+ (aq) + 4HCO3-(aq). \\ ---soil in inzijggebied \\ ---aerobic \ zone \ in \ Plio-Pleistocene \ aquifer \\ ---soil in \ seepage \ area \end{array}$

(3) Reactions in the reductive environment:

(3a) Iron reduction

 $Fe(OH)3(s) + 1/4 CH2O(s) + 2H + -ads \rightarrow Fe2 + (aq) + 1/4CO2(aq/g) + 11/4H2O(l)$

(3b) De-nitrification

 $4NO3-(aq) + 5CH2O(s) \rightarrow 2N2(g) + 2CO2(aq/g) + 4HCO3-(aq) + 3H2O(l)$ ---Anaerobic zone in the aquifer of soil seepage area

(3c) Sulfate reduction

-CO2 rise, -water is harder because of release of the Mg²⁺ and Ca²⁺ -PH rise because of CO2 release.

-PH increase production by HCO3-

- Ground water nitrogen poorer

-PH rise because of the use of the H+ and the outcome of the HCO₃⁻

 $2 \text{ SO42-(aq)} + 4\text{CH2O}(s) + \text{H} + (aq) \rightarrow \text{H2S}(aq/g) + \text{HS-(aq)} + 2\text{HCO3-(aq)} + 2\text{H2O}(l) + 2\text{CO2(aq/g)} + 2\text{H2O}(l) + 2\text{CO2(aq/g)} + 2\text{H2O}(l) + 2\text{CO2(aq/g)} + 2\text{H2O}(l) + 2\text{H2O}(l) + 2\text{CO2(aq/g)} + 2\text{H2O}(l) + 2\text{H2$

(3d) Acetoclastische methanogenesis (linked to ethanol fermentation): C2H4O2 (aq) \rightarrow CH4(g) + CO2(aq/g) (3e) Reductive methanogenese (link to hydrogen production)

 $CO2 (aq/g) + 4H2(g) \rightarrow CH4(g) + H2O (l)$

---Both forms of methanogenesis take place in strictly anaerobic soils in seepage areas or in the anaerobic zone in the Plio-Pleistocene aquifer, provided SO42--concentrations low.

(4) CEC:

(4a) Ca2+ (aq) + Na+ -ads(s) ₹ Na+(aq) + Ca2+-ads(s) ---hard contact zone ground water with marine sediments.

(4b) Na+ (aq) + Ca2+-ads(s) ₹Ca2+ (aq) + Na+ -ads(s) ---contact zone saline ground water with fluvial sediments Plio-Pleistocene aquifer

(4c) Kat+ (aq) + H+ -ads(s) \neq H+(aq) + Kat+-ads(s) ---contact zone HCO3-water with peat -water is softened by removing Ca²⁺

-water is harder by producing Ca²⁺

-PH decreases by releasing H⁺ -Part HCO3 in ground water is converted to CO2 as a result of pH drop -Water hardness decreases t.g.v. cation

Ground water contamination

According to the mentioned process, the different chemical components in the ground water are carried by water through the process of infiltration. It may be adsorbed from atmosphere, soil and rocks. Such process may easily indicated that the human acts on or near the surface, where the water through, may bring certain elements into the ground water. For instance, the fertilizers that used by the farmers during cultivation processes have quite high possibilities to be combined with the water and eventually infiltrate to the ground water. Also like the nitrate concentration in the ground water, both human activity (agriculture, industry, house hold) and natural formation can be the sources. No matter what is the source of those elements, when some of the elements' concentrations in the drinking water, like nitrate, exceed a certain value, the water is harmful for the human health. The situation like this, the water can be looks as contaminated. The S. County (2008) concluded that ground water can be contaminated in many ways and through variety of compounds, both of natural origin and man-made. County's conclusion is also partly proved the conclusion of the literature study of this research: Both human and nature bring the ground water impurities.

In County's (2008) theory the concentration of natural impurities depends on the nature of the geological material through which the groundwater moves and the quality of the recharge water. He named some naturally occurring pollutants of ground water: Microorganisms, Dissolved solids and chlorides, Radionuclides, Radon, Nitrates and nitrites, Heavy metals, Fluoride.

Most concern over ground water contamination has centered on pollution associated with human activities, including municipal, agriculture, Industrial and residential uses (S. County, 2008). During the water goes through the soil to the underground water table, the contaminants caused by human activities like over fertilizer, landfill can be moved through the water flow to the ground water.

Here, this research was mainly looking for the potential risks of the ground water quality in the project area, eliminate the possible natural origin of the risk and focused on the risk might brings by different land use. Also, considering the situation in the project area, the potential risks are not same as County mentioned. Thus not all the elements in the ground water need to be analyzed. In next paragraph, the result after comparing a few selected elements concentration of the ground water in the natural condition and land use changed condition (mainly changed into agriculture land) will be illustrate.

4.2 Each station's selected elements concentration status

Table 3 separately shows the result of all the element concentrations from each station within the past 25 years (1985-2009). The different symbols represent different statuses which are defined at the beginning of the table. The detailed trend graphs of each element's concentration can be found in the Appendix III.

As the table shows: ammonium and total hardness concentration of both station Aalten and Klooster exceed the limit value; the nitrate, pH and SI concentration of Van Heek are exceed the limit value; also the bicarbonate concentration of both Van Heek and Aalten are higher than the limit value.

Those elements high concentration can cause different problems for three stations groundwater uses for dinking water source. Thus those elements high concentration are the risks for the groundwater quality.

The reason for cause those elements' high concentration is various. But in conclude it is caused either agriculture land use or natural soil component. The detail information of their causes is discussed in the Chapter 5.

