PUBLIC SUPPLY WELL FIELDS AS A VALUABLE GROUNDWATER QUALITY MONITORING NETWORK

Igor Mendizabal

VRIJE UNIVERSITEIT

PUBLIC SUPPLY WELL FIELDS AS A VALUABLE GROUNDWATER QUALITY MONITORING NETWORK

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan
de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. L.M. Bouter,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Aard- en Levenswetenschappen
op dinsdag 22 november 2011 om 15.45 uur
in de aula van de universiteit,
De Boelelaan 1105

door

Igor Mendizabal Fernandez de la Bastida

geboren te Beasain, Spanje

promotor: prof. dr. P.J. Stuijfzand

To Bertha, Nayra and Amey

Leescommissie:
dr. Maria Teresa Condesso de Melo
dr. ir. Kees Meinardi
dr. Boris van Breukelen
dr. Pauline van Gaans
prof. dr. Kristine Walraevens

Contents

Preface

This thesis is the result of a very intense, busy and instructive period: Exciting research, great discussions, many colleagues, good friends and an exceptional guidance. The thesis is now finished, but it could never have been accomplished without the valuable help provided by many people, which I try to acknowledge in the following lines, with the risk of forgetting somebody, to whom I herewith apologize.

To start with Prof. dr. Pieter J. Stuyfzand, the promotor. Dear Pieter, after my experience at Gemeentewaterleidingen Amsterdam I decided to widen my horizons with the master in hydrogeology and to finish the master with a thesis on groundwater quality, under your supervision. You became professor at the VU University of Amsterdam during the project and offered me the extension of the master thesis towards a PhD, which results are presented in this book. My most sincere thanks, not only for offering me the opportunity, but also for your involvement, both scientifically and personal, in your multiple roles as promotor and copromotor at the VU and colleague and project leader at KWR. I experienced this time as a luxurious and instructive period. I was your only PhD student for a few years (now you have to divide your time amongst more than 15) and you were very involved, both in research and personal spheres. We could always find the time to discuss, either during our drive back home from KWR, or when we shared office at VU, or any time I required your advice. Thanks for your friendship and for your critical advice. You were always there and I hope this friendship will continue now the PhD is finished.

The financial funds for carrying out this investigation were mainly provided by the Joint Research Program of the Dutch Waterworks (BTO) and Delft Cluster, project number CT05.30. But how did I get here? Everything began thanks to Dr. Carmen Gomez Artola and prof. Dr. Fernando Lopez Vera from the Autonomous University of Madrid, who triggered my fascination towards groundwater. The theory on water particles flowing through tiny pores within sediments and the fact that this water could be abstracted in such large volumes as to supply a whole city with drinking water made such an impression on me that I decided to become a hydrologist as soon as I finished my master's degree on geochemistry in the Autonomous University of Madrid.

Theo Olsthoorn, Piere Kamps and Jos Moorman (Jos, I know you are reading these acknowledgements even before the summary and conclusions …) gave me the means to step out from the geochemical laboratory towards hydrogeology, fieldwork and modeling during my three years at Gemeentewaterleidingen Amsterdam (today Waternet). Thanks for helping me understand the ins and outs of hydrogeology, groundwater modeling and time series analysis. And of course, for demanding me to learn Matlab, which unfortunately deprives you too often from sleeping hours during the night and free weekends, but without which, the results presented in this thesis could never have been accomplished.

Maarten Waterloo, Boris van Breukelen, Vincent Post and Koos Groen are acknowledged for the many lunch discussions at VU (and Jacinta for the delicious meals on Thursdays). It is not common that a PhD student joins the staff for lunch and I experienced it as a privilege. Thanks for your advice and suggestions and for reviewing numerous parts of this book.

Colleagues at KWR, thanks for the great moments during the past six years. Special thanks to my room mates Bernard, Ruud and Flip. Bernard, thanks for showing me the way during my first days with KWR, for making the time to assist me with all my 'kleine vraagjes' that were often not so 'klein', regarding GIS problems I faced during this research, for the kilometers we swam together during lunch breaks and for being such a great person. And Flip and Ruud thanks for your support during my last period at KWR. Thanks Jos for the first piece of code and Inke for your help with HyCA; Kees van Beek for your advice and the old archive of reports concerning PSWFs, which you might still want back for your postdoc position; Kees Vink, Klaasjan and Gijsbert for the good moments; Pim for the numerous KWR reports and bibliographic searches; Vassili and Gerard for your help during the tedious data digitalization process; Wim for your graphics and design and Kim for numerous GIS data. And Jan Willem, thanks for your support during difficult periods.

Cor Merks, my team leader at my current position as hydrologist at PWN, for imposing the finishing of the PhD as one of my main targets for 2011. Letting me work on the PhD one day a week made it possible to finish it within 2011 indeed.

Dutch waterworks are greatly acknowledged, not only for their financial support throughout this project, but also for believing in me when I proposed the largest ever organized national sampling campaign in The Netherlands. We sampled all active public supply well fields for chemical analysis of macroparameters, trace elements and stable isotopes, during the first trimester of 2008. And we succeeded in such a tremendous effort, mainly thanks to the involvement of many people. With apologies for anybody forgotten in such a long list, my sincere gratitude goes to Harry Boukes, Ben Beerens, Toon van Alphen, Edwin Gerritsen and Harrie Melsen (Brabant Water); Martin de Jonge (Vitens), Stephan Teunissen, Manfred Harmsen, Ferry von Bannisseht, Alle Broersma, John Doorn, Gerrit-Jan Vierhuizen, Laura Keizers, Jos van Laarschot, Martijn Becks, Antoon Bongers, Eibert van de Brug, Paul Peters and Roel van der Aart (Vitens Laboratorium Leeuwarden); Caspar van Genuchten (Oasen); Birgitta Putters, Hans Eijkelhardt, Guus Stassen, Jan-Daan Duimel, Wiel Ramakers, Wen Akkermans, Paul Verstappen, Ed Hermse, Marcel Wijnhoven, Gerrit Janssen and Ron Burhenne (WML); Jet Lebbink (PWN); Piere Kamps (Waternet); Ed van der Mark (DZH); Peter Hendriks and Ramon Imamdi (Het Waterlaboratorium); Richard Schuitemaker (Evides); Nico van der Moot (Waterleiding Maatschappij Drenthe); Theo Vlaar (Waterbedrijf Groningen); Harm de Kleine, Arjan de Jonge and Albert Jan Roelofs (Waterleiding Laboratorium Noord); Susanne Wuijts, Monique van der Aa and Arthur de Groot (National Institute for Public Health and the Environment - RIVM); Jon Visser, Hubbert Vonhoff and Suzan Verdegaal (Laboratorium VU).

Numerous additional data were also provided by many people from different institutions. Many thanks to Ane Wiersma, Ronald Harting and Gu Oude Essing (Deltares) for geological data; Maria Juhàsz-Holterman and Wouter Swierstra (WML); Martin de Jonge and Rob Breedveld (Vintes); Rob Lafort (Evides) and Ans Versteegh and Harald Dik (RIVM) for additional historical data of Public Supply Well Fields; Mariëtte van Vlerken (Vitens); Harrie Timmer (Oasen) and Jochem Fritz (DZH) for hydrogeochemical characteristics of public supply well fields; Martin de Jonge (Vitens); Birgitta Putters and Linda Ruijpers (WML); and Mark Bakker (TU-delft) for hydrological response curves of PSWFs; Harald Dik and Susanne Wuijts (RIVM) for well head protection areas of all active public supply well fields; Peter Stoks; Gerrit van de Haar and Karina Pikaard (RIWA) for surface water quality data; Hans van der Meij and Gerrit van der Meer (Deltares) for data from the national groundwater quality monitoring network; Ton van der Linden and Herman Prins (RIVM) for data regarding pesticides; Theo van der Heijden (Wageningen UR/Alterra/Centrum Geo-Informatie Geodesk) for the land use map of The Netherlands; and Paul Baggelaar (Icastat) and Eit van der Meulen (AMO) for the computer program Trendanalist.

And of course Bertha, thanks for believing in me even before I started the PhD and for your support.

Amsterdam, The Netherlands

June, 2011

Igor Mendizabal

Summary

Groundwater is an extremely valuable and reliable source of drinking water for public and individual supply, which is becoming extremely vulnerable to human interference because of its hydrogeological structure, the increasing demographical pressure and the multitude and variety of anthropogenic activities that threaten its quality. During the last decades, many countries have set up extensive national groundwater quality monitoring networks, in order to preserve and protect drinking water resources. The specific goals of such monitoring networks include: determining the current quality of the groundwater, identifying trends in groundwater quality, and defining the regional natural background concentrations in groundwater. The first goal is usually easy to achieve with a recently developed monitoring network, but the resulting time periods are usually insufficient to achieve the other two goals.

A monitoring network that is available in most countries and which can work towards all three goals simultaneously because of widespread spatial distribution and long periods of time is the monitoring network for public supply well fields (PSWFs). These well fields are monitored on a regular basis as an integral part of the quality surveillance of national drinking water supply. The monitoring network, which is operational in the Netherlands since 1898, is used in this thesis to address, among others, the three goals mentioned above. The hydrochemical status quo and development of trends in raw groundwater used for drinking water purposes is first established for individual PSWFs and subsequently upscaled to groundwater bodies (GWB) on a national scale.

This doctoral study is primarily based on: (1) an individual monitoring campaign of 241 well fields carried out in 2008, involving a very detailed inorganic analysis of primary components, a number of trace elements, and some environmental isotopes; and (2) a database of historical quality data regarding all raw waters extracted in the Netherlands (mostly from well fields, but also from surface water intake points and surface water from reservoirs) in the period 1898-2008.

Chapter 2: Guidelines for interpreting hydrochemical data from PSWFs

PSWFs form an extremely valuable network for monitoring groundwater quality because they offer (a) information on the raw water quality over a uniquely long period (beginning in 1898); (b) an extensive analytical package; and (c) representativeness for an enormous volume of groundwater, for which even the pumped volumes have been registered. However, there are also important complications with interpretation (also important in terms of the Water Framework Directive), which have been translated in this publication into guidelines. These guidelines cover the following aspects: (1) changes in monitoring methods, pre-treatment, detection limits and units over the past 100 years; (2) prevention of different types of short-circuiting, in particular to the pumped aquifer via leaking clay plugs, within the pumped aquifer via the well screen or gravel pack during inactivity, and through leaking valves in transport pipes near pumped wells; (3) interaction of water with well materials, resulting in abnormally high concentrations of copper, PAHs and Pb; (4) adaptations of a well field under threatening conditions, such as by closing bad wells, expanding towards areas of better quality, switching to artificial recharge or river bank filtration, subsurface iron removal, changing the pumping regime; and (5) mixing groundwaters of differing composition, origin and age.

Two solutions are offered for the last aspects. The origin of the water can be determined by means of semi(natural) tracers. The use of the heavy, stable isotopes of water (^{2}H and ^{18}O) to quantify the mixing rate of Rhine bank filtrate with normal groundwater is demonstrated. Determination of the origin is discussed in more detail in Chapter 4.

The second solution involves the presentation of a new method for determining the hydrological response curve (cumulative travel time distribution). This method departs from an analytical hydrological calculation on the basis of the depth of the well screens, among other data. The result is then hydrochemically corrected on the basis of a single tritium analysis of the raw water in the year X and a known tritium input function for the aquifer. The result is a significantly improved prediction of the percentage of young water containing tritium (infiltrated after 1953). This method can also be used to validate/calibrate hydrological response curves obtained using three-dimensional hydrological models.

Examples are given to demonstrate that (a) PSWFs are a very welcome addition to the relatively shallow Dutch National Groundwater Quality Monitoring Network; (b) well field adaptation measures strongly influence trends; and (c) the natural background levels of the quality of deep groundwater can be determined by studying the trends. Trends and natural background levels are studied in more detail in Chapter 6.

Chapter 3: HyCA, the all-in-one approach for hydrochemical analysis of water quality data

This Chapter presents HyCA (HydroChemical Analysis), a new computer program for efficient hydrochemical analysis of large water quality databases in 4D (x, y, z, t). HyCA was primarily developed within the framework of this doctoral study in order to set up, control, analyze and interpret an extremely large database, namely the database of water quality data from the national network of PSWFs. The emphasis laid on the inorganic chemistry and on well fields where groundwater is withdrawn. However, the withdrawal points for surface water have also been included, and HyCA has been designed such that other quality parameters, including organic micro contaminants, microorganisms, and radio nuclides are accommodated in the database. The program is also applicable to any types of water and sampling technique. As a result, it is a user friendly multiuse tool that is already being used in numerous fronts.

Chapter 3 describes the structure of HyCA, how it differs from somewhat comparable programs available in the market, and what it is capable of in terms of data management, data presentation (including visualization) and data interpretation.

HyCA is developed within the MATLAB environment, but operates separately (no license required). HyCA offers basic facilities from Menyanthes, ChemCal and PHREEQC-2 (no licenses required), and numerous additional new functions. A fast database accepts nearly all input types (including ASCII, Excel, DINO and DAWACO). A vast range of selections, calculations, and plots can be executed with just a few mouse clicks.

HyCA is suitable for everyone who works with water quality data at any level. It can answer questions about analytical reliability, mineral saturation, water types, degree of contamination, and redox levels; and it can produce tables, maps, profiles, plots, and more.

New and existing data analysis techniques have been combined into a single software package, reducing time-consuming data manipulation steps and enabling a wide variety of computations to be carried out with just a few mouse clicks, simplifying data analysis. This integration of possibilities results in an incredibly fast visual screening of the database and an exceptionally rapid production of maps and plots. This, along with the availability of elements of hydrochemical facies analysis, differentiates HyCA from alternative commercial programs like Aquachem. Without HyCA, the content of this thesis would have been entirely different.

Chapter 4: Hydrochemical typology of PSWFs

In the past, Dutch well fields were classified on the basis of the aquifer type (phreatic, semiconfined, limestone) and source type (precipitation, artificial recharge, or river bank filtration). In this Chapter, a new international typology is introduced for PSWFs, which builds on the hydrochemical facies analysis of Stuyfzand (1993). The classification is based on the spatial distribution of groundwater bodies with specific origins (hydrosome) and characteristic hydrochemical zones within each hydrosome (facies), which typifies the water quality from that PSWF on the basis of specific characteristics.

The type of water body, that is to say its origin, is determined on the basis of geomorphological and potentiometric maps combined with (semi)natural tracers. The simultaneous use of several tracers (multitracing) is preferred in order to increase the certainty of the results obtained. In this regard, the contrast of the various tracers (such as Cl, ^{18}O, Cl/Br, EC, Mg, Mo, B) between infiltrated Rhine water (R) and autochthonous groundwater (G) is quantified as based on measurements of 100% R and 100% G. This is done using a new key figure: the absolute value of the difference in average values divided by the root of the product of both standard deviations. In order to quantify the mixing rate of R and G, the suitable tracers (with a sufficient contrast) are weighted and averaged according to the score on contrast.

The hydrochemical facies is determined by a combination of three indices (age, redox state and alkalinity), specifically developed for PSWFs. The age index is derived from the percentage of young water (%Y), defined as water infiltrated after 1953, related to increased tritium activity since then. The %Y follows from the calculated hydrological response curve (see Chapter 2) and indicates the chance of recent pollutants. The redox index determines the oxidation or reduction state of water, and as such, the chance of (a) (bio)degradation of numerous organic pollutants; (b) (re)mobilization, precipitation or degradation of inorganic pollutants; and (c) the toxicity of certain compounds. The redox index is determined on the basis of all redox-sensitive main components of water (O_2, NO_3, SO_4, Fe, Mn, NH_4, H_2S and CH_4).

The alkalinity index, which in the Dutch situation primarily focuses on the concentration of HCO_3, indicates to which degree the water reacts especially with calcium carbonate and organic material.

These three facies parameters are also used to quantify the intrinsic vulnerability of PSWFs (see Chapter 5). For this purpose, the redox index was further refined.

All 206 PSWFs active in 2008 are classified according to this hydrochemical typology. This results in the differentiation of eleven water bodies and eleven facies parameters. The resulting water bodies, defined as much as possible in accordance to the Water Framework Directive are: Northern, Eastern, Bentheimer sandstone, Central, Southern, Flanders, Western, Coastal Dunes, Limestone, Artificial recharge (sub-types Rhine, Meuse, IJsselmeer, other) and River bank filtration (sub-types Rhine, Meuse, other). The facies parameters are: young, intermediate and old; (sub)oxic, anoxic, deep anoxic, and mixed; and very low, low, intermediate, and high alkalinity.

The classification results are presented by means of maps in planar view and three cross sections over the country, with a clear explanation of patterns and processes affecting each water body. The results offer direct insight into the vulnerability of PSWFs (see Chapter 5) and constitute a valuable tool for optimizing groundwater quality monitoring programs. The (potential) presence of certain pollutants strongly depends on the type of groundwater body and the hydrochemical facies. The maps facilitate communication between researchers, water managers, and politicians; and aid in solving complex groundwater management problems on a variety of scales, from a single well, well field or region up to the national or European level. The hydrochemical typology of well fields can also be applied to monitoring wells.

Chapter 5: Quantifying the vulnerability of PSWFs

The theme of this Chapter is a new method to quantify the intrinsic vulnerability of PSWFs (VIP) and their specific vulnerability towards a particular contaminant X (VIP_X), either a main component, trace element, or micropollutant.

Intrinsic vulnerability is defined as the sensitivity of the PSWF to contamination as a result of unfavorable characteristics of the system (such as a short travel time and limited buffering capacity of the aquifer), regardless of the type of pollutant or land use. When PSWFs change, because of either expansion or adaptation measures (see Chapter 2), VIP also changes. VIP is therefore not a 100% static characteristic. It is calculated from the hydrochemical facies parameters of age, redox level and alkalinity (see Chapter 4), plus the fraction of surface water in the pumped water. This results in a score ranging between 0 for old, deeply anoxic, high alkalinity groundwater and around 30 for young, (sub)oxic, acidic groundwater. The redox level defined in Chapter 4 is further developed in this chapter, by refining the sulphate-reducing conditions and by subdividing the mixed redox state.

Specific vulnerability is defined as the sensitivity of the PSWF to contamination by a particular compound X, not only because of unfavorable characteristics of the system, but also because of the strain placed on the system. The latter is mainly influenced by land use and the behavior of contaminant X in the soil. As a result, VIP_X is much less static than VIP. VIP_X combines VIP with four aspects: the current concentration of X in the pumped water, the mobility or mobilization of X in the hydrochemical environment as determined on the basis of the redox state and alkalinity of the raw water, the land use within the well head protection area or water catchment area, and the pollution risk for X as determined by its concentration in shallow groundwater and/or the infiltrated surface water.

The proposed method requires both simple data and data that are more difficult to obtain. The easily obtained data are: (1) the quality of the raw water pumped, shallow groundwater from observation wells (preferably within the well head protection area or water catchment area), and surface water prior to its infiltration in case of PSWFs receiving contributions from artificial recharge or river bank filtration; (2) a land use map of the area; and (3) an (inter)national drinking water standard or otherwise some baseline value. Data which is more difficult to obtain has to do with the age distribution of the extracted water and the fraction of infiltrated surface water in the pumped water. These data can be estimated using the new method introduced to determine the hydrological response curve (see Chapter 2) and multitracing (see Chapter 4), respectively.

The national survey on the intrinsic vulnerability of 241 Dutch PSWFs (175 single PSWFs plus 33 PSWFs subdivided into two partial abstractions), carried out in 2008, reveals that 50% have a low VIP (<1), 41% have an intermediate VIP (1-4), and 9% have a high VIP (4-10). PSWFs with VIP <1 are mainly observed at greater depth, in (semi)confined aquifers or in the exfiltration zones of large hydrosomes. The very vulnerable PSWFs have shallow well screens and are pumping from either acidified, phreatic sandy aquifers, (sub)oxic, artificially recharged coastal dunes, (sub)oxic river banks or oxic limestone.

The national survey of the specific vulnerability of these 241 well fields in terms of Cl, NO_3, SO_4, Al, As, Ni, bentazone, carbendazim, and MCPP (mecoprop) revealed relatively high values for Cl and bentazone, which behave conservatively (redox and alkalinity indifferent). PSWFs pumping shallow groundwater from areas with a high density of intensive agriculture are the most vulnerable to bentazone. High vulnerability to Al and Ni is seen in areas with intensive agriculture and forest and in areas with groundwater of low alkalinity.

In principle, VIP and VIP_X are not based on site specific hydrological or geochemical parameters, but on standard factors exclusively derived from the water composition. This makes it a robust objective method that can be applied elsewhere and could therefore serve as a means to standardize vulnerability assessment of PSWFs. The method is established in a simple computer algorithm which can easily be modified, in order to modify normalization in terms of drinking water standards and the land use.

Chapter 6: Natural background levels and historical trends

This Chapter examines historical hydrochemical data of PSWFs between 1898 and 2008, in order to derive the natural background concentration levels of and the water quality trends in the raw water delivered by PSWFs. Water quality parameters with a sufficiently long data record that are considered indicators of specific processes were selected for trend analysis: Cl (general pollution and salinization); NO3 (agriculture); SO4, HCO3 and total hardness (together indicating acidification or hardening). This data set was extended with EC, pH, Na, K, Fe, Mn and SiO2.

The natural background levels are derived from data series prior to 1940 if they did not show a trend during the first six years of extraction. The philosophy behind this criterion is that PSWFs rarely undergo changes during the first six years of operation and that general environmental pollution within and around water catchment areas did not reach problematic levels before 1940.

Trends have only been determined for the period 1960-2005 and for those PSWFs which were active during this period, in order to obtain a homogenous population and period. Within this population and period, the following trends have been differentiated: large, intermediate and small upward trends; large, intermediate, and small downward trends; no trend; and convex and concave trend reversals (from upward to downward and from downward to upward, respectively). Clear convex trend reversals have been observed at PSWFs which extract a significant fraction of surface water from the Rhine either via artificial recharge or river bank filtration. This trend reversal is primarily due to the large number of sanitation measures in the entire Rhine basin. Other reversing trends have been observed in shallow groundwaters, such as declining SO4 concentrations due to decreasing atmospheric SO4 inputs since the early 1970s and reduced NO3 concentrations due to improved agricultural practices. These improvements are only evident in a very limited number of shallow PSWFs, due to longer travel times and more mixing with older groundwater.

On the basis of the trends observed, trend bundles are defined as combinations of trends in several quality parameters which can be connected to a particular anthropogenic influence. The following seven trend bundles are defined: Dominated by surface water; with acidification due to atmospheric deposition; influenced by agriculture above a calcareous aquifer with pyrite; influenced by agriculture above a calcareous aquifer without pyrite; influenced by salinization; no trend; and other.

A dimensionless normalized concentration change index (NCC) is introduced in order to quantify and map concentration changes in relation to the natural background levels.

Finally, a simple method is presented for scaling up natural background concentration levels obtained for individual PSWFs to the level of groundwater bodies at a national scale, with differentiation of hydrochemical zones defined as based on the hydrochemical system analysis presented in Chapter 4. The results in terms of natural background concentrations, trends for guide parameters, trend bundles, and the normalized concentration change index are presented on national maps of the Netherlands.

Samenvatting

Grondwater is een zeer waardevolle, betrouwbare bron voor drinkwaterbereiding, maar blijkt langzamerhand steeds kwetsbaarder voor menselijke beïnvloeding via overexploitatie en een veelvoud aan kwaliteitsbedreigende activiteiten. In veel landen zijn enkele decennia geleden ter bewaking en bescherming van de drinkwaterbronnen nationale grondwaterkwaliteitsmeetnetten ingericht en beheerd. Specifieke doelen van die meetnetten zijn: het vaststellen van de actuele grondwaterkwaliteit, identificatie van trends in grondwaterkwaliteit, en bepaling van de regionale natuurlijke achtergrondconcentraties in grondwater. Het eerste doel wordt meestal eenvoudig gehaald met een dergelijk meetnet, maar de resulterende tijdreeksen zijn dikwijls te kort om de andere twee doelen te bereiken.

Een meetnet dat in de meeste landen beschikbaar is en de drie doelen tegelijk kan dienen, dankzij een goede ruimtelijke spreiding en lange tijdreeksen, is het meetnet van puttenvelden voor de openbare drinkwatervoorziening. Deze puttenvelden worden namelijk regelmatig bemonsterd als onderdeel van de nationale drinkwaterkwaliteitsbewaking. Het meetnet dat in Nederland sinds 1898 operationeel is, wordt in dit proefschrift gebruikt om o.a. bovengenoemde drie doelen te adresseren. De hydrochemische status quo en trendmatige ontwikkelingen van grondwater voor drinkwaterproductie kunnen eerst vastgesteld worden voor afzonderlijke puttenvelden en vervolgens opgeschaald worden naar het niveau van een grondwaterlichaam op nationale schaal.

Voorliggend promotie-onderzoek is vooral gebaseerd op: (1) een eigen in 2008 uitgevoerde meetcampagne van 241 puttenvelden, met zeer uitvoerige anorganische analyse op hoofdbestanddelen, vele sporenelementen en enkele natuurlijke isotopen; en (2) een database met historische kwaliteitsgegevens van alle ruwe wateren van Nederlandse winningen (grotendeels puttenvelden, doch ook innamepunten oppervlaktewater en oppervlaktewater uit spaarbekkens) in de periode 1898-2008.

Hoofdstuk 2: Richtlijnen voor interpretatie van hydrochemische data van puttenvelden.
Puttenvelden vormen een zeer waardevol meetnet grondwaterkwaliteit, omdat zij kunnen bogen op o.a. (i) uniek lange tijdreeksen van kwaliteitsgegevens van het ruwe water (startend in 1898); (ii) een zeer breed analysenpakket; en (iii) representativiteit voor een zeer groot volume grondwater, waarvan zelfs de opgepompte hoeveelheid geregistreerd is. Er zijn echter ook belangrijke complicaties in de beoordeling (ook van belang voor de KRW) die in deze publicatie zijn vertaald in richtlijnen. Deze betreffen de volgende aspecten: (1) veranderingen in meetmethoden, voorbehandeling, detectielimieten en eenheden tijdens de afgelopen 110 jaar; (2) het voorkomen van diverse typen van kortsluitstroming, met name naar het afgepompte pakket via lekkende kleiproppen, binnen het afgepompte pakket via putfilter en omstorting tijdens stilstand en door lekkende kleppen in transportleidingen nabij pompputten; (3) interactie van water met putmaterialen, leidend tot abnormaal hoge concentraties van o.a. koper, PAK en Pb; (4) adaptaties van een puttenveld aan bedreigende omstandigheden, door b.v. slechte putten te sluiten, uit te breiden waar de kwaliteit goed is, overschakeling op kunstmatige infiltratie of oeverfiltratie, ondergrondse ontijzering, verandering van onttrekkingsvolume e.d; en (5) de menging van grondwater met verschillende samenstelling, herkomst en ouderdom.

Voor laatstgenoemde aspecten worden 2 oplossingen geboden. De herkomst van het water kan m.b.v. (semi)natuurlijke tracers worden vastgesteld. Getoond wordt hoe dit met de zware, stabiele isotopen van water (^{2}H en ^{18}O) werkt bij het kwantificeren van de mengverhouding van Rijnoeverfiltraat met normaal grondwater. Meer in detail komt herkomstbepaling terug in Hoofdstuk 4.

De tweede oplossing zit in de presentatie van een nieuwe methode ter bepaling van de responscurve (cumulatieve reistijdverdeling). Deze methode gaat uit van een analytische hydrologische berekening op basis van onder andere, de diepteligging van de putfilters. Het resultaat ervan wordt vervolgens hydrochemisch gecorrigeerd op basis van een enkele tritium analyse van het ruwe water in jaar X en een bekende tritium inputfunctie voor de aquifer. Het resultaat is een aanzienlijk betere voorspelling van het percentage jong, tritiumhoudend water (geïnfiltreerd na 1953). Deze methode is tevens bruikbaar ter validatie/calibratie van responscurves die met 3D hydrologische modellen zijn verkregen.

Aan de hand van voorbeelden wordt getoond dat (a) puttenvelden een zeer welkome aanvulling vormen op het relatief ondiepe Landelijk Meetnet Grondwaterkwaliteit; (b) puttenveldadaptaties een zeer sterke invloed uitoefenen op trends, en (c) natuurlijke achtergronden van de diepere grondwaterkwaliteit achterhaald kunnen worden door bestudering van de trends. Trends en natuurlijke achtergronden zijn nader onderzocht in Hoofdstuk 6.

Hoofdstuk 3: HyCA, de alles-in-1 benadering voor hydrochemische analyse van waterkwaliteitsgegevens.

In dit hoofdstuk wordt HyCA (acronym voor HYdro-Chemische Analyse) gepresenteerd. Het betreft een nieuw computerprogramma voor efficiënte hydrochemische analyse in 4D (x, y, z, t) van grote databestanden met waterkwaliteitsanalyses. HyCA is primair ontwikkeld in het kader van voorliggend promotie-onderzoek omdat daarin een zeer groot databestand opgebouwd, gecontroleerd, geanalyseerd en geïnterpreteerd diende te worden, namelijk het databestand met vrijwel alle analyseresultaten van het ruwe water van de Nederlandse bronnen voor de openbare drinkwatervoorziening. Daarbij lag het accent op de anorganische chemie en op puttenvelden waar grondwater wordt onttrokken. Niettemin zijn ook de onttrekkingspunten van oppervlaktewater meegenomen en is HyCA zodanig ontworpen dat ook enkele duizenden andere kwaliteitsparameters, waaronder organische microverontreinigingen, micro-organismen, en radionucliden een solide plaats in de database innemen. Het programma is natuurlijk ook toepasbaar gemaakt voor alle mogelijke watersoorten op welke wijze dan ook bemonsterd. Daarmee is het een algemeen bruikbaar computergereedschap geworden, dat inmiddels op veel fronten dankbaar wordt ingezet.

In hoofdstuk 3 wordt uiteengezet waaruit HyCA is opgebouwd, waarin het afwijkt van enigszins vergelijkbare programma's, en wat het allemaal kan op het vlak van data management, data presentatie (incl. visualisatie) en data interpretatie.

HyCA boogt op Matlab (maar draait los daarvan; geen licentie vereist), basisfaciliteiten uit Menyanthes, CHEMCAL en PHREEQC-2 (geen licenties vereist) en vele nieuwe functies. Een supersnelle database accepteert vrijwel alle invoer (o.a. ASCII, Excel, DINO en DAWACO). Allerhande selecties, berekeningen en plots vergen slechts enkele muisklikken.