Table	3. Result of t	he data analysis			
Code	of the element cond	centration situation			
95% of the data	is under the detection	on limit ⁸	U		
within around 25	years it has an incr	ease trend	1		
within around 25	years it has an decr	ease trend	Ļ		
more 50% of the	data exceed the lin	nit value	Ε		
more 50% of the	more 50% of the data within the limit value				
	Eleme	nts concentration s	ituation		
Elements (Dutch)	Van Heek	Aalten	Klooster		
Aluminium	U	U	U		
Ammonium	U	↓ E	↓ E		
Arseen	U	U	↓ N		
BAM	U	U	U		
Cadmium	U	U	U		
Chloride	↓ N	↓ N	† N		
Chroom	U	U	U		
Cyanide Totaal	U	U	U		
DOC	1	1	1		
IJzer	↓ N	↓ N	↑ E		
koper	U	U	U		
Lood	U	U	U		
Mangaan	↓ N	↓ E	† N		
Natrium	↓ N	↓ N	↓ N		
Nikkel	U	U	U		
Nitraat	↑ Е	U	U		
Nitriet	U	U	U		
pН	↑ Е	↓ N	↓ N		
Si-index	↑ E	† N	† N		
Sulfaat	$\uparrow N^{(a)}$	† N	† N		
TOC	↓ N	↓ N	↓ N		
Totale hardheid	† N	↑ E	↑ E ^(b)		
Waterstofbicarbonaat	↑ E	† N	↑ E		
pesticide					
MCPP	U	U	U		
Bentazon	U	U	↓ N		

 $^{^{8}}$ The detection limit and the limit value are according to the Vitens drinking water guideline.

4.3 The physical environment comparison

No matter the human impact or natural evolution, the physical environment of the project area determines the ground water quality element concentration. In this project, the differences among three pumping stations' physical environment are mainly land use and soil structure (soil formation). Figure 12 illustrates the differences. Given those differences, the effects can be displayed and analyzed based on former research: Impact of agriculture (2003)⁹, Nitrogen and the Hydrologic Cycle (1996)¹⁰, etc.

Agricultural land use can cause high sulfate (consulting from M. Van Aken), heavy metal (Kenneth Tanji and Laura Valoppi, 2003), phosphor, nitrate, pesticide as well as pesticide metabolite concentrations in the ground water (British Geological survey, 2003), originating from the use of fertilizers and pesticides.

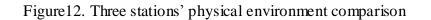
Thus, combining the land use of these three stations, the ground water situation is:

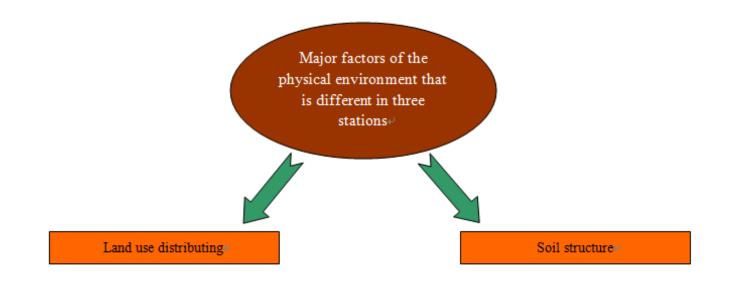
Element	
Sulfate	
Nitrate	Concentration situation.
Heavy mental	Concentration situation: Klooster and Aalten > Van
Phosphor	Heek
pesticide	IICCK
Pesticide metabolite	
Other elements related with agriculture	
Table 4. the conjecture situation	

In soil with very high sand and low organic matter contents, the ammonium and nitrate iron will move in the direction of the water flow (1996, Larry C. Brown and Jay W. Johnson). By combining the soil information from the three stations, the ground water is expected to have a higher ammonium and nitrate concentration in Van Heek than in the other two stations.

⁹ Birtish Geological survey, 2003, The Impact of agriculture

^{10 1996,} Larry C. Brown and Jay W. Johnson





e	Klooster₽	Aalten∉	Van <u>Heek</u> e	¢
Agriculture 🧧	70‰	67%	9‰	Ð
Urban 🤟	4‰₽	19%	2‰	¢
Forest and nature	26‰	12‰	80%+9%ª•	ç
The data of Van <u>Heek</u> comes from KIWA report, 1998,				
Nitraatvoorspelling van Heek; the data of Klooster and				
Aalten come from Vite	ens in the yea	r of 2000₽		

Main soil type: sand 🖉			
Name of the station#	Soil particles of 1-30m under	ę	
	the ground@		
kloostere	Fine	ę	
Aalten@	Fine	ę	
Van Heek#	Coarse or moderately coarse	¢	
Information from: <u>www.dinoloket.nl</u> +			

^a 80% of forest area and 9% of grass land↔

5 Discussion

By combining the results from the hydro-geo-chemical literature study, the results from the ground water data analysis, and the supposition of physical environment analysis, several discussions are held pertaining to the following parts:

5.1 The cause of higher ammonium concentration in Klooster and

Aalten

The cause of this difference might be due to the land use and soil composition of the three stations. There are three possibilities:

Firstly, it might because the sandy soil contains the least amount of organic soil matter to react in the ammonification process (this has been proven by the previous research where there is almost no organic matter in the marine sediments in the project area).

Secondly, the deeper sandy layers provide the possibility for oxygen to exist in the deeper soil layers that allows a nitrification reaction to happen in deeper depths. This may cause the ammonium (assuming there is ammonium impute because of the agricultural land use) to totally change into nitrate (the chemical reaction formula (1b)).

Thirdly, it also can be the fact that Van Heek is the only station of the three where there is no surface water filtration (consulting from M. Van Aken).

For the second reasoning, the high nitrate concentration in the ground water of Van Heek might be enough evidence of the inference. But the reason for the high nitrate concentration in Van Heek has also other explanations (detailed information can be found in the next part---Nitrate). Thus, the reason why Van Heek has a much lower ammonium concentration compared to the other two stations is still on the stage of inference.

5.2 The cause of high nitrate concentration in Klooster

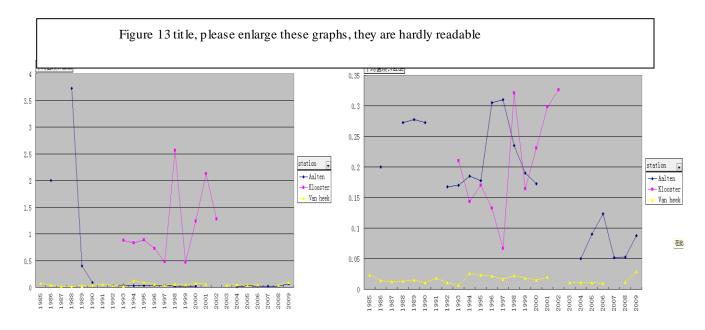
The nitrate concentration in this project area is opposite to the situation of ammonium concentration: only Van Heek has been tested for high nitrate concentrations.

The previous research (Nitraatonderzoek Montferland) confirmed that the high nitrate concentration in Van Heek is because it is a hilly region with much deeper sand layers (caused by the marine push land formation) which provides quicker filtration rates. But, as mentioned in the former paragraph that the nitrate concentration is quite high, it may also be because of the deep sandy layers providing enough oxygen. This gives the possibility of complete nitrification where the ammonium changes into nitrate. Lower organic matter sandy soil also can be the cause of higher nitrate concentrations in Van Heek.

All in all, no matter what caused the high nitrate concentration in Van Heek, comparing the average concentration value of Van Heek with the nitrate concentration value of the ground water in the pure agricultural land regions (290mg/l) and the nitrate concentration of ground water in the pure nature/ forest areas (37mg/l), it is lower than 290 mg/l but much higher than 37 mg/l, which means it is still influenced by the agricultural land.

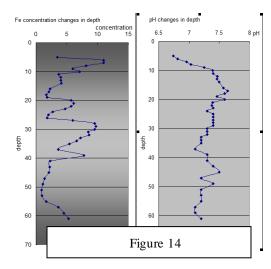
5.3 Iron and Manganese concentration in the project area

The Iron concentrations of the three stations are totally different. Klooster had a high concentration in the first two years, however after that it maintained a lower concentration similar to that found in Van Heek. As for Aalten, it fluctuates between 0.5 mg/l and 2.5 mg/l. Now looking at the manganese concentration levels, Figure 13 shows that it is not very high in this project area. Considering the station's situation, it shares a similar situation to Van Heek with its low and stable concentration; however, for the other two stations, both of them fluctuate. Figure 13 illustrates this.



Vitens does underground de-ironing at Aalten and Klooster. This process, for

oxygen enriched water, is filtered in the underground which starts the oxygenation of iron where it becomes solid and stays in the underground. Therefore, the found iron concentrations at Aalten and Klooster can't be seen as representative of the period after underground de-ironing initiated. But the reason for the fluctuation of manganese might be related to the pH level of the water. Because Mn has similar pH reactions as iron, and there is a lack of Mn concentration information in the monitory points. makes Iron it



concentrations in the well without de-ironing process an example. Figure 14 displays the monitory point data at Klooster in 1997. In the first 5-30 meters, the concentration change of iron and pH are inversely related. This explains the iron reduction process. But there are a lot of elemental changes related to pH, as the pH line does not inversely relate with iron changes in depth.

6 Conclusion:

The ultimate objective of this research is to gain an understanding of geo-hydro-chemical process of groundwater evolution and address this knowledge to a given district, Achterhoek, to assess the land use of Achterhoek whether affect on the groundwater quality.

The results of this project, including literature study findings and groundwater quality data analysis as well as project area physical environment analysis, shows that the project area's agricultural land use, especially fertilizer apply, causes stresses on local groundwater quality. High nitrate concentration in the Van Heek and high ammonium concentration in the Aalten and Klooster are the most apparent evidences.

Furthermore, for the elements which are exceed the Vitens limit value, especially for ammonium, nitrate and sulfate. Their concentration level for the future will hardly decrease under the Vitens target value if there are still agriculture land use input related elements in the project area. Though there is long time delay in the land effects and some of the elements' concentrations have already decreased.

All in all, based on all the findings, in order to ensure there is enough reliable water sources for the future needs, the agriculture land use coverage in the project area should be reduced.

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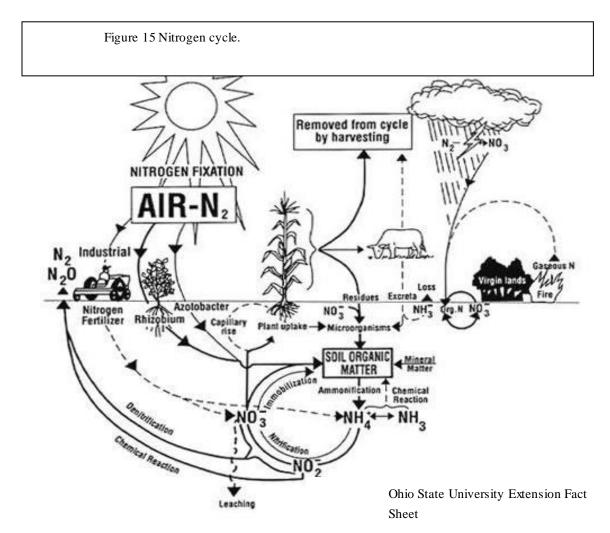
Website FAO: <u>http://www.fao.org/</u>

Appendix I

In appendix I, 25 elements introduction are listed.

Nitrate and ammonium

Both nitrate and ammonium are a different form of nitrogen. A simplified nitrogen cycle (figure 15) illustrates many of the complex interactions of various forms of nitrogen, including: atmospheric nitrogen (N^2), ammonia (NH_3), **ammonium ion (NH_4^+**), nitrite ion (NO_2^-), and **nitrate ion (NO_3^-)**. Each nitrogen form has characteristics that relate to plant utilization and possible impacts on water resources. (1996, Larry C. Brown and Jay W. Johnson)



The form of nitrogen that most plants can use are the ammonium ion (NH_4^+) and nitrate ion (NO_3^-) , as shown in Figure 15. Ammonium is converted to nitrite and nitrate forms rather quickly by nitrifying bacteria, such as *Nitrosomonas .sp* and *Nitrobacter .sp*, which add oxygen to the ammonium ion and convert it to nitrate. In contrast to the nitrate ion, the ammonium ion has a strong attraction for soil, and therefore is considered to be immobile in most soils. However, in soils with

very high sand and low organic matter contents, the ammonium ion will move in the direction of water movement (1996, Larry C. Brown and Jay W. Johnson).