HyCA is geschikt voor iedereen die met waterkwaliteitsgegevens te maken heeft, op elk niveau. Het levert antwoord op vragen over betrouwbaarheid, controles, mineraalevenwichten, watertypen, verontreinigingsgraad, redoxniveau en produceert tabellen, kaarten, profielen, plots enzovoort.

Nieuwe en bestaande data-analysetechnieken zijn zodanig in een enkel softwarepakket bijeengebracht, dat tijdrovende datamanipulaties tot het minimum beperkt blijven en slechts enkele muisklikjes nodig zijn voor uiteenlopende uitwerkingen die de data-analyse vergemakkelijken. Deze integratie van mogelijkheden leidt tot een extreem snelle visuele screening van de database, en tot een uiterst snelle productie van kaarten en plots. Daarin en in de beschikbaarheid van onderdelen van de hydrochemische facies analyse onderscheidt HyCA zich van alternatieve commerciële programma's zoals Aquachem. Zonder HyCA zou de inhoud van dit proefschrift er overigens totaal anders hebben uitgezien!

Hoofdstuk 4: Hydrochemische typologie van puttenvelden

Nederlandse puttenvelden zijn in het verleden ingedeeld op basis van het aquifertype (freatisch, semispanningspakket, kalksteen) en soort voeding (neerslag, kunstmatig infiltraat of oeverfiltraat). In deze bijdrage is een nieuwe internationale typologie voor puttenvelden ontworpen die voortborduurt op de hydrochemische faciesanalyse van Stuyfzand (1993). De indeling is gebaseerd op het type waterlichaam (hydrosoom) waaraan onttrokken wordt, en de hydrochemische facies daarbinnen, die de waterkwaliteit van het puttenveld op basis van specifieke kenmerken nader typeert.

Het type waterlichaam, d.w.z. de herkomst, wordt bepaald aan de hand van geomorfologische en potentiometrische kaarten in combinatie met (semi)natuurlijke tracers. Bij voorkeur worden meerdere tracers beschouwd (multitracing), opdat de herkomstbepaling aan zekerheid wint. Daarbij dient het onderscheidend vermogen van de verschillende tracers (zoals Cl, ^{18}O, Cl/Br, EGV, Mg, Mo, B) tussen b.v. geïnfiltreerd Rijnwater (R) en gebiedseigen grondwater (G) te worden gekwantificeerd op basis van metingen aan 100% R en 100% G. Dit gebeurt door een nieuw kengetal: de absolute waarde van het verschil in gemiddelde waarden gedeeld door de wortel van het product van beide standaardafwijkingen. Ter bepaling van de mengverhouding van R en G worden dan de geschikte tracers (met voldoende onderscheidend vermogen) gewogen gemiddeld naar de score op onderscheidend vermogen.

De hydrochemische facies wordt bepaald door een voor puttenvelden aangepaste combinatie van drie indices, namelijk van de ouderdom, redoxtoestand en alkaliniteit. De ouderdomsindex is gebaseerd op het percentage jong water (%Y), dat gedefinieerd is als geïnfiltreerd na 1953 in verband met verhoogde tritiumactiviteit sedertdien. Het %Y volgt uit de berekende responscurve (zie Hoofdstuk 2), en indiceert de kans op recente verontreinigingen. De redoxindex bepaalt de oxidatie of reductie toestand van water, en daarmee de kans op (a) (bio)degradatie van vele organische verontreinigingen, (b) (re)mobilisatie, precipitatie of afbraak van anorganische verontreinigingen, en (c) toxiciteit van bepaalde verbindingen. De redoxindex is vastgesteld op basis van alle redoxgevoelige hoofdcomponenten van water (O_2, NO_3, SO_4, Fe, Mn, NH_4, H_2S en CH_4).

De alkaliniteitsindex, die in de Nederlandse situatie voornamelijk op de concentratie HCO_3 boogt, geeft de mate van reactie van water met kalk en organische stof aan.

Genoemde 3 faciesparameters worden tevens gebruikt om de intrinsieke kwetsbaarheid van puttenvelden te kwantificeren (zie Hoofdstuk 5). Daartoe is de redoxindex echter verder verfijnd.

Met de aldus gedefinieerde hydrochemische typologie zijn alle 206, in 2008 actieve puttenvelden ingedeeld. Dit resulteerde in het onderscheiden van 11 waterlichamen en 11 faciesparameters. De waterlichamen zijn zoveel mogelijk gekozen in overeenstemming met de nationale KRW-indeling: Noordelijk, Oostelijk, Bentheimer zandsteen, Centraal, Zuidelijk, Vlaanderen, West, Kustduinen, Kalksteen, Kunstmatig infiltraat (subtypen Rijn, Maas, IJsselmeer, overig) en Oeverfiltraat (subtypen Rijn, Maas, overig). De faciesparameters betreffen: jong, middelbaar en oud; (sub)oxisch, anoxisch, diep anoxisch en gemengd; en zeer lage, lage, matige en hoge alkaliniteit.

Vervolgens zijn de resultaten van indeling gepresenteerd middels een kartering in bovenaanzicht met 3 profielen en met een heldere toelichting van patronen en processen voor elk waterlichaam. De resultaten bieden ondersteuning bij het voorspellen van de kwetsbaarheid van winningen (zie Hoofdstuk 5) en het optimaliseren van monitoringsystemen van de grondwaterkwaliteit. Het voorkomen van bepaalde verontreinigingen hangt namelijk sterk af van het type grondwaterlichaam en de hydrochemische facies. De kaarten faciliteren de communicatie tussen onderzoekers, waterbeheerders en politici, en helpen bij het oplossen van complexe grondwaterbeheerproblemen op schalen variërend van een enkele put, puttenveld of regio tot nationale of Europese schaal. De hydrochemische typologie van puttenvelden is tevens toepasbaar op waarnemingsputten.

Hoofdstuk 5: Kwantificering van de kwetsbaarheid van puttenvelden

Een nieuwe methode ter kwantificering van de intrinsieke kwetsbaarheid (VIP) van puttenvelden (voor drinkwatervoorziening) en hun specifieke kwetsbaarheid (VIP_X) voor verontreinigende stof X (hoofdbestanddeel, sporenelement of organische microverontreiniging), vormt het thema van dit hoofdstuk.

Onder intrinsieke kwetsbaarheid wordt verstaan de gevoeligheid van het winsysteem voor verontreiniging vanwege ongunstige systeemeigenschappen (zoals korte reistijd en gering bufferend vermogen ondergrond), onafhankelijk van het type verontreiniging en landgebruik. Wanneer puttenvelden veranderen, door uitbreiding of adaptaties t.g.v. bedreigingen, dan verandert ook VIP. VIP is dus geen 100% statische eigenschap. VIP wordt berekend uit de hydrochemische faciesparameters ouderdom, redoxniveau en alkaliniteit (zie Hoofdstuk 4), plus de fractie oppervlaktewater in het opgepompte water. Dit resulteert in een score tussen 0 voor oud, diep anoxisch grondwater met hoge alkaliniteit, en ca. 30 voor jong, (sub)oxisch, zuur grondwater. De bepaling van het redoxniveau is verder uitgewerkt t.o.v. Hoofdstuk 4, door het sulfaatreducerende milieu te verscherpen en een gemengde redoxtoestand nader onder te verdelen.

Onder specifieke kwetsbaarheid verstaan wij de gevoeligheid van het winsysteem voor verontreiniging door een specifieke stof, niet alleen vanwege ongunstige systeemeigenschappen, maar ook vanwege de belasting van het systeem met die stof. Daarbij spelen het landgebruik en gedrag van verontreiniging X in de bodem wel degelijk een rol. VIP_X is dus een veel minder statische eigenschap dan VIP. VIP_X combineert VIP met vier aspecten: de huidige concentratie van X in het opgepompte water; de mobiliteit of mobilisatiepotentie van X in het hydrogeochemisch milieu zoals vastgesteld op basis van de redoxtoestand en alkaliniteit van het ruwe water; het landgebruik binnen het intrek- of waterwingebied; en het verontreinigingsrisico voor X, zoals bepaald uit zijn concentratie in ondiep grondwater en/of in het infiltrerende oppervlaktewater.

De voorgestelde methode vereist eenvoudig en moeilijker te verkrijgen data. Relatief eenvoudig zijn: (1) de kwaliteit van ruwwater van de winning, ondiep grondwater bemonsterd via waarnemingsputten (bij voorkeur binnen het waterwin- of intrekgebied), en oppervlaktewater in geval het puttenveld bijdragen kent van kunstmatig infiltraat of oeverfiltraat; (2) een landgebruikkaart van het waterwin- of intrekgebied; en (3) een (inter)nationale drinkwaterstandaard of anders een natuurlijk achtergrondniveau. Minder eenvoudig te verkrijgen data betreffen de leeftijdsverdeling van het opgepompte water en de fractie geïnfiltreerd oppervlaktewater in het opgepompte water. Deze data kunnen geschat worden met respectievelijk de nieuwe methode ter bepaling van de responscurve (zie Hoofdstuk 2) en multitracing (zie Hoofdstuk 4).

De nationale verkenning van de intrinsieke kwetsbaarheid van 241 puttenvelden (175 single plus 33 stuks met onderverdeling in 2 deelwinningen) in Nederland in 2008 onthult dat

50% een lage VIP (<1) scoort, 41% een middelmatige VIP (1–4), en 9% een hoge VIP (4–10). Winningen met VIP <1 betreffen voornamelijk de diepere of puttenvelden in (half)afgesloten aquifers of winningen in exfiltratiezones van zeer grote hydrosomen. De zeer kwetsbare puttenvelden hebben ondiepe putfilters en onttrekken uit verzuurde, freatische zandaquifers, (sub)oxische kustduinen met kunstmatige infiltratie, (sub)oxische oeverfiltraatsystemen of oxische kalksteen.

De nationale verkenning van de specifieke kwetsbaarheid van de 241 puttenvelden, t.a.v. Cl, NO_3, SO_4, Al, As, Ni, bentazon, carbendazim en MCPP (mecoprop), leverde o.a. relatief hoge VIP_X-waarden voor Cl en bentazon, die zich conservatief gedragen in de bodem. Puttenvelden die ondiep grondwater onttrekken in gebieden met hoge dichtheid aan intensieve landbouw, scoren de hoogste kwetsbaarheid voor bentazon. Hoge kwetsbaarheden voor Al en Ni komen voor in gebieden met intensieve landbouw en bos, en met lage alkaliniteit van het grondwater.

VIP en VIP_X zijn in principe niet gebaseerd op locatiespecifieke hydrologische of geochemische parameters, maar uitsluitend op de gemeten water-kwaliteit. Dat maakt de methode robuust, objectief en overal toepasbaar. De methode is vastgelegd in een eenvoudig computeralgoritme, dat makkelijk gewijzigd kan worden, b.v. om de normalisatie op drinkwaternormen en de typen landgebruik te veranderen.

Hoofdstuk 6: Natuurlijke achtergrond en trends van de waterkwaliteit van puttenvelden

In dit hoofdstuk worden hydrochemische data van puttenvelden uit de periode 1898-2008 gebruikt om uit tijdreeksen de natuurlijke achtergrondwaarden van en trendmatige ontwikkelingen in de ruwwater-kwaliteit te destilleren voor puttenvelden met voldoende gegevens. Het betreft kwaliteitsparameters met een voldoende lang datarecord die bovendien gidsparameters vormen voor specifieke milieuthema's: Cl (algemene verontreiniging, verzilting in het bijzonder), NO_3 (vermesting), SO_4, HCO_3 en totale hardheid (verzuring of opharding), eventueel aangevuld met EGV, pH, Na, Fe, Mn en SiO_2.

Natuurlijke achtergrondwaarden konden worden ontleend aan de tijdreeksen vóór 1940 indien zij gedurende de eerste zes jaar van onttrekking geen trend vertoonden. De filosofie hierachter is dat puttenvelden gedurende de eerste zes jaar zelden veranderingen ondergaan en dat de algemene milieuverontreiniging binnen en in de omgeving van waterwingebieden pas na 1940 stevige vormen begon aan te nemen.

Trends zijn alleen vastgesteld voor de periode 1960-2005, voor die winningen die in deze periode actief waren. Dit om een homogene populatie en periode te verkrijgen. Daarbij zijn onderscheiden: sterk, matig en zwak stijgende trends, dito dalende trends, geen trend, convexe en concave trendomkering (resp. van stijgend naar dalend; en van dalend naar stijgend). Duidelijke convexe trendomkeringen zijn vastgesteld bij puttenvelden die een significante fractie oppervlaktewater uit de Rijn winnen, via hetzij kunstmatige infiltratie, hetzij oeverfltratie. Deze omkering is vooral te danken aan de vele saneringsmaatregelen in het hele stroomgebied van de Rijn. Andere trendomkeringen zijn reeds waargenomen in ondiepe grondwateren, zoals dalende SO_4 concentraties dankzij een afnemende atmospherische SO_4 input sinds begin jaren 70 en een reductie van NO_3 concentraties vanwege verbeterde landbouwkundige praktijken. Deze verbeteringen manifesteren zich echter in een zeer beperkt aantal ondiepe puttenvelden, omdat de meeste puttenvelden langere reistijden en meer menging met ouder grondwater kennen.

Op basis van de waargenomen trends zijn zogenaamde trendbundels onderscheiden, d.w.z. combinaties van trends in meerdere kwaliteits-parameters die in verband te brengen zijn met een bepaalde antropogene beïnvloeding. Het betreft de volgende typen trendbundels met als trefwoorden: Oppervlaktewater gedomineerd; met verzuring door atmosferische depositie; beïnvloed door landbouw boven een kalkhoudende aquifer met pyriet; beïnvloed door landbouw boven een kalkhoudende aquifer zonder pyriet; beïnvloed door verzilting; zonder trend; en overig.

Een genormaliseerde concentratieveranderings-index (NCC) is geïntroduceerd om concentratie-veranderingen ten opzichte van de natuurlijke achtergrond dimensieloos te kunnen kwantificeren en in beeld te kunnen brengen.

Tenslotte is een eenvoudige methode gepresenteerd om natuurlijke achtergrondconcentraties op te schalen van individuele puttenvelden naar nationale grondwaterlichamen, met onderscheid tussen hydrochemische zones op basis van de Hydrochemische Systeemanalyse zoals gepresenteerd in hoofdstuk 4. De resultaten ten aanzien van natuurlijke achetrgrondconcentraties, trends van gidsparameters, trendbundels en de genormaliseerde concentratieveranderingsindex, zijn op nationale kaarten van Nederland weergegeven.

Chapter 1

1 General introduction

1.1 Background

Groundwater is of major societal significance for many well-known reasons. One of the most important ones is that groundwater normally offers a direct and hygienically safe source of drinking water for public and individual supply. Groundwater resources, however, are becoming extremely vulnerable to human interference because of their hydrogeological structure, the increasing demographical pressure and the multitude and variety of anthropogenic hazards. For this reason, demanding legislation has been implemented (EU, 2000; 2006b; 2008; USEPA, 1974; 1996), in order to guarantee the protection of such valuable resources, by enforcing governments to monitor and assess the quality and quantity of their waters on the basis of common criteria and to identify and reverse groundwater pollution trends.