The nitrate ion (NO $_3$ ⁻) is the most water-soluble form of nitrogen as well as the form least attracted to soil particles. Therefore, its interaction with the hydrologic cycle is very important since it moves in the same direction as water. Thus, the nitrate ion (NO₃⁻) can move through the soil as water percolates downward beyond the reach of plant roots to the ground water (1996, Larry C. Brown and Jay W. Johnson). In forestry areas, the nitrate concentration in the ground water should be lower than 37mg/l whilst in agricultural areas it should be 290mg/l. (data from KIVR report)

Aluminum

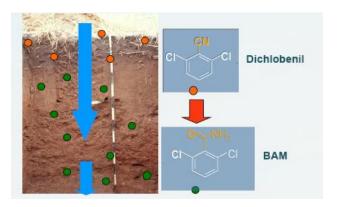
Aluminum forms during mineral weathering of feldspars, such as and orthoclase, anorthite, albite, micas and bauxite, and subsequently ends up in clay minerals. River water generally contains about 400 ppb of aluminum. Aluminum mainly occurs as $Al_3^+(aq)$ under acidic conditions, and as $Al(OH)_4^-(aq)$ under neutral to alkalic conditions. Other forms include $AlOH_2^+(aq)$ and $Al(OH)_3(aq)$. Regular aluminum concentrations in ground water are about 0.4 ppm, because it is present in soils as water insoluble hydroxide. At pH values below 4.5 the solubility rapidly increases, causing aluminum concentrations to rise above 5 ppm. This may also occur at very high pH values. (Source: website of Lenntech¹¹, April 2010)

Arsenic

Arsenic is a chemical element with the symbol "As." It is found naturally in rocks in the earth's crust. Arsenic is recognized as a poison and cancer causing substance (carcinogen). It occurs within organic compounds (combined with hydrogen and carbon), and within inorganic compounds (combined within sulphur, chlorine or oxygen). In water, arsenic has no smell or taste and can only be detected through a chemical test.

BAM

An important ground water pollutant is 2,6-dichorobenzamide (BAM), a metabolite of the herbicide 2,6-dichlorobenzonitrile (dichlobenil) (figure 16). BAM is a very persistent



¹¹ Lenntech: Lenntech Water treatment & purification Holding BV. Website: http://www.lenntech.com

molecule with a half life ranging between 2 to 16 years and very soluble in water. (Source: Aswini Sekhar and others, 2009).

Cadmium

Cadmium (Cd) is found in very low concentration in most rocks, as well as in coal and petroleum. It can be present in ground water through contact with dissolved rocks and minerals (Nova Scotial Environment, 2008).

The Nova Scotial Environment also concluded other sources of cadimium in ground water:

- mining and smelting operations
- industrial operations
- burning of fossil fuels
- fertilizer application
- sewage sludge disposal
- corrosion of galvanized pipes
- leaching of landfills

Chloride

Chloride is an element found in most common salts. It occurs naturally in some sedimentary bedrock layers, particularly shale layers. This kind of chloride is a remnant of the seawater present at the time the rocks were formed. Chloride is very soluble in water and moves freely with water through soil and rocks. Chloride is not readily consumed by microorganisms, so it is more persistent than nitrates (Source: U.S. Geological Survey, 2005). In the forest site, the Chloride concentration in the ground water should be lower than 14mg/l. In the agricultural site it should be around 60mg/l.

Chrome

Chromium dissolved in ground water occurs naturally in the environment as CR (VI) anion chromate (CrO_4^{2-}) and various Cr (III) hydrolysis species $[Cr(OH)_2^+, Cr(OH)_3^0$ and $Cr(OH)_4^-]$ (Source: HRC TB 2.7.5¹²).

Total Cyanide

Cyanide occurs as a ground water contaminant at various current and former industrial sites, including electroplating facilities, aluminum production plants, manufactured-gas plants (MGP), and gold mining industries.

¹² HRC: Hydrogen release compound; HRC TB: HRC technical bulletin. HRC TB 2.7.5: chromium remediation in ground water.

Iron and Manganese

Iron and manganese are metallic elements present in many types of rock. Iron has the symbol "Fe" and manganese has the given symbol "Mn." Both are commonly found in water and are essential elements required in small amounts by all living organisms. Concentrations of iron and manganese in ground water are often higher than those measured in surface waters. The most common sources of iron and manganese in ground water are naturally occurring, for example from weathering of iron and manganese bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron and manganese to local ground water (Source: British Columbia government website).

Copper and Nickel

Copper and nickel are the same as zinc in that it occurs in large quantities in rocks. Their concentration in ground water are usually well below the amount that could potentially occur (based on solubility). Consequently, their concentration in geologic materials generally limits its concentration in the ground water. (Source: Minnesota pollution control agency)

Lead

Lead is a main-group element with symbol Pb (Latin: plumbum) and atomic number 82 (Source: Wikipedia). Lead is used as a major anti-knock additive in gasoline.

Sodium

Sodium is a highly soluble chemical element with the symbol "Na." It is often naturally found in ground water, which is because most rocks and soils contain sodium compounds from which sodium is easily dissolved. The most common sources of elevated sodium levels in ground water are:

- Erosion of salt deposits and sodium bearing rock minerals
- Naturally occurring brackish water of some aquifers
- Salt water intrusion into wells in coastal areas
- Filtration of surface water contaminated by road salt
- Irrigation and precipitation leaching through soils high in sodium
- Ground water pollution by sewage effluent
- Seepage of leachate from landfills or industrial sites.

This information comes from The British Columbia Ground water association.

Sulfate

Sulfate is a chemical commonly found in air, soil and water. Since it is soluble (easily dissolved) in water, sulfate is found at high concentrations in many aquifers and in surface water. There are many potential sources of sulfate. Gypsum is an important source in many aquifers having high concentrations of sulfate. Reduced forms of sulfur are oxidized to sulfate in the presence of oxygen (in some cases nitrate can also replace oxygen). This process often occurs when sulfide minerals are mined. In the past century, atmospheric fallout has become an important source of sulfates to soils and, eventually, to ground water. Other sources of sulfur include the decomposition of organic matter sources, such as volcanoes. Some other main sources are fertilizer use and land application of animal wastes.

Organic carbon

The organic carbon is the foundation of most of life on earth, but it has a very low concentration in the ground water. Gounot (1994) found that total organic carbon concentration is no more than 1 mg/l in the early ground water, also normally the organic carbon concentration will relate with the distance to the recharge area. The dissolved organic carbon is a broad classification for organic molecules of varied origin and composition within aquatic systems (Wikipedia).

Total hardness

Water hardness is primarily the amount of calcium and magnesium, and to a lesser extent, iron in the water. Water hardness is measured by adding up the concentrations of calcium, magnesium and converting this value to an equivalent concentration of calcium carbonate (CaCO3) in milligrams per litre (mg/L) of water. The optimum range of hardness in drinking water is from 80 to 100 mg/L. Water hardness in most ground water is naturally occurring from weathering of limestone, sedimentary rock and calcium bearing minerals. Hardness can also occur locally in ground water from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas. The information is from The British Columbia Ground water association.

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One of the major environmental issues is acidification. Acidification caused by atmospheric emissions of CO2, NOx, SOx, NHx. Normally NOx, SOx, NHx in the atmosphere will be oxide. Then they (also the CO2) will be dissolved in the cloud droplets to make the rain acid. Since 1940, the atmospheric emissions of CO2, NOx, SOx, NHx increased.

Appendix II

The Climate information of Achterhoek is noted in the table below. The data are from FAO website

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			Prc.	Wet	Tmp. Tmp. Tm				Rel.	C	Wind		
Month	Prc.	Prc.	CV		mean		min.		hum.	Sun shine	(2m)	ETo	ETo
	mm/m	mm/d	%	days	°C	°C	°C	days	%	%	m/s	mm/m	mm/d
Jan	65	2.1	42.9	18.2	1.9	4.3	-0.5	15.9	89.6	15.2	3.2	11	0.4
Feb	45	1.6	60.1	12.7	2.5	5.4	-0.4	15.9	84.8	25.5	3.2	17	0.6
Mar	61	2.0	45.9	17.1	5.3	8.9	1.8	12.6	81.1	27.1	3.1	35	1.1
Apr	49	1.6	52.7	14.7	8.1	12.6	3.6	7.8	75.3	35.4	3.0	59	2.0
May	61	2.0	45.6	14.2	12.6	17.5	7.7	2.5	73.4	39.5	2.5	88	2.8
Jun	72	2.4	46.9	15.8	15.3	20.1	10.5	0.0	76.0	35.4	2.4	95	3.2
Jul	73	2.4	48.8	14.5	17.0	21.8	12.3	0.0	76.5	36.0	2.4	101	3.3
Aug	65	2.1	47.6	13.8	17.0	22.0	12.1	0.0	76.5	39.5	2.3	91	2.9
Sep	59	2.0	60.6	15.1	14.1	18.5	9.8	1.1	82.4	34.1	2.4	57	1.9
Oct	57	1.8	56.2	14.3	10.5	14.2	6.9	3.6	85.3	31.1	2.5	33	1.1
Nov	69	2.3	41.1	17.0	5.8	8.5	3.1	9.0	88.6	19.6	3.1	16	0.5
	74	2.4	56.7	18.8	3.3	5.5	1.1	13.7	90.4	14.0	3.1	10	0.3
Dec													

Click here to use these values to calculate a soil water balance and crop water requirements.

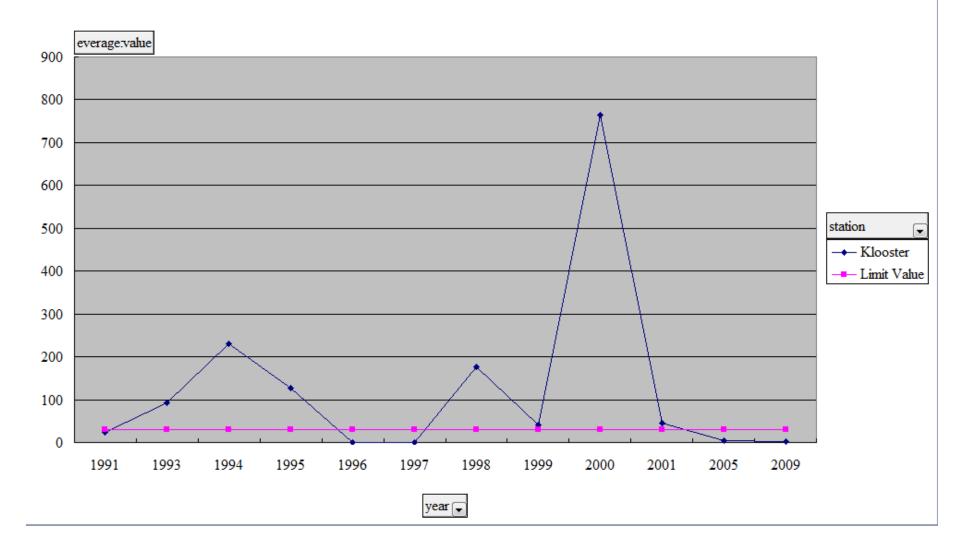
Appendix III

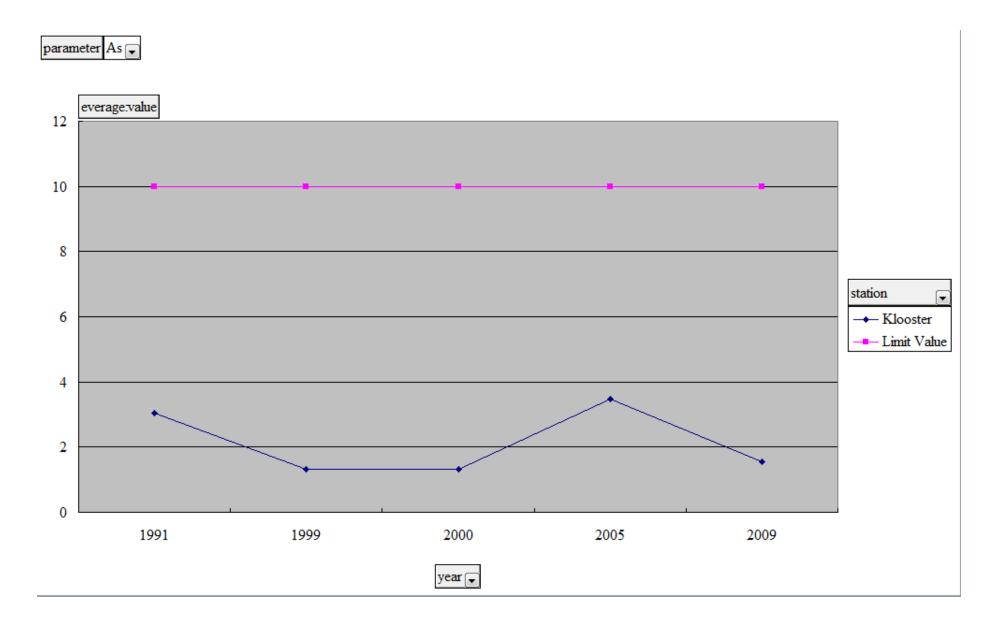
In the appendix III, 17 elements concentration tends graph are listed. For reset of the elements, because their 90% of the concentration values are under the detection limit which is not enough to make the trend graph.