Numerous national groundwater quality monitoring networks (NGQMNs) are being developed for this purpose, not only in the US (Rosen and Lapham, 2008) and Europe like in Denmark (Juhler and Felding, 2003), The Netherlands (van Duijvenbooden et al., 1993) and the UK (Ward et al., 2004), but also in other countries, a.o. Egypt (Dawoud, 2004), Korea (Kim et al., 1995; Lee et al., 2007), New Zealand (Daughney and Reeves, 2005) and South Africa (Parsons and Tredoux, 1995). Such networks are regularly monitored to fulfill three main purposes: (1) establish the actual groundwater quality in relation to soil use, soil type and hydrogeological conditions (Boumans et al., 2005; Frapporti et al., 1993; Fraters et al., 1998; Meinardi, 2003; Pebesma and de Kwaadsteniet, 1997; Reijnders et al., 1998; van den Brink et al., 2007); (2) identify trends in groundwater quality (Batlle Aguilar et al., 2007; Boumans et al., 2005; Broers and van der Grift, 2004; Burow et al., 2007; 2008; Daughney and Reeves, 2006; Frapporti et al., 1994; Reynolds-Vargas et al., 2006; Stuart et al., 2007; Visser et al., 2009; Xu et al., 2007); and (3) establish the regional natural background level of concentrations in groundwater (Coetsiers et al., 2009; Edmunds et al., 2002; Edmunds and Shand, 2008; Fraters et al., 2001; Lee and Helsel, 2005; Limbrick, 2003; Wendland et al., 2008).

The actual groundwater quality is successfully established with data gathered via these networks. However, groundwater quality trend detection and quantification of natural background levels (NBLs) are hindered by insufficient length of time series, which in most cases do not cover the period of interest (Visser, 2009). Such networks are operational for 20 to 30 years at most, while the main groundwater quality deteriorating processes, due to intensive agriculture, urbanization, industrial activities and atmospheric pollution, threaten groundwater resources for more than 60 years.

A monitoring network that is available in most countries and constitutes an attractive (inter)national monitoring system for evaluating the chemical state of groundwater and fulfill the above mentioned three purposes is the network of public supply well fields (PSWFs). A PSWF is a coherent set of pumping wells delivering groundwater to be distributed to the public as drinking water, either without or after treatment. PSWFs are monitored on a regular basis as an integral part of the quality surveillance of national drinking water supply, in compliance with the relevant national drinking water act (EU, 2000; 2006b; 2008; USEPA, 1974; 1996). In The Netherlands, where the period of record begins in 1898, such network provides valuable information on the quality status of groundwater around year 1900 and its evolution through more than a century. The earliest data provide a valuable means to establish the natural background composition of groundwater resources used for drinking preparation purposes. Advantages of the PSWF network may consist of long data records, extensive analytical programs, and representativity for the relatively large volumes of water pumped, which are registered as well. The main disadvantage, however, is the more elaborate interpretation of such data, due to misleading effects resulting from variable pumping schemes during sampling and/or well field adaptation measures, which mask the effects of environmental problems by dilution, reallocation or changing the water sources. Guidelines to avoid these problems are introduced in (Mendizabal and Stuyfzand, 2009, Chapter 2).

1.2 Aim and research questions

The aim of this thesis is, in line with the above arguments, to determine the hydrochemical status and quality developments of the groundwater used in The Netherlands for drinking water production purposes, as based on 110 years of PSWF monitoring. For this purpose, first the hydrochemical status of individual PSWFs is diagnosed and results are then upgraded to the groundwater body (GWB) level on a national scale. The following aspects are covered:

- Analyzing the potential of PSWFs as a groundwater quality monitoring network.
- Developing tools for the efficient analysis of large groundwater quality databases.
- Defining a new classification of PSWFs, according to their reaction to anthropogenic pollutants.
- Establishing the actual hydrochemical status of PSWFs and GWBs.
- Quantifying the vulnerability of PSWFs and GWBs towards numerous pollutants.
- Quantifying the natural background levels of PSWFs and GWBs, regarding selected parameters.
- Quantifying groundwater quality trends for PSWFs regarding selected parameters, and translating them into trend bundles related to specific hydrochemical processes affecting the quality of the delivered water.

To this end, two large water quality datasets are used: (1) a national sampling campaign carried out in 2008, where all active PSWFs in the Netherlands were sampled for extensive chemical analysis on macroparameters, trace elements and stable isotopes; and (2) the National Network of Public Supply Well Fields, an extensive database created for this research, containing numerous properties of all Dutch PSWFs, the raw water quality delivered and the volumes pumped since 1898.

1.3 Thesis outline

The main body of this thesis consists of seven chapters. Chapters 2 to 6 correspond to papers that have either been published in or submitted to a peer-reviewed journal. Chapters 2, 3 and 5 address respectively objectives 1, 2 and 5. Objectives 3 and 4 are addressed in chapter 4 and objectives 6 and 7 in chapter 6. The synthesis in chapter 7 summarizes and integrates the main results of the thesis.

In Chapter 2, hydrochemical data records from public supply well fields are shown to be a valuable national monitoring network for evaluating the quality status of groundwater. This network has been regularly monitored for more than 100 years, but it does present the complications of interpreting mixed samples of waters with different age, origin and recharge conditions, and also of changes in abstraction regime. Guidelines for the proper interpretation of such data are presented, supported by some examples of application.

In Chapter 3, new software is presented for the efficient management, control, analysis and presentation of water quality data in four dimensions (X, Y, Z, t). HyCA (Hydrochemical Analysis) is a computer program primarily developed within this thesis, in order to facilitate the analysis and interpretation of large databases, such as the Dutch network of PSWFs. The results of this thesis would have never been the same without such a tool.

In Chapter 4 a new international PSWF typology is presented, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The origin is determined by environmental tracers or geomorphological and potentiometric maps, the facies by combining age, redox and alkalinity indices. This typology forms the basis for the analyses performed in Chapter 5 and Chapter 6 and to upgrade results obtained for individual PSWFs to the GWB level on a national scale.

The results obtained in Chapter 4 are further developed in Chapter 5 into VIP, a single Intrinsic Vulnerability Index towards anthropogenic Pollution, and VIP_X, a Specific Vulnerability Index towards Pollutant X, with X being either a main constituent, trace element or organic compound. VIP combines the age, redox and alkalinity indices introduced in Chapter 4 with the surface water fraction of the pumped water. VIP_X takes also into account specific characteristics of parameter *X* and the land use and pollution risk of X within the groundwater catchment area.

In Chapter 6, NBLs are calculated for selected parameters, by applying statistical trend detection methods to historical water quality data series from PSWFs, both at the PSWF and GWB level. Trends are normalized to drinking water standards and aggregated into specific trend bundles to identify the responsible hydrochemical processes.

The synthesis in chapter 7 summarizes the main conclusions from the foregoing chapters to provide an overview of the methods developed to establish the actual hydrochemical status and quality developments of groundwater as used for drinking water production in The Netherlands.

Chapter 2

2 Guidelines for interpreting hydrochemical patterns in data from public supply well fields and their value for natural background groundwater quality determination[1]

Abstract

Hydrochemical data records from public supply well fields (PSWFs) may constitute a valuable national monitoring network for evaluating the quality status of groundwater. The advantages and disadvantages of such networks are analyzed, as compared to dedicated networks that use specific monitoring (observation) wells with short well screens and without protracted high volume pumping. The term *well field adaptation* (WFA) is introduced as the capacity of a PSWF to adapt to a changing environment. The WFA-record itself is shown to be a general indicator of environmental problems affecting the groundwater system.

Guidelines are presented to better interpret PSWF water quality data, by analyzing (a) the chances on bias in using data from a well field, (b) the WFA-record, (c) historical changes in hydrochemical methods, (d) the origin of the groundwater mixture, and (e) the approximate age distribution of the water. A simple approximation is given for calculating the hydrological response curve (HRC) of a well (field), which yields the cumulative frequency distribution of the age of the raw water. With a single tritium analysis of the raw water in year x and a known tritium input function for the aquifer, this HRC can be corrected to better predict the percentage of young, tritiated water (infiltrated after 1953).

The many complications connected to interpreting PSWF data are illustrated (ranging from a single sample to a time series of >100 years) and it is shown that notwithstanding various drawbacks, valuable observations and conclusions can be obtained.

---

[1] This chapter was published as Mendizabal, I., Stuyfzand, P.J., 2009. Guidelines for interpreting hydrochemical patterns in data from public supply well fields and their value for natural background groundwater quality determination. Journal of Hydrology, 379(1-2): 151-163.

2.1 Introduction

The Water Framework Directive (EU, 2000; 2008) and its daughter Groundwater Directive (EU, 2006a), enforce all EU member states to monitor and assess the quality and quantity of European waters on the basis of common criteria and to identify and reverse trends in groundwater pollution. Member states are required to achieve good chemical status of their waters by the year 2015. For this purpose, extensive monitoring is required and national groundwater quality monitoring networks (NGQMNs) are being developed, not only in Europe (a.o. Denmark (Juhler and Felding, 2003), The Netherlands (van Duijvenbooden et al., 1993) and the UK (Ward et al., 2004)), but also in, e.g. Egypt (Dawoud, 2004), Korea (Kim et al., 1995; Lee et al., 2007), New Zealand (Daughney and Reeves, 2005), South Africa (Parsons and Tredoux, 1995) and the US (Rosen and Lapham, 2008).

Such networks are regularly monitored and resulting data used to: (1) establish the actual groundwater quality in relation to soil use, soil type and hydrogeological conditions (Boumans et al., 2005; Frapporti et al., 1993; Fraters et al., 1998; Meinardi, 2003; Pebesma and de Kwaadsteniet, 1997; Reijnders et al., 1998; van den Brink et al., 2007); (2) identify trends in groundwater quality (Batlle Aguilar et al., 2007; Boumans et al., 2005; Broers and van der Grift, 2004; Burow et al., 2007; 2008; Daughney and Reeves, 2006; Frapporti et al., 1994; Reynolds-Vargas et al., 2006; Stuart et al., 2007; Visser et al., 2009; Xu et al., 2007); and (3) establish the regional natural background compositions of groundwater (Coetsiers et al., 2009; Edmunds et al., 2002; Edmunds and Shand, 2008; Fraters et al., 2001; Lee and Helsel, 2005; Limbrick, 2003; Wendland et al., 2008).

The first goal is successfully accomplished with groundwater quality data gathered throughout these networks. The studies on detection and quantification of trends in groundwater quality, however, often showed difficulties (Visser, 2009), mainly because the period of interest in groundwater studies is usually longer than the period of record (Loftis, 1996). Furthermore, the regional natural background composition of shallow groundwater is hard to define in many areas, due to its contamination. The problem is usually solved through backward trend analysis of young groundwaters or by selecting, if available, a data subset from older monitoring networks that is assumed to reflect the natural composition, as evidenced by hydrological and geochemical tracers (Edmunds, 2008). A recent review of the complications connected to these methods revealed that the data set selection is a crucial step in determining the natural background and that old analyses are the only direct reference to establish the natural background concentration for groundwater units having only anthropogenically influenced, young groundwater at present (Griffioen et al., 2008).

A monitoring network that is available in most countries and is also useful to determine temporal and regional groundwater quality patterns is the network of public supply well fields (PSWFs), which are monitored on a regular basis as an integral part of the quality surveillance of national drinking water supply. Long-term monitoring data from PSWFs have been successfully used, often in combination with data from private drinking water supply wells, to determine contamination problems mainly deriving from agricultural practices (Goss et al., 1998; Squillace et al., 2002; Stuart et al., 1995). In addition, national surveys on a.o. fluoride (Lalumandier and Jones, 1999; Stas et al., 1937) or iodine (Gezondheidsraad, 1932) in drinking water provide a national overview of the groundwater quality. This network presents numerous advantages and disadvantages, as compared to dedicated networks that use specific monitoring (observation) wells. The main advantage of PSWFs amongst NGQMNs is their longer period of record, which in many cases fully covers the period of interest. In The Netherlands, where the period of record begins in 1898, such network provides valuable information on the quality status of groundwater at the beginning of the 20th century and its evolution through more than a century. Furthermore, concentrations measured in the early years are a good estimation of the natural background of the pumped aquifers. The main disadvantage, however, is the more elaborate interpretation of such data, due to numerous complications inherent to historical data and to PSWFs themselves.

In this contribution, new guidelines are presented to interpret water quality data obtained from national PSWF networks, by taking into account the following aspects: (a) the chances on bias in using data from a well field, (b) historical changes in the well field, (c) changes in hydrochemical methods in the course of time, (d) the origin of the groundwater mixture (local precipitation, river bank filtrate (RBF), artificially recharged surface water (AR) or recent/ancient sea water), and (e) the approximate age distribution of the water pumped. The latter is needed to understand the proportion of young, potentially more contaminated water and dilution phenomena due to mixing with old groundwater. The value of groundwater quality time series obtained from PSWFs as compared to NGQMNs is illustrated, by means of three examples. Although they refer to the situation in The Netherlands, where the quality and volume of groundwater abstracted by all active PSWFs have been continuously monitored since 1898, the guidelines and methods here presented are expected to be applicable in any other country where PSWFs have been monitored.

2.2 Well fields and their data collection

2.2.1 Public supply well fields (PSWF)

A PSWF is defined as a coherent set of not privately owned pumping wells delivering groundwater to be distributed to the public as drinking water, either without or after treatment. PSWFs can be classified into various types according to: (1) the origin of the groundwater; (2) the properties of the aquifer; (3) the land use incl. anthropogenic sources in the capture zone, if any; and (4) the hydrologic characteristics of the PSWF. These factors, summarized in Table 2.1, mainly dictate the quality of the raw water delivered by a PSWF, by a succession of processes from recharge to abstraction. A special factor is the source water (see guideline 4), which can be fresh autochthonous groundwater (either actual or paleo groundwater deriving from local precipitation), RBF and/or AR. In particular cases even brackish to saline groundwater may be admixed. The origin of the water pumped is a special factor indeed, because it dictates which input signal is relevant for the PSWFs output signal. The properties of the PSWF itself also play a particular role, by determining the mixing ratio of waters of different age and origin during pumping.

According to these criteria, PSWFs in The Netherlands can be classified in five groups: Phreatic, (semi)confined, AR, RBF and limestone. Their main properties are summarized in Table 2.2 and their spatial distribution is given in Fig 2.1. Most AR is located in the coastal dunes, RBF in the Rhine Delta and limestone in South Limburg. Most PSWFs in Twente and the Achterhoek are phreatic and pump water from a shallow aquifer, while most PSWFs in the Central Graben (area within the faults) pump deep tertiary aquifers, at 100-200 m-MSL (meters below Mean Sea Level).

Table 2.1: Main factors determining the water quality abstracted by public supply well fields (PSWF).

Source[a]	Aquifer properties				Land use	Well field characteristics
	Type	Material	Genesis	Reactivity		
G	Phreatic	sand	Eolian	Organic matter	Nature	Hydrological response curve
P	Semiconfined	Sandstone	Glacial	Pyrite	Agriculture	Capture zone
RBF	Confined	Limestone	Fluviatile	Calcite/dolomite	Pasture	Recharge / pumping rate ratio
AR		Effusive rock	Marine	Gypsum	Urban	Depth to brackish/salt interface
S		Other	Other	Glauconite	Industrial	Depth to groundwater table

[a] G: fresh, autochthonous, recent groundwater; P: fresh, autochthonous paleo groundwater; AR: artificially recharged water; RBF: river bank filtrate; S = saline/brackish groundwater.