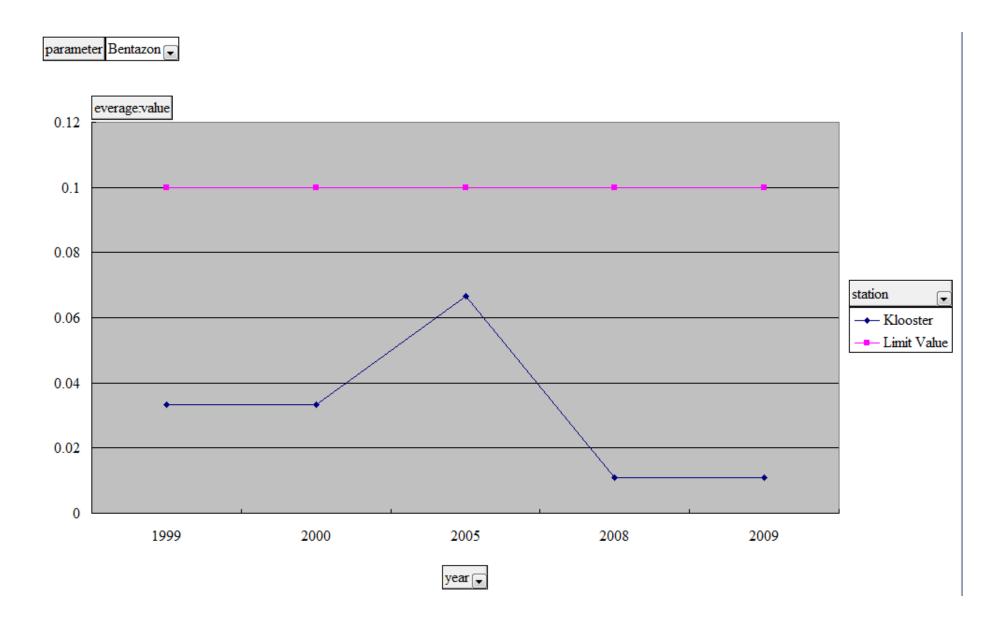
List of the graphs:

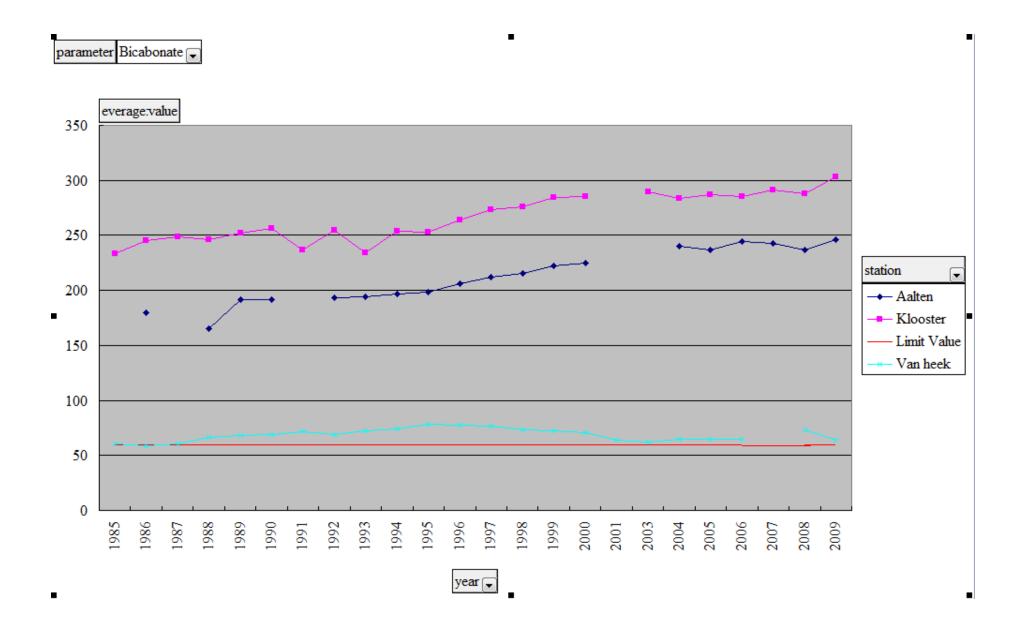
- Aluminum
- Arsenic
- Bentazon
- Bicarbonate
- Chloride
- DOC
- Iron
- Manganese
- Sodium
- Ammonium
- Nitrate
- pH
- Total Hardness
- Sulfate
- Si- index
- TOC