From the 1187 Mm^3 (Million cubic meters) of drinking water produced in 2000, PSWFs covered 79 % of the production. The rest was prepared from surface water directly taken from rivers or lakes. From the 940 Mm^3 drinking water produced by PSWFs, 46 % was pumped from (semi)confined aquifers. These are also the most protected against anthropogenic pollution from the surface. AR systems have the largest capacity (19 % of the total production with only 9 PSWF) and they also present the lowest closing rate. The production of phreatic PSWFs decreased drastically in 8 years (from 335 Mm^3 in 1992 to 205 Mm^3 in 2000) due to their higher vulnerability towards a.o. agriculture and urbanization. Limestone PSWFs are also very vulnerable, as shown by their high closing rate.

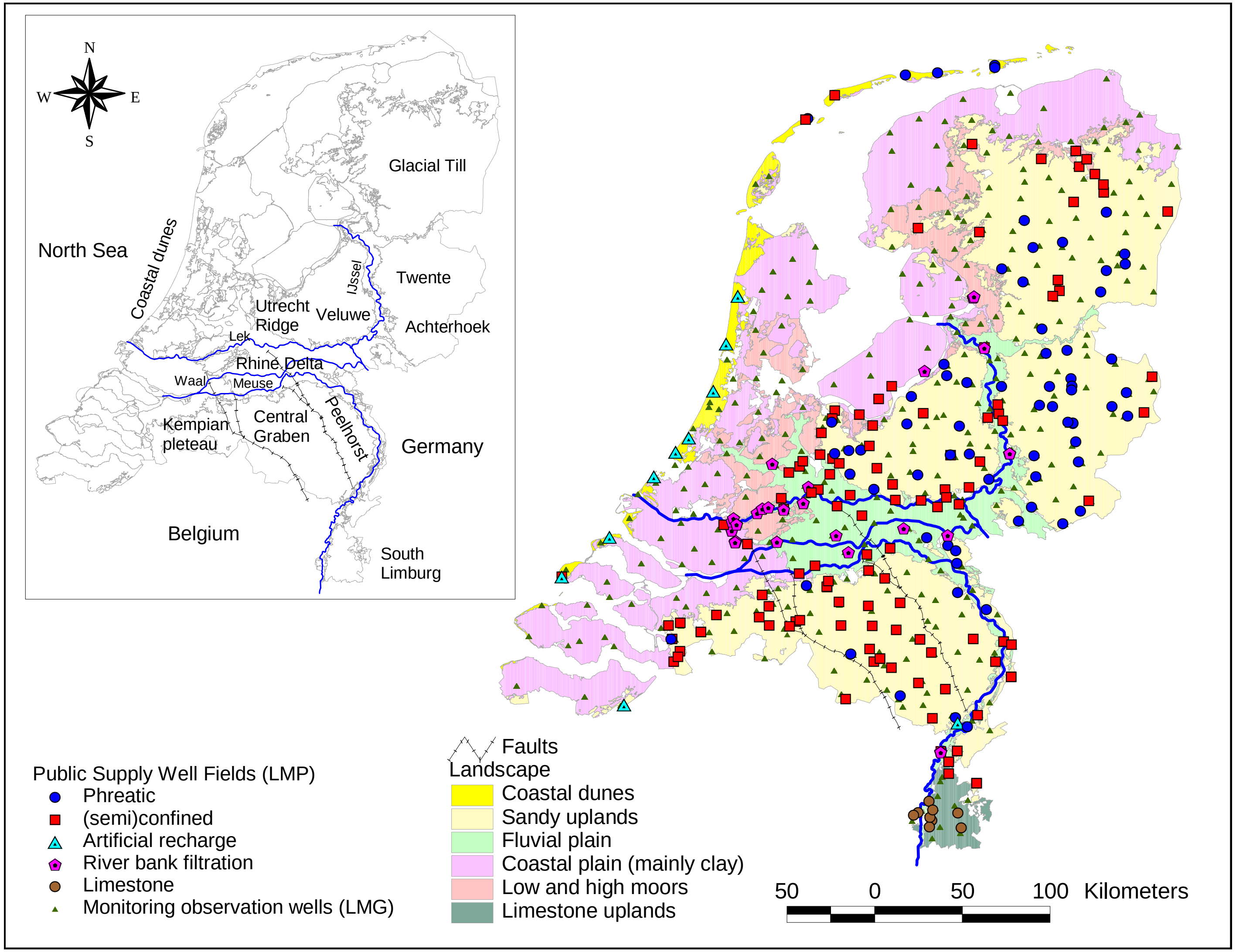


Fig 2.1: Spatial distribution of the National Network of PSWFs projected on top of a landscape map of The Netherlands. Classification according to source water and aquifer type in: phreatic, (semi)confined, AR, RBF and limestone. The Dutch National Groundwater Quality Monitoring Network (LMG) is also shown.

Table 2.2: General characteristics of the five types of water resources for public drinking water supply in The Netherlands, anno 2008.

PSWF type	Sand and gravel				Limestone
	G		AR	RBF	
	Phreatic	(Semi)confined			
Number of PSWFs	121	147	12	38	24
First year of operation of first PSWF	1881	1881	1940	1921	1894
Number of active PSWFs	69	93	9	21	9
Number of closed PSWFs	52	54	3	17	15
% Of closed PSWFs	43	37	25	45	63
Mean raw water production per PSWF [Mm^3/y] [a]	2.5	4.3	14.3	4.2	1.8
Total amount of drinking water produced [Mm^3/y] [a]	205	437	180	97	22
% Of total amount of drinking water produced [a]	22	46	19	10	2
Mean nr. of wells/collection points	10	12	303	15	7
Mean land surface [m ASL]	20	12	11	2	80
Mean abstraction level [m BLS]	26-65	62-112	9-41	24-54	19-60
Mean aquifer Level [m BLS]	9-90	55-142	1-44	18-81	12-92
Mean aquifer thickness [m]	81	87	43	64	80
Age spectrum [y]	2-200	20-25000	0.1-0.3	1-50	2-200

[a] Water production in year 2000. ASL = Above Sea Level; BLS = Below Land Surface.

For comparison, Fig 2.1 also shows the spatial distribution of the Dutch NGQMN (LMG in its Dutch abbreviation). LMG was established in 1979 by RIVM, the Dutch National Institute for Public Health and the Environment, in order to quantify human impact on groundwater quality over space and time. The network comprises 400 piezometer nests evenly distributed throughout the country, with a higher density in areas relevant for drinking water production (Reijnders et al., 1998; van Duijvenbooden, 1987). All wells were constructed using a standardized drilling method, dimensions and well completion, with 2 m long screens at about 9, 15 and 24 m BLS (below land surface). The upper (9 m BLS) and lower piezometers (24 m BLS) are sampled and analyzed for macro and micro constituents every 1-4 years, depending on the vulnerability of the groundwater (Wever, 1998). The other piezometer is sampled occasionally. LMG has been supplemented since 1989 with 12 Provincial Groundwater Quality Monitoring Networks (PMG, not shown on the map), which follow the same construction and sampling standards for optimal integration. PMG fulfills additional purposes, like the groundwater quality surveillance of specific nature reserves. Both networks are well distributed over the entire country, except for the areas with marine clay deposits from the Holocene transgression, where drinking water production is not feasible.

2.2.2 Data records

In The Netherlands, the raw water quality and volumes pumped from all PSWFs are reported four times a year to the authorities, conform Dutch legislation (Waterleidingbesluit, 1984). These routine data have been stored initially, in the period 1898-1991, in data reports (VWN/VEWIN, 1898-1992) and data files of RIVM. Since 1992 the data are stored in a national digital database (REWAB). All nondigital data have been digitalized for this study, including both the routine data and selected data from occasional national surveys, for instance on iodine (Gezondheidsraad, 1932), fluoride (Stas et al., 1937) and tritium (Glastra et al., 1989). The result is a digital record of water quantity and quality for all PSWFs since 1898.

When important hydrochemical data on raw water quality are lacking, it is optional to resort to data on drinking water quality deriving from the same well field. Of course, the effects of water treatment should be known; they determine which parameters of the analysis can be used.

2.2.3 Sampling

PSWFs should be sampled with special care to obtain water samples that are hydrochemically representative for the well field. Samples are usually obtained from specific sampling points (faucets) on individual wells or on transport mains that discharge the water from various or all pumping wells. The most representative sample is obtained from a collection point where the waters from all wells have been mixed already, before entry into the water treatment facility, and preferably when all wells or a representative set of wells have been active for at least a couple of hours. The latter is a practical rule lacking theoretical basis, although this refreshening time normally is in line with the rule for monitoring wells requiring the evacuation prior to sampling, of at least three times the water content of the well screen plus riser. In a PSWF with wells tapping different aquifers additional samples from the individual aquifers will help in the interpretation. However, this is not always feasible. On the other hand sometimes only individual wells can be sampled and the water quality of the well field must be calculated as the average of all individual wells, volume weighted. The pumping scheme of the individual wells within the well field is also crucial (Hem, 1985). It is common practice to apply pumping schemes in order to optimize the functioning of the PSWF in relation to water supply needs, water treatment, well clogging or salinization prevention. This may introduce a large variability in water quality depending on the wells activated.

Chemical analyses of water samples from PSWFs require a more cautious interpretation than those obtained from conventional observation wells, and require two additional properties to be involved: the hydrological response curve (HRC), which is explained in guideline 5, and the area contributing recharge to the water body pumped by the well, which is also referred to as the well head protection area (WHPA) by different authors.

2.2.4 Well head protection area (WHPA)

The WHPA is the surface and subsurface area surrounding a water well or well field supplying a public water system, through which contaminants are likely to move toward and reach such water well or well field (USEPA, 1997). The surface area is identical to the water catchment area of the well field. When interpreting water quality data from well fields, the land use within the catchment area and the changes in both the area and the land use should be known.

WHPA's are delineated by several methods, ranging from simple analytical approaches to complex computer models. USEPA (1998) provides a detailed literature review on methods used until 1998. Analytical approaches have been developed for selected ideal cases (Broers and van Geer, 2005; Ceric and Haitjema, 2005; Haitjema, 1995; van Leeuwen et al., 1998; van Ommen, 1986). The simplest one is a fixed-radius WHPA (Ceric and Haitjema, 2005), which applies to a fully penetrating, single extraction well, screened in a confined aquifer of infinite areal extent without regional flow component. The most elaborate option is to obtain the WHPA from a numerical groundwater model, which is more appropriate in complex geohydrological settings (Franke et al., 1998). The optimal method is usually the one that simplifies the flow system as much as possible while still preserving its geological and hydrologic characteristics (Paradis et al., 2007).

2.3 Guideline 1: check for specific bias inherent to data from pumping wells

2.3.1 Short-circuiting via wells

Well construction is a crucial element in the evaluation of chemical analyses of groundwater in general. It is perhaps even more crucial in case of groundwater from pumping wells, because of a larger diameter of their bore hole and larger pressure drops for a longer time in their vicinity, as compared to monitoring wells. When aquitards (or aquicludes) are perforated during well construction, they should be properly restored by clay plugs or cement grout, to prevent cross-flow between aquifers through the annular space between the well casing and the aquitard (Driscoll, 1986). When such seals are absent or do not perform properly, waters of normally lower quality from overlying aquifers will flow towards the well screen through the annular space, induced by large pressure drops generated within the well. Holes, cracks and casing joints can also act as cross flow enhancers.

Short-circuiting is indicated when, for instance, a significant tritium activity is measured in water from a well that was calculated to contain water that infiltrated 100% before 1953 (see "Tritium validation and calibration"). Other evidence may derive from microbiological analyses when positive for viruses or bacteria originating at the surface, in water pumped from deep confined aquifers or water calculated to be older than for instance 100 years (Stuyfzand and Bannink, 2003).

Another source of short-circuiting is the well screen itself when there are significant pressure differences within the pumped aquifer or between 2 or more aquifers, in case of one well tapping various aquifers. The cross flow will strike when the well does not pump. This results in leakage of groundwater from one aquifer (layer) into the other, which can be recognized during the initial pumping phase as a slow change in water quality away from the water that leaked in (normally water from shallower aquifers with lower quality or a less anoxic character).

A side effect of cross-flows through the gravel pack or well screen is the mixing of for instance deep anoxic water with shallow (sub)oxic water. This mixing can also occur, without any cross flow, in wells screened in different aquifers, wells tapping a chemically stratified aquifer or wells pumping waters of different origin (Houben and Treskatis, 2007; Stuyfzand, 2007). The mixing of both waters within the well provokes the formation of chemical precipitates of a.o. $Fe(OH)_3$, which plug the well screen and substantially reduce well yield. The process is known as chemical well clogging and is one of the main hydrochemical problems waterworks must face. The formation of precipitates slightly reduces concentrations of mainly Fe, Mn, As and PO_4 (Houben and Treskatis, 2007). Also, periodical maintenance of clogging wells may result in water samples that bear some effects of the regeneration itself (like reaction products of the acids or oxidants used), if taken too early after regeneration.

2.3.2 Leaky valves (well field scale)

Another point of concern is the leakage through valves in temporarily inactive wells. When wells are inactive, they are isolated from the transport network by valves. High pressures in this network combined with defects in the valves due to corrosion, iron precipitation or malfunctioning can turn the inactive well into an unexpected infiltration well, bringing into the aquifer water flowing through the transport network that originates from a different area of the well field. When the well functions again, the involuntarily infiltrated water will be pumped out first and this will dictate the quality of the pumped water. Depending on the volume infiltrated during the inactive period, it may take a long time before the sampled water quality resembles the real quality of the aquifer.

2.3.3 Interaction with well materials

Samples from older PSWFs may also be handicapped by the release of heavy metals like Cu from copper well screens, and PAHs from asphalted iron or steel screens and risers. These non-inert materials were frequently used until the 1960s, after which more inert materials like polyvinylchloride (PVC), high density polyethylene (PE) or glass fiber have been used. Effects of interaction with well materials are more pronounced in well fields tapping acid groundwater and shortly after reactivation of inactive wells.

2.4 Guideline 2: determine well field adaptation (WFA)

In the 19th century, PSWFs usually abstracted groundwater of good quality from phreatic aquifers. Increasing pollution during the 20th century forced waterworks to look for more protected resources, and growing population and drinking water demands also forced them to increase their capacity. We define the term well field adaptation as “*The capacity of a PSWF to adapt to the environment in order to produce enough water volume to fulfill the drinking water demand, with sufficient quality for preparation of drinking water at the lowest cost and avoiding expensive treatment”*. Well field adaptation is a process comparable to the adaptation of any living creature to survive in a dynamic environment. When adaptation measures are not sufficient to improve the water quality to sustainable standards, the well field fails and is permanently closed or equipped with enhanced treatment systems. Some typical adaptation measures are listed in Table 2.3.

The interpretation of hydrochemical data obtained from PSWFs is hindered by these adaptation measures, but the adaptation record also provides substantial information on the effects of anthropogenic influences on water resources. Extensions (adding new wells to the well field) and reallocations (adding new wells and closing the old ones) to deeper aquifers point towards stresses from the surface like acidification, urbanization and eutrophication, while extensions or reallocations to shallower aquifers point towards salinization of deep aquifers by excessive pumping and subsequent upconing of deeper brackish water. Implementation of AR in an aquifer is usually triggered by salinization due to excessive pumping and/or by an unacceptable decline of groundwater tables. RBF is applied to counteract river water quality deterioration, mainly due to urbanization and industrialization. Interception wells within a well field usually solve pollution spills and point pollution sources.

If a well produces water with high Fe and Mn concentrations, the quality is sometimes improved by application of Subsurface Iron Removal (SIR). SIR is applied to approximately 10 % of all PSWFs in The Netherlands. The method consists of the injection of a limited volume of aerobic water into the aquifer through the abstraction well, followed by the abstraction of a greater volume of groundwater, with much lower iron and manganese concentrations (Hallberg and Martinell, 1976), which precipitate as hydr(oxides) around the well. During subsequent abstraction, dissolved Fe and Mn adsorb to the hydr(oxides) and are removed from the pumped groundwater. When the adsorption complex becomes saturated, Fe and/or Mn concentrations are again detected and a new injection is applied. The method produces numerous changes in the water quality (Appelo et al., 1999; van Beek and Vaessen, 1979) that must be taken into account. Sulfides and organic material probably present are also oxidized, with the consequent increase of SO_4 and heavy metals like As, Ni, Co and Zn. Furthermore, all mentioned oxidation processes and adsorption of Fe and Mn are acidifying processes that release protons, modifying the concentrations of all pH dependent species.

Table 2.3: Well field adaptation measures, their application in The Netherlands and implications for trend analysis of water quality. The second column shows the environmental or technical problems that are to be solved by the specific adaptation measures.

Well field adaptation measures	Counteracted environmental or technical problem	a	Consequences for trend analysis	
			Increase	Decrease
Extension with new wells in a deeper aquifer	Acidification, urbanization, eutrophication and salinization	+++	pH, HCO_3	Oxid., pollutants
Moving to deeper aquifer		+		
Extension with new wells in same aquifer outside impacted areas		++	-	Salinity, pollutants
Moving to same aquifer outside impacted areas		+		
Extension with new wells in shallower aquifer	Salinization		Oxid.	Ca, salinity
Moving to shallower aquifer		-		
Interception wells	Point pollution sources and spills	+++	-	Pollutants
Sanitation measures within the WHPA, incl. the banning of specific activities				
Abandoning a specific bad quality well	All	+		
Change from surface water to AR or RBF	Urbanization, industrialization	ca 5%		
Change from groundwater to AR	Salinization, declining groundwater tables	15%	Pollutants	-
Well regeneration	Clogging	+++	Co, Ni	Fe, Mn, NH_4, PO_4
Subsurface Iron Removal (SIR)	Clogging, treatment	+		
Variability in pumping scheme	Water demand and treatment, well clogging, salinization		-	Salinity

[a] estimated importance in The Netherlands.

2.5 Guideline 3: check for historical changes in hydrochemical methods

Hem (1985), Matthess (1982) already warn for the effects of historical changes in hydrochemical methods. In PSWFs in The Netherlands, various chemical parameters have been reported in different units during the century. Nitrate, for example, was reported as mg N_2O_5/L before 1915, as mg NO_3/L until 1970 and as mg N/L afterwards. Historical data must be checked for these inconsistencies and it is not uncommon that unit conversions have been applied twice, which is extremely difficult to identify. A listing of parameters with variable units encountered in The Netherlands is given in Table 2.4, together with the conversion factors required to recalculate them. Missing decimal points in ancient books or typing errors during digitalization of large databases are common errors that require correction. Such errors are not only common in historical PSWF data series, but also in NGQMNs. Frapporti et al. (1994), for example, reported changes in sampling and analytical procedures, due to a relocation (including renovation) of the laboratory responsible for the analyses.

Another point of concern is the handling of censored data (values above or below a specific detection limit). Simple substitution methods ($<x$ by either 0, $x/2$ or x) are widely used, but have no theoretical basis and lead to undesirable and unnecessary errors when computing basic statistics (Helsel, 1990). Moreover, they produce bias when detection limits vary in time and space. The data record shows on average a continuous decrease in detection limits in time, corresponding to improved analytical methods. This trend, however, shows fluctuations sometimes in detection limits because available resources and budgets determine which analytical method is good enough for the information required. Also, the many laboratories and waterworks involved in a national survey, apply different analytical methods, which yields an additional spatial variability in detection limits. Hence, censored data with values far above present detection limits should be discarded. For this purpose, a threshold of 2 times the 10th percentile was defined for every parameter in the database and censored values above this threshold were rejected. This exercise removed from the database misleading values like Hg <5 µg/L reported in 1989. When multiplied by 0.5, this censored value would become 2.5 µg/L, which would be the maximum value of the database with Hg values of 0.005-0.25 µg/L.

Table 2.4: Listing of parameters with variable units in the annual reports of the Dutch Waterworks Association (VWN/VEWIN, 1898-1992). Three periods are discerned, with boundaries around 1915 and 1970. The conversion factors to recalculate between columns are also given. Although units in column C are more actual, units in column B are more commonly used in groundwater literature.

A		B		C		Conversion	
Before 1915		1915-1970		After 1970		A -->B	C -->B
NaCl [a]	mg/L	Cl	mg/L	Cl	mg/L	0.61	1
-	-	EC	uS/cm (18 °C)	EC	mS/m (20 °C)		1.05
N_2O_3	mg/L	NO_2	mg/L	NO_2-N	mg N/L	1.21	3.29
N_2O_5	mg/L	NO_3	mg/L	NO_3-N	mg N/L	1.15	4.43
NH_3	mg/L	NH_4	mg/L	NH_4-N	mg N/L	1.06	1.29
P_2O_5	mg/L	PO_4	mg/L	PO_4-P	mg P/L	0.34	3.07
Fe_2O_3	mg/L	Fe	mg/L	Fe	mg/L	0.70	1
Mn_2O_3	mg/L	Mn	mg/L	Mn	mg/L	0.70	1
CaO	mg/L	Ca	mg/L	Ca	mg/L	0.72	1
MgO	mg/L	Mg	mg/L	Mg	mg/L	0.60	1
SiO_2	mg/L	SiO_2	mg/L	SiO_2-Si	mg Si/L	1	2.14
$KMnO_4$	mg/L	$KMnO_4$	mg/L	$KMnO_4$-O_2	mg O_2/L	1	3.95
TH [b]	D[c]	TH	D[c]	TH	mmol/L	1	5.60

[a] Only for some waterworks. [b] TH = Total Hardness; [c] D = German degrees.

Pretreatment and preservation of samples and analytical procedures are nowadays standardized, much improved and more specific. Samples are filtrated in the field over 0.45 µm filters and acidified when necessary, which was not necessarily the case in the past. PO_4 for example was measured in non acidified samples probably before the 1990s, which is a major problem in samples containing iron, if not analyzed immediately, due to losses of PO_4 by sorption to precipitating iron hydroxides. Most older analyses are therefore unreliable with respect to PO_4 and should not be taken into consideration (Stuyfzand, 1987b). Analytical techniques have also improved especially regarding trace compounds. In individual cases, however, they worsened due to the selection of more rapid methods and refraining from duplicate analysis. SO_4 for example was determined by precipitation with Ba until the 1970s, which was a more precise method than many ultrarapid spectrometric methods applied nowadays.

Hence, historical data should be checked on errors and hydrochemical consistency before starting any trend analysis. This is a tedious and time consuming exercise, but necessary in order to avoid erroneous interpretations and conclusions. The process is substantially fastened by the use of specialized software like HyCA (www.hyca.nl), a program developed within the framework of this research project to facilitate the correction, management and interpretation of water quality data and the presentation of results. HyCA presents a fully automated routine to plot trends and maps, and to calculate indicators like the ionic balance, specific electrical conductivity, redox environment, saturation indices for different minerals and outliers. This facilitates the identification and correction of errors mentioned here.

2.6 Guideline 4: how to determine the origin of the water

As already mentioned in "Well fields and their data collection", the source water is a crucial factor for the proper interpretation of PSWF data. RBF and AR can often be distinguished from autochthonous groundwater (locally or regionally infiltrated rainfall) by means of specific origin tracers. Kass (1998), Clark and Fritz (1997) provide an overview of generally applied water tracing techniques. The technique is briefly illustrated with an example from The Netherlands, where PSWFs abstracting RBF are separated from PSWFs pumping autochthonous groundwater. Complications of the method in the Rhine delta are mentioned as well.

In The Netherlands, RBF and AR have been successfully distinguished from autochthonous groundwater (locally or regionally infiltrated rainfall) by means of a.o. δ^{18}O, Cl, the Cl/Br ratio, Mg, and the Fe/Mn ratio (Stuyfzand, 1989a). The contrasting low δ^{18}O content of Rhine water (δ^{18}O = -9.5 ‰) as compared to autochthonous groundwater in The Netherlands (δ^{18}O = -7.6 ‰) is related to the high contribution (ca. 70%) of the inland mountainous areas in Switzerland and Germany to the Rhine's discharge in The Netherlands, and the depletion of the heavier oxygen isotope ^{18}O upon its preferential raining out from oceanic air when moving inland and uphill. The high Cl/Br ratio in the Rhine (500-820) is caused by the low Br content of salt waste released by the salt mining industry in the Elzas to the Moesel River, which discharges into the Rhine River in Germany. Combination of both tracers yields the most reliable identification. Fig 2.2 shows the results obtained for PSWFs located in the Rhine delta, composed of the branches Lek, Waal and Yssel (Fig 2.1). Also given is the percentage of RBF, quantified as:

$$\%RBF = 100\frac{(C_M - C_G)}{(C_R - C_G)} \qquad (2.1)$$

where C_M, = δ^{18}O or any other tracer in the sample, C_G = ditto, in the autochthonous groundwater (δ^{18}O = -7.6 in The Netherlands); C_R = ditto, in the influent (δ^{18}O = -9.5).

The following complications were encountered in The Netherlands when using δ^{18}O. On the one hand, δ^{18}O levels in autochthonous groundwater may deviate from -7.6 ‰, especially when infiltrated during a glacial period (-9 ‰) or when infiltrated in swampy areas with high evaporation losses (-4 to -6 ‰). Minor deviations arise in The Netherlands due to differences in distance to the North Sea coastline (0.5 – 250 km), different altitudes (-7 to 321 m+MSL) and land uses. On the other hand, there is a recent trend of increasing δ^{18}O levels in the Rhine (-9.9 ‰ in the 1960-1970s, to -9.1 ‰ in the period 1997-2006) due to climate change and various changes in water management in the Rhine catchment area (Stuyfzand, 2008b). This trend necessitates to also address the age of the water pumped, or to use more tracers.

2.7 Guideline 5: how to calculate the Hydrological Response Curve

The Hydrological Response Curve (HRC) is the cumulative frequency distribution of the age of the water pumped by a well (field). The HRC is crucial for the interpretation of water quality data obtained from PSWFs, but its accurate determination requires the collection of numerous data and intensive modeling procedures. In a national inventory such data and models are frequently lacking for too many PSWFs, so that simple approximations are needed to calculate their HRC, and for comparison or consistency, also for the others. Therefore, in the following paragraph a simplified method is presented to approximate the HRC of a PSWF. It is mainly based on the thickness and porosity of the pumped aquifer, the depth of abstraction, and recharge rate. Such data are easy to estimate on a national scale. The method is developed for 'normal' PSWFs, either phreatic or confined. RBF and AR require different methods, due to their direct connection to surface water infiltrating via a line source.

2.7.1 General HRC equation

The travel time of groundwater (*t*) to a well field consists of an unsaturated (t_{UNS}) and saturated (t_d) part. In the following analytical approximation of *t*, the pumped aquifer is assumed to be homogeneous, isotropic, of infinite length and with uniform recharge, and the well field is schematized into a single abstraction well with an equal water delivery along the whole well screen.

Assuming a constant thickness of the unsaturated zone, the travel time in the unsaturated zone (t_{UNS} in year) can be approximated according to Stuyfzand (1993) by

$$t_{UNS} = \left(hV + \varepsilon c\right)/N \qquad (2.2)$$

where *h* = average thickness of the unsaturated zone (m); *V* = mean moisture content of the unsaturated zone (fraction by volume); ε = porosity of the capillary fringe (fraction by volume); *c* = thickness of the capillary fringe (m); *N* = groundwater recharge (m/y).

For details on how to calculate *V* from grain size data and *N*, reference is made to van Lanen (1984). Normal values for medium grained sandy deposits in The Netherlands, with *N* = 0.8 m/y, are: *V* = 0.07, ε = 0.4 and *c* = 0.3 m (Stuyfzand, 1993). The effect of differences in unsaturated zone thickness induced by the variable relief around the PSWF could be incorporated using the method proposed by Schwientek et al. (2009).

The travel time of groundwater in the saturated zone (t_d in year) of a phreatic aquifer at depth *d* (m below the groundwater table) (Fig 2.3), given the above mentioned conditions, can be calculated according to Vogel (1967) (see also (Appelo and Postma, 1983)) by:

$$t_d = \frac{nD}{N}\ln\left(\frac{D}{D-d}\right) \qquad (2.3)$$

with *n* = effective porosity; *D* = aquifer thickness (m).

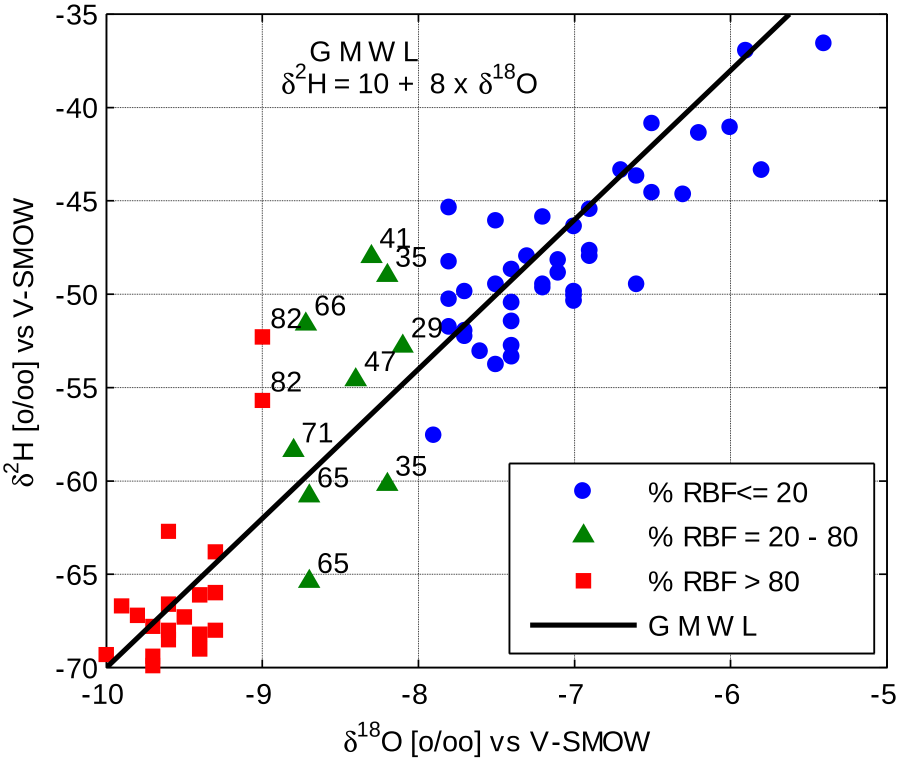


Fig 2.2: Tracer plot of δ^2H versus δ^{18}O, for PSWFs located in the Rhine delta (see Fig 2.1 for location). Isotopic concentrations are reported as per mil deviation from the Vienna Standard Mean Ocean Water (V-SMOW). Classification according to average % RBF obtained with Eq. (2.1) for δ^{18}O. The % RBF is indicated for PSWFs with values > 20, except for the ones with 100%. GMWL = Global Meteoric Water Line.