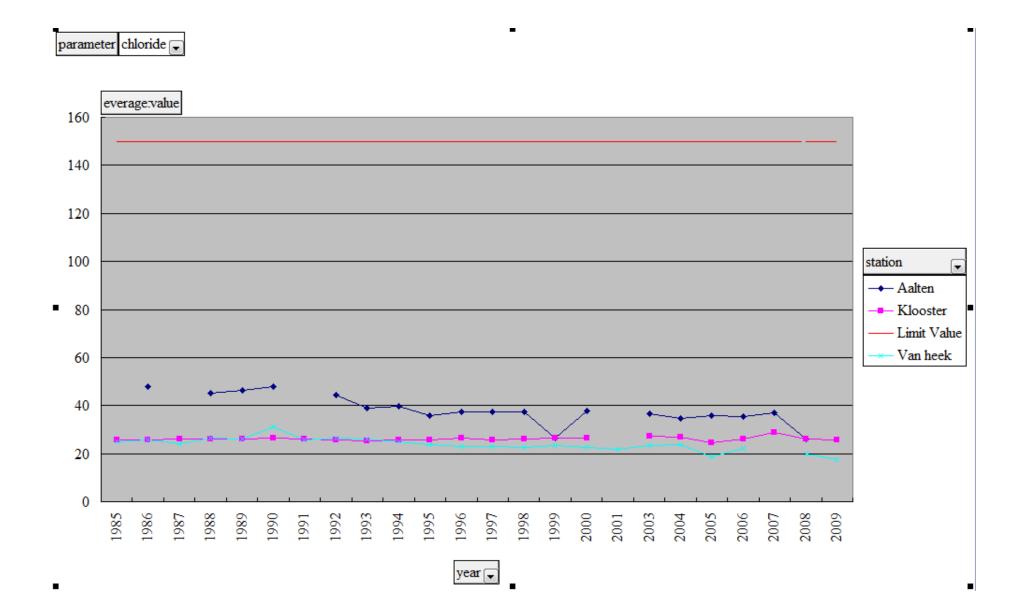
parameter Al 🖵

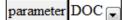


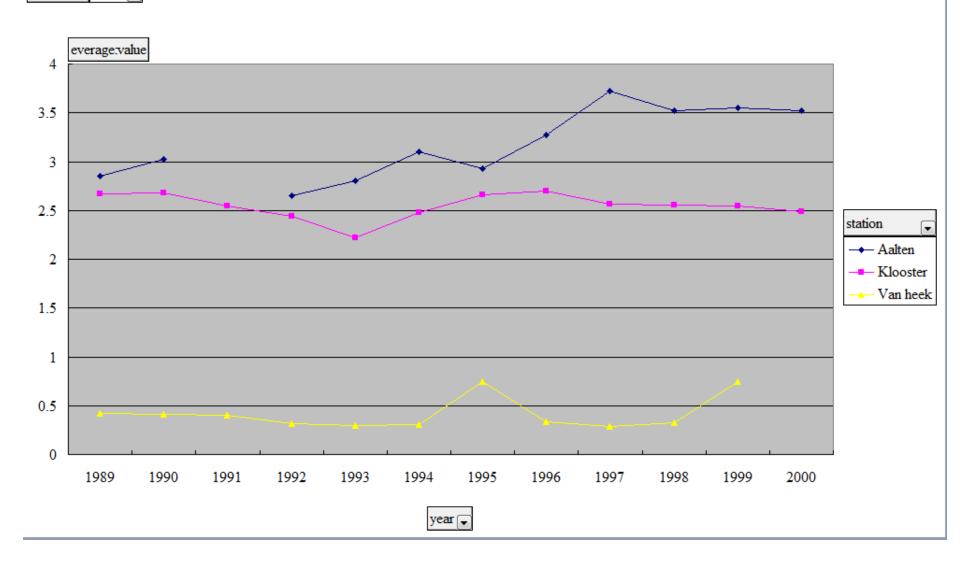


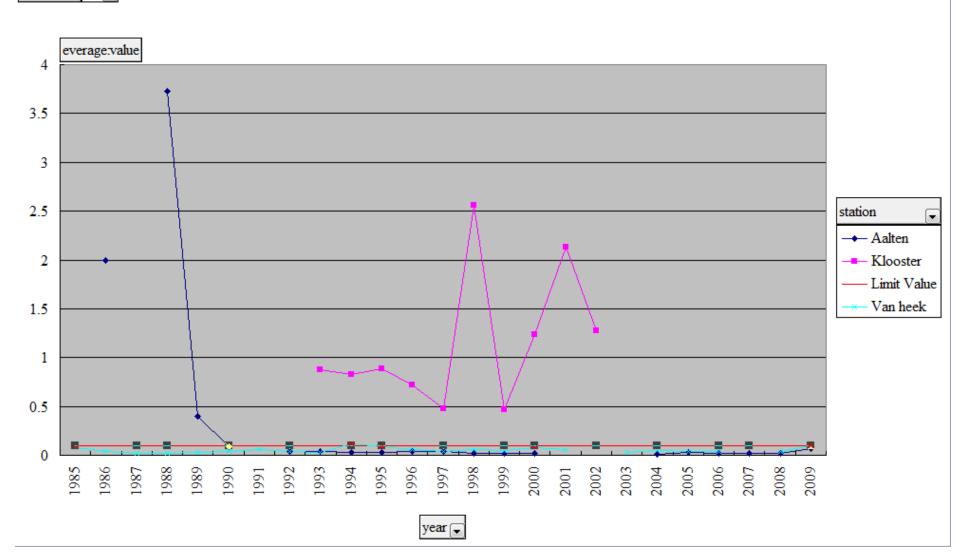






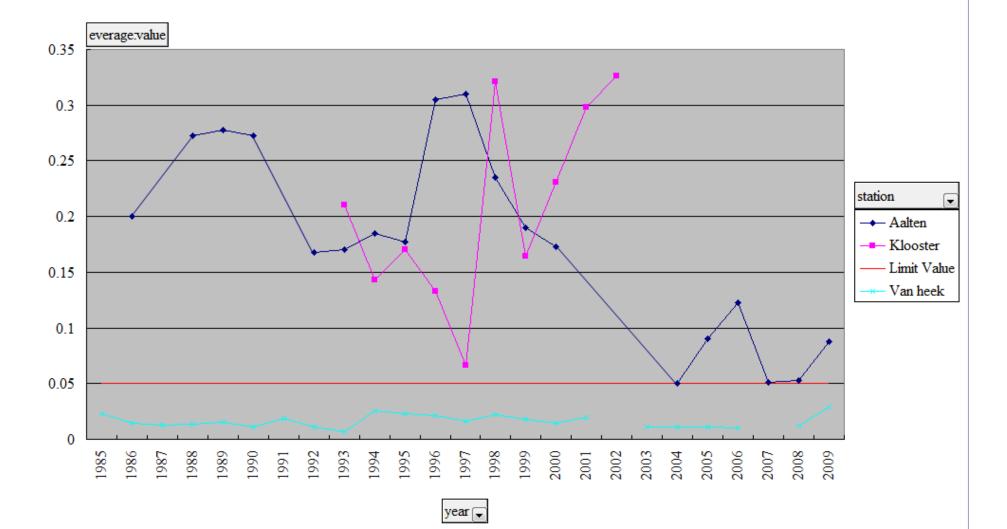


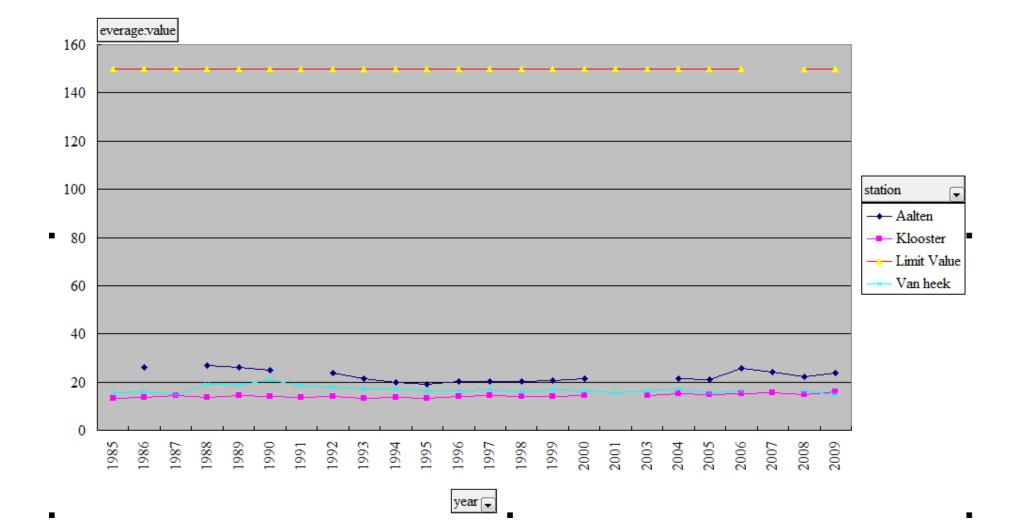