This expression does not take into account any impact on flow by groundwater pumping. For calculating the HRC the term d in Eq. (2.3) needs to be replaced by:

$$d = d_U + 0.01 P_X (d_L - d_U) \qquad (2.4)$$

where d_L = lower well screen level (m below groundwater table); d_U = upper well screen level (m below groundwater table); P_x = percentile *x* in the HRC (0-100%). Replacing *d* in Eq. (2.3) by Eq. (2.4) and adding Eq. (2.2) yields the following HRC for a phreatic PSWF:

$$t_P = t_{UNS} + \frac{nD}{N} \times \ln\left(\frac{D}{D - (d_U + 0.01 P_X (d_L - d_U))}\right) \qquad (2.5)$$

For practical purposes the following conditions are set: $d_L \leq 0.999 D_A$ or $d_L \leq 0.999 D$ (Fig 2.3), where D_A = thickness of phreatic aquifer (m).

In case of a (semi)confined aquifer, a term needs to be added to take into account the travel time from the edge of the confining layer to the PSWF (Fig 2.3), what yields the following HRC for a semiconfined PSWF:

$$t_C = t_{UNS} + \frac{nD}{N} \ln\left(\frac{D}{D - (d_U + 0.01 P_X (d_L - d_U))}\right) + \frac{nD_B}{N} \frac{(x_B - \Delta x)}{x_o} \qquad (2.6)$$

where D_B = thickness of the semiconfined aquifer (m); x_o = distance between the groundwater divide and the last flow line feeding the top of the confined aquifer (m); x_B, Δx = distances from the groundwater divide to respectively the well and the edge of the confining layer (m) and D = thickness of phretic+semiconfined aquifers.

If we neglect the latter term in Eq. (2.6) due to lack of data, then Eq. (2.6) yields only minimum travel times in its HRC. This information is, however, still very valuable. For instance, a t_C > 55 years in 2008 strongly reduces the chance on pollutants that were introduced after 1953.

An important characteristic number in the HRC is the percentage of ‘Young’ groundwater (%Y), which is defined as water that infiltrated after 1953 and therefore (still) contains a significant tritium activity (Fig 2.4) and relatively many modern pollutants. This %Y is obtained from the HRC, by rearranging Eq. (2.5) and Eq. (2.6) to:

$$\%Y = \frac{100\left[D(1 - e^{(t_{UNS}+G-Y)N/nD}) - d_U\right]}{(d_L - d_U)} \qquad (2.7)$$

with $G = nD_B\,(x_B - \Delta x) / (Nx_0)$ (year; G=0 for phreatic); Y = reference date (for sample taken after 1953; for instance August 30, 1984 = 1984.66 – 1953).

2.7.2 Tritium validation and calibration

The natural background activity of tritium in central Europe is 5 (TU) (Tritium Units), but after nuclear tests in the 1950s and 1960s, activities up to 1700 TU were reached in bulk precipitation in The Netherlands (Stuyfzand, 1993). In Fig 2.4 the measured tritium activities (with a reconstruction prior to 1970) and the same activities after a correction for radioactive decay are shown. The correction to a specific reference date (t_R) is as follows

$$^3H_R = {}^3H_A\; e^{-0.6931\,(t_A - t_R)/12.264} \qquad (2.8)$$

where t_A = date of the tritium analysis (for instance August 30, 1984 = 1984.66); ^3H_A = tritium activity at date of analysis; and ^3H_R = tritium activity corrected for decay at reference date. 12.264 = half-life of tritium (years) (Akulov and Mamyrin, 2004).

A single tritium measurement of the mixed water from the well field can be used to roughly calibrate the HRC, by multiplying the whole HRC with the ratio of the predicted tritium activity (on the basis of the HRC and the annual tritium input corrected for decay to year of measurement) and the measured tritium activity:

$$t_C = ({}^3H_{HRC-1} / {}^3H_M)\,t \qquad (2.9)$$

$$^3H_{HRC-1} = 0.01[({}^3H_{IN})_1 + ({}^3H_{IN})_2 + \ldots\ldots + ({}^3H_{IN})_{99} + ({}^3H_{IN})_{100}] \qquad (2.10)$$

where t_C = corrected HRC; t = original HRC as calculated by Eq. (2.5) or Eq. (2.6); ^3H_M = tritium activity measured in the mixed water from the well field on reference date t_R (TU); $^3H_{HRC-1}$ = predicted mean tritium activity for the well field on reference date t_R (TU); $(^3H_{IN})_X$ = predicted tritium activity for percentile X on reference date t_R (TU).

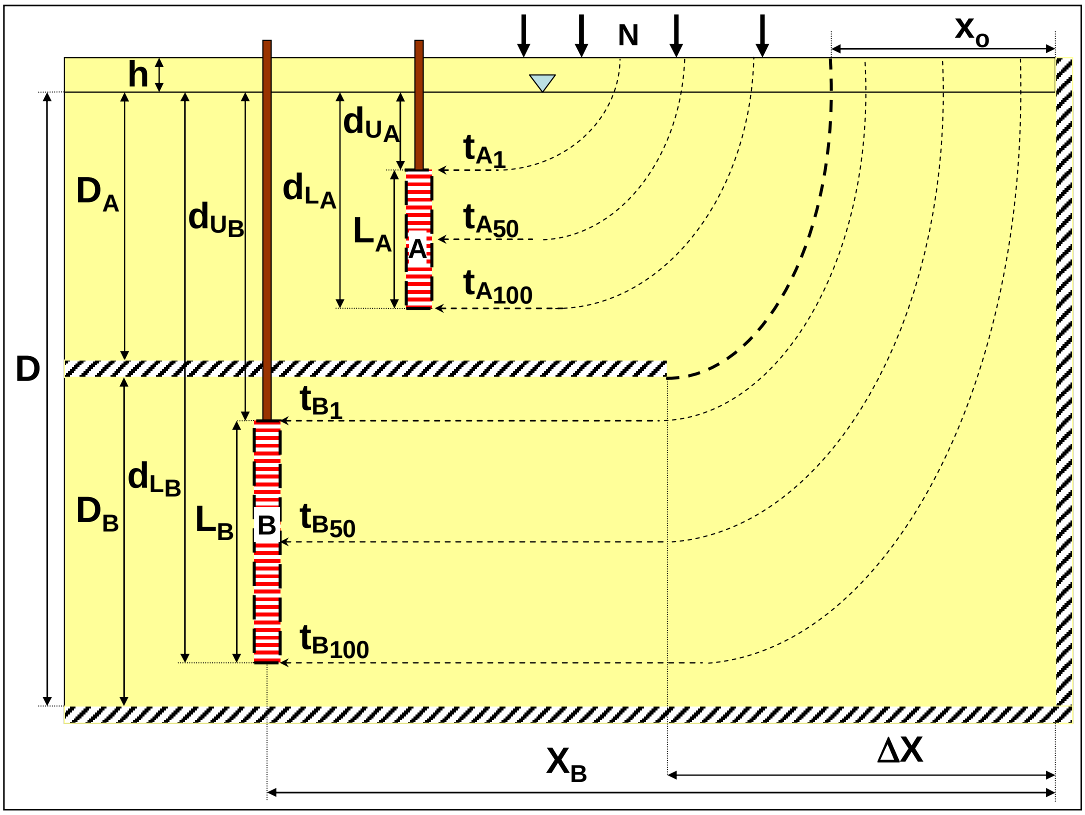


Fig 2.3: Cross section showing groundwater flow towards a phreatic (A) and a semiconfined (B) PSWF, both schematized by a single abstraction well.

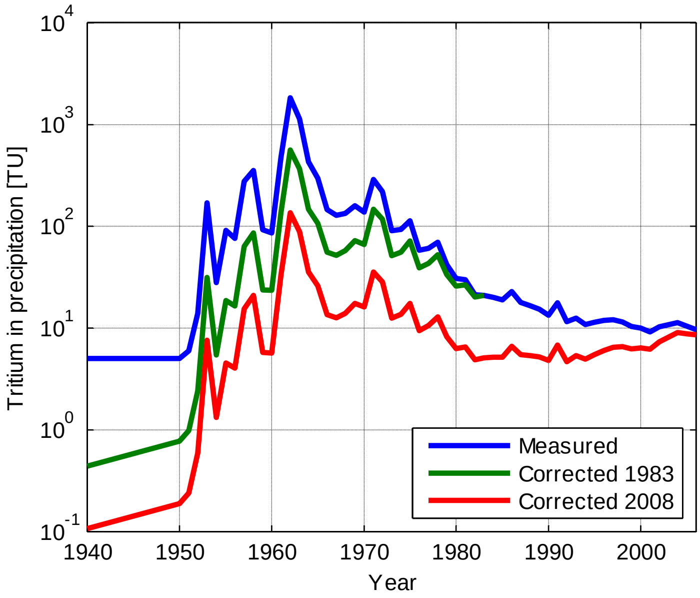


Fig 2.4: Tritium activity in bulk precipitation at station Groningen in the northern Netherlands and corrected for radioactive decay in 1983 and 2008. Period 1940-1969 = reconstructed after Stuyfzand (1993); period 1970-2006 = data obtained from the water isotope system for data analysis, visualization and electronic retrieval (WISER) of the International Atomic Energy Agency (IAEA).

Thus, the calculation of ${}^{3}H_{HRC-1}$ is based on the tritium values from the input curve (annual means corrected for decay to reference date t_R; Fig 2.4), and the calculated travel times for each percentile from the uncorrected HRC. The reference date and travel times need to be rounded off in order to match the corresponding year of the tritium input.

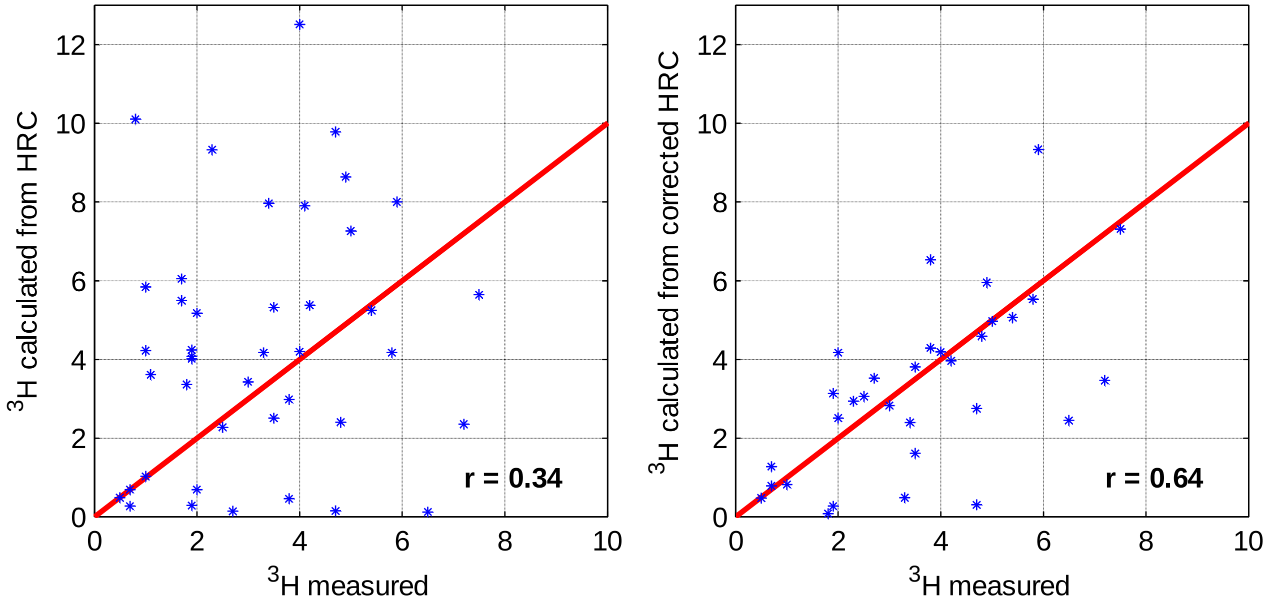


Fig 2.5: Correlation between tritium activity measured on the reference date and the mean tritium activity predicted from uncorrected (left) and corrected (right) HRC. The improvement is quantified by the Pearson's linear correlation coefficient.

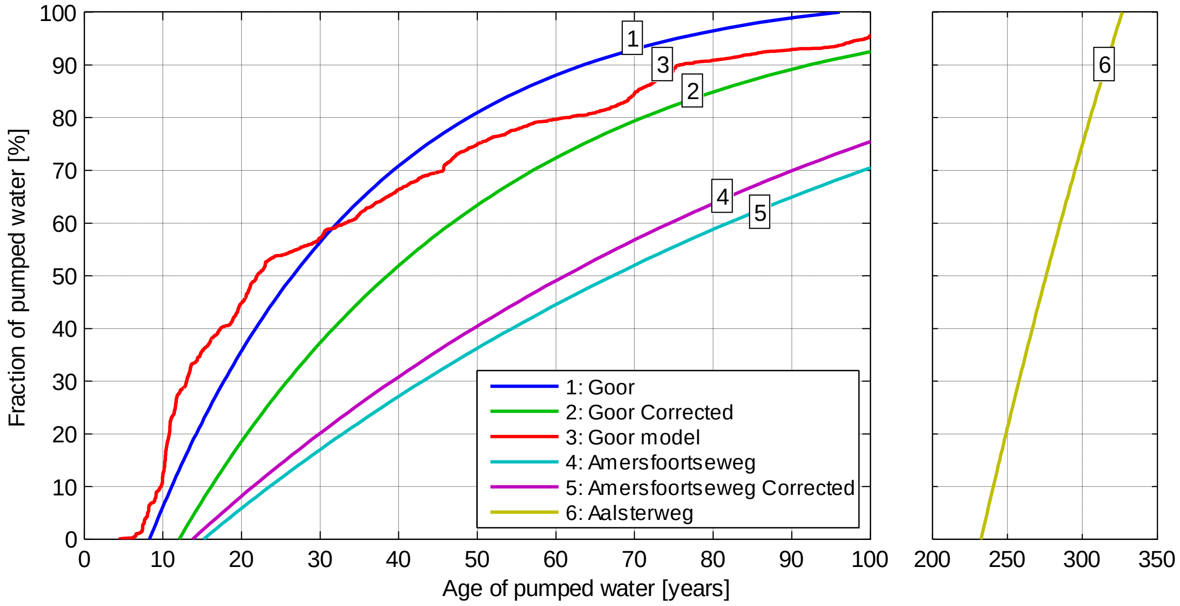


Fig 2.6: HRC obtained before and after correction for the measured tritium activity in the pumped water, for three different PSWFs: (a) Goor: shallow, phreatic with ${}^{3}H$ = 42 TU; (b) Amersfoortseweg: shallow (semi)confined with ${}^{3}H$ = 21 TU; and (c) Aalsterweg: deep confined with ${}^{3}H$ < 2 TU (no correction needed). For Goor also the HRC as obtained from a 3D groundwater model is shown.