parameter Fe 🖵

parameter Mn 💌



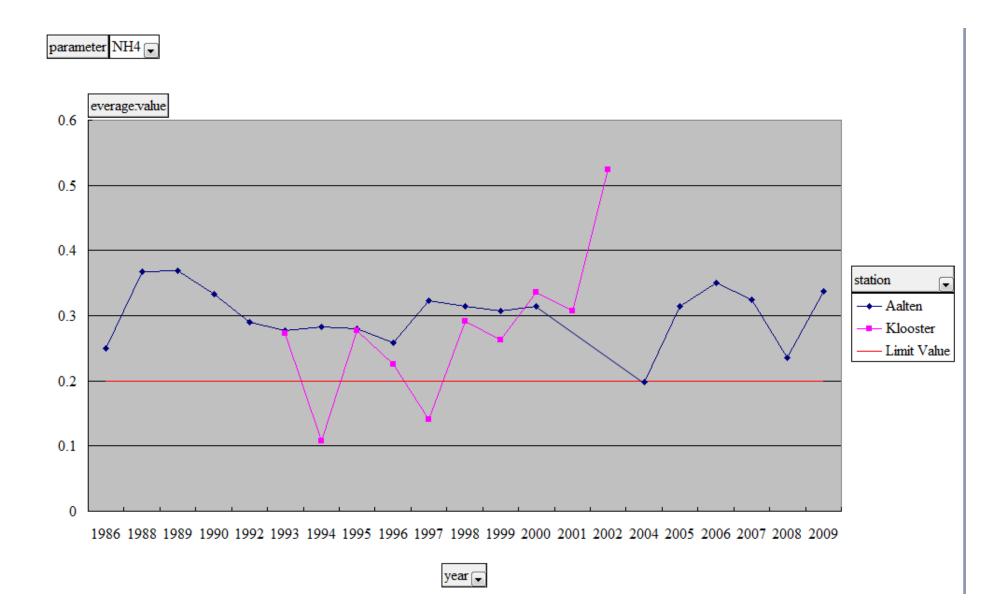


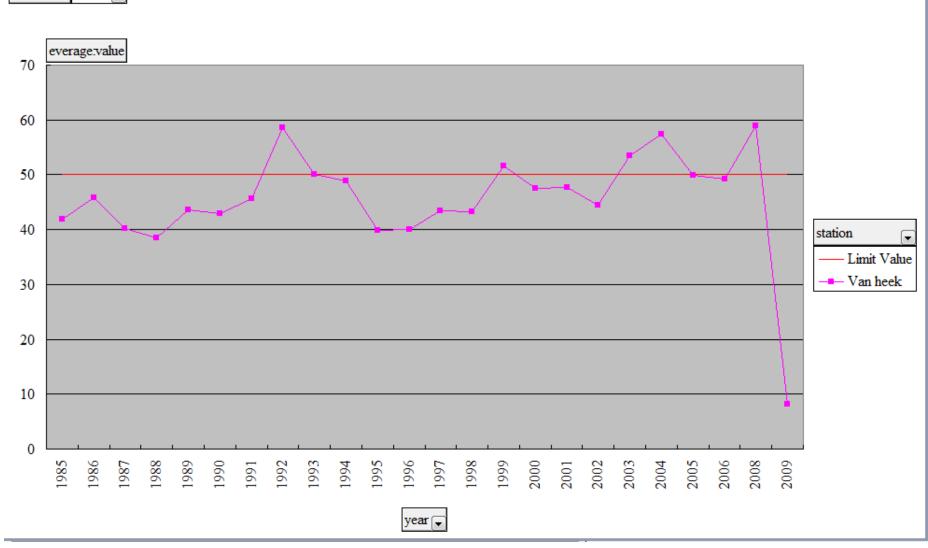
-

parameter sodium 🖵

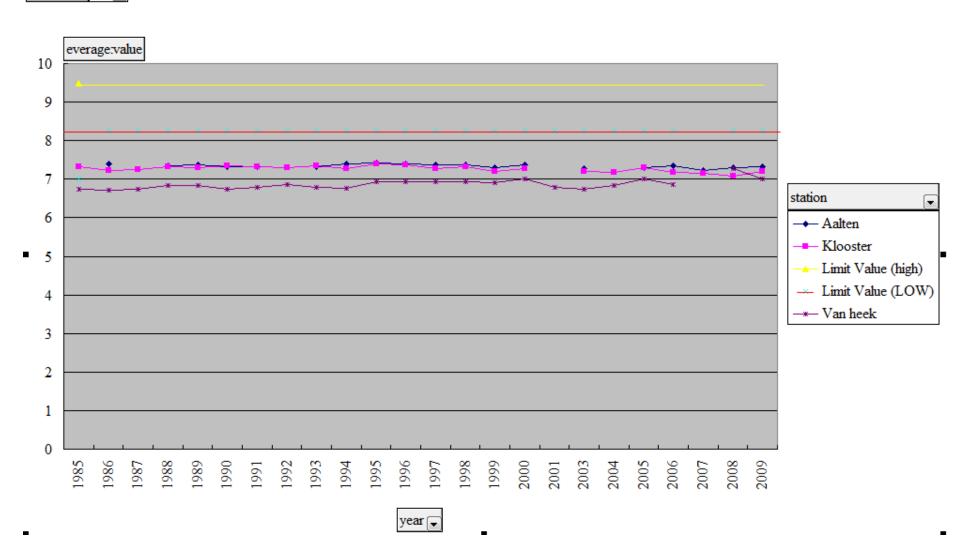
53

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parameter nitrate 🖵



parameter pH 💌