The tritium corrected HRC yields a much better fit of the measured and predicted tritium activities (Fig 2.5), which justifies the correction. Deviations remain, however, due to the rough approximation of the HRC and deviations from the assumed boundary conditions. Results obtained for three different PSWFs in The Netherlands are shown in Fig 2.6.

The tritium activities measured in PSWFs Goor, Amersfoortseweg and Aalsterweg in 1983 were respectively 42, 21 and <2 TU. HRCs were calculated for average situations of n = 0.35 and R = 0.4 m/y. Note that the tritium correction displaces the HRC towards longer travel times in the case of Goor and towards shorter travel times in Amersfoortseweg. Aalsterweg is a deep PSWF that pumps very old water from tertiary sediments ($^3H < 2$ TU; no correction needed). It is important to realize that hydrodynamic dispersion has been neglected in our approach, which would decrease the low ages and increase the high ages in all 3 cases. For Aalsterweg all ages should be raised by the time needed for subhorizontal transport in the (semi)confined aquifer ($X_B – ΔX$; Fig 2.43).

2.8 The value of PSWFs as compared to NGQMNs

Following the guidelines here presented, PSWFs constitute a valuable monitoring network to determine temporal and regional patterns in groundwater quality. In this paragraph, the value of PSWFs is illustrated as compared to NGQMNs, by means of two examples: (1) The spatial distribution of potassium obtained from both networks in The Netherlands; and (2) The length of the time series gathered from both networks, in order to establish the natural background concentration of groundwater. The third example illustrates how the WFA-record helps to interpret a long but disturbed water quality record obtained from PSWFs.

2.8.1 Spatial distribution of potassium

The concentration of potassium (*K*) in bulk precipitation is about 0.2 mg/L (KNMI-RIVM, 1978-1988), but concentrations in groundwater can be much higher, due to both natural and anthropogenic sources. Natural *K* sources in groundwaters are (1) marine influences (*K*=400 mg/L in sea water), (2) dissolution of *K* rich minerals like feldspars, and (3) cation exchange between groundwater and the soil matrix in freshening aquifers. The main anthropogenic sources are (1) the application of manure (either animal or artificial) in agricultural areas and (2) leaky sewer systems in urbanized areas. *K* concentrations in groundwater are reduced by plant uptake (*K* is an essential plant nutrient) and sorption. The spatial distribution of *K* in both PSWFs and LMG is shown in Fig 2.7. Note that PSWFs correspond to the depth of abstraction (see Fig 2.1 for different types of PSWFs) and LMG to the shallow filter, around 9 m BLS.

In general, LMG presents much higher concentrations than PSWFs. The high *K* concentrations in LMG in the marine clays in the western part of the country are due to the presence of brackish to salty groundwater. This fact also explains why groundwater abstraction for drinking water preparation is absent in this area. High concentrations are also found in sandy uplands with intensive agriculture. The high concentrations in these shallow groundwaters are, however, substantially reduced in the PSWFs, mainly due to a decrease in *K* concentration with depth due to sorption and increasing age and due to mixing of waters of different origin (incl. land use). PSWFs in Twente (see Fig 2.1 for location) present higher concentrations than the ones in the Achterhoek because the pumped aquifer is much thinner and there is less space for groundwater flow, sorption and mixing with deep groundwater.

Observation wells located within the Rhine fluvial plain present low *K* concentrations. The levels are slightly higher in PSWFs with RBF (white dot) and AR (black dot), due to raised *K* in the rivers (*K* = 5-6 mg/L).

The lowest *K* concentrations (<2 mg/L) are encountered in PSWFs in the glacial till plateau and the ice pushed ridges of Utrecht and the Veluwe. They pump Pleistocene nonmarine aquifers that are not influenced by agriculture, because they pump relatively old water and/or due to the absence of agriculture in the WHPA.

A curious inversion effect is observed in the Central Graben, where shallow observation wells and shallow PSWFs present lower concentrations than deep PSWFs, which mainly abstract water from deep tertiary aquifers. The higher *K* concentrations are probably related to desorption of *K* in a freshening aquifer and the natural weathering of glauconite, which is abundant in those deposits.

Only two PSWFs exceed the drinking water norm of 12 mg/L.

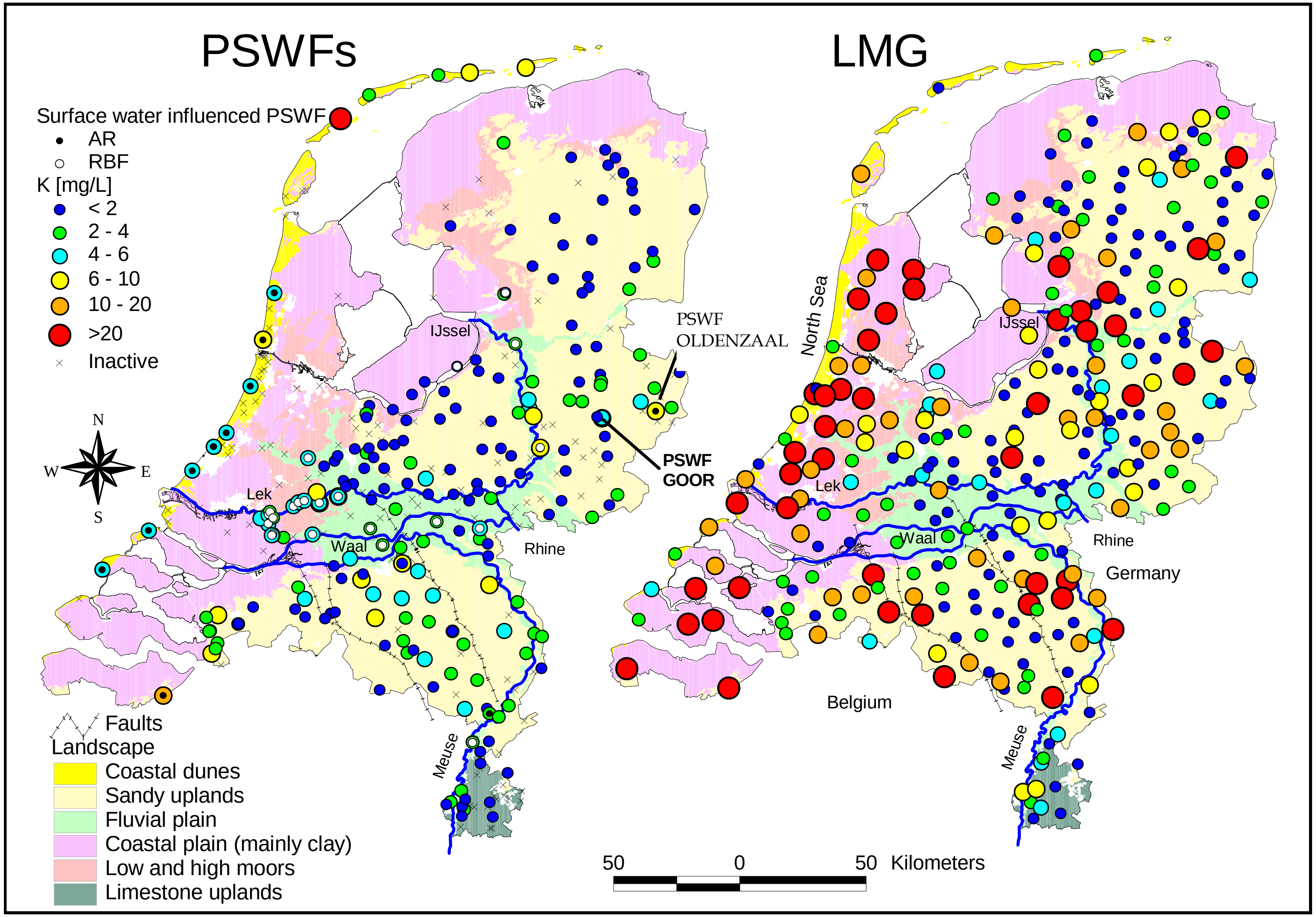


Fig 2.7: Potassium concentrations in PSWFs in 2008 and LMG in 2003, projected on top of a landscape map of The Netherlands. PSWFs with a strong influence of surface water are marked (black dot for AR and white dot for RBF).

2.8.2 Natural background composition

PSWF Goor (Fig 2.7, left) is active since 1915 in the eastern part of The Netherlands, with a capacity of 1.5 Mm^3/y. The well field comprises 10 wells screened at 17-27 m BLS. The wells pump anoxic water from a 20 m thick aquifer, consisting of coarse fluvioglacial sands. The slightly calcareous aquifer is covered by a discontinuous sandy clay layer of large reduction capacity at 10-12 m BLS and a 10 m thick layer of fine sands on top. The WHPA of Goor covers 109,600 m^2, 24 % of which is urbanized by the village Goor, and 58 % is agricultural land. The closest piezometer nest of LMG is LMG226, situated 2 km to the west and regularly monitored at 8 and 24 m BLS. The surface level at the location of PSWF and LMG226 is 11 m ASL. Time series of major parameters measured in the PSWF and both well screens are shown in Fig 2.8. Data of macro parameters and some trace elements measured in 1996 are given in Table 2.5.

LMG226-8 shows clear influences of agriculture, with high concentrations of NO_3, with one sample exceeding three times the EU drinking water norm of 50 mg/L. The effect is masked in LMG226-24 and the PSWF by the strong denitrification capacity of the aquifer (by organic matter and pyrite), which reduces all NO_3 to gaseous N_2. NO_3 concentrations in the pumped water of the PSWF are also reduced by dilution with waters from natural areas or waters that infiltrated before intensive farming started, and by local horizontal dewatering of shallow, polluted groundwater. This means that although NO_3 concentrations in shallow groundwaters under agricultural areas can rise above the drinking water norm, concentrations in pumped waters are generally much lower and only occasionally exceed the norm.

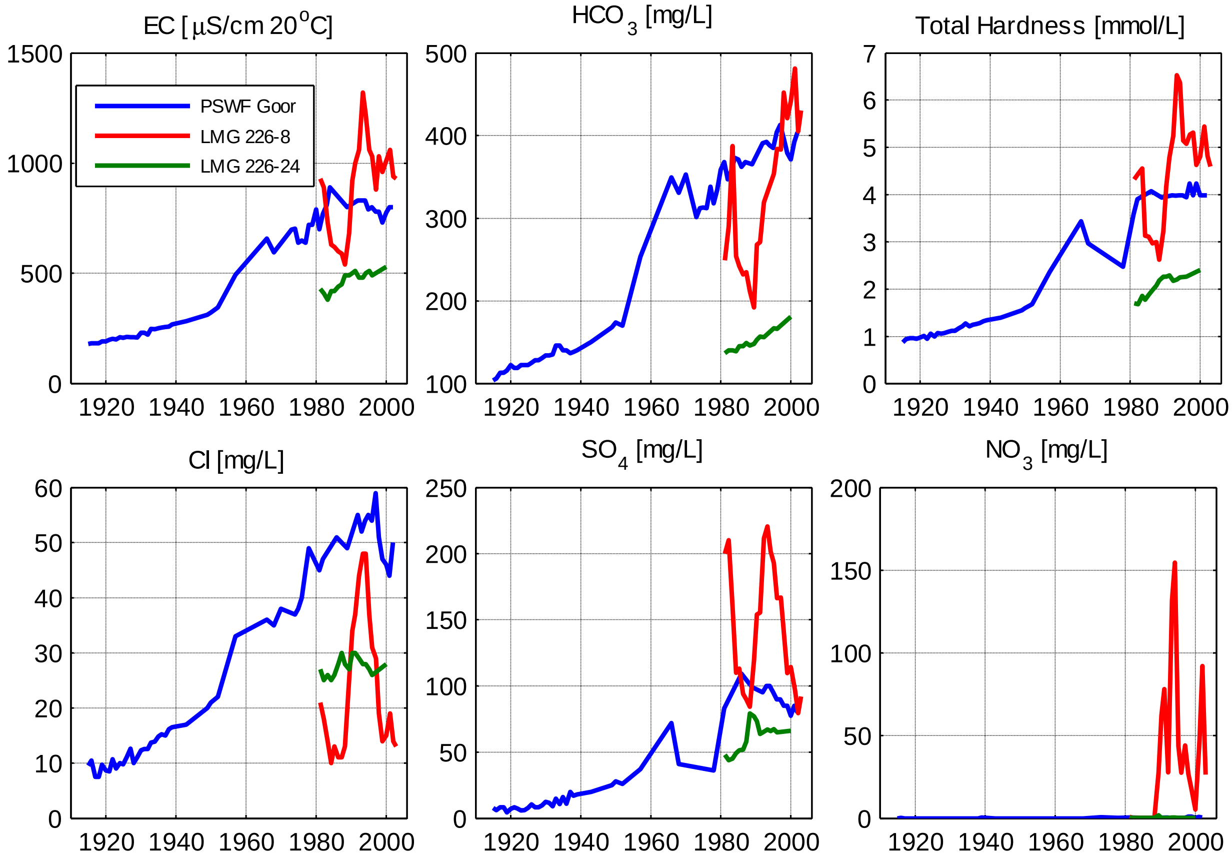


Fig 2.8: Time series of major parameters of groundwater obtained from PSWF Goor (17-27 m BLS), and 2 piezometers of LMG226 of the National Groundwater Monitoring Network, at resp. 8 and 24 m BLS.

Agricultural practices and, to a smaller extent, atmospheric deposition of SO_4 and NO_3 also introduce high loads of acidifying substances. These are buffered by dissolution of calcite, yielding high HCO_3 concentrations and total hardness values >4 mmol/L. The effect is accentuated by liming by farmers, for reducing soil acidity. The high SO_4 concentrations are due to inputs from agriculture (in the form of animal manure), atmospheric deposition of SO_4 and probably some pyrite oxidation by NO_3. The effect of these anthropogenic influences is not so strong in LMG226-24, which has lower values for all the parameters, due to the increasing depth and the protecting effect of the semiconfining layer. The water sample from the PSWF represents an average water quality from a large catchment area including both moderately deep and shallow groundwaters. As such it is more representative for the regional character of the system than the localized observation wells.

Fig 2.8 also reveals that the natural backgrounds of the different water quality parameters in the aquifer can be much better inferred from the historical data record of the PSWF, starting in 1915, than from the 20 years of measurements available in NGQMN. The quality measured in the pumped water in 1915 is given in Table 2.5.

2.8.3 WFA-record

The WFA-record (see guideline 2) is a general indicator of environmental problems affecting the groundwater system and provides substantial information on the effects of anthropogenic influences on water resources. As an example, the consequences of expansion and reallocation for the quality of the water delivered by PSWF Oldenzaal (Fig 2.7, left) are illustrated here. The well field was established in the centre of the town of Oldenzaal in 1906. Increased water demands forced the installation of a second well field in the same semiconfined aquifer but just outside town, in 1928. Water quality steadily worsened, probably due to infiltrating sewage from cesspits and effluents or spills from local industries. In 1954 the first well field was abandoned because of an unacceptable water quality. In 1963 a third well field was added further away from town, in an agricultural area, in the same semiconfined aquifer. This, in combination with the installation of a sewer system in Oldenzaal, significantly improved the situation, as evidenced by a sharp decline in Ca and SO_4 (Fig 2.9).

Table 2.5: Water quality data measured in 1996 at PSWF Goor and 2 piezometers of LMG226 (belonging to the Dutch Groundwater Quality Monitoring Network). For comparison, the water quality at the PSWF in 1915 is given, which approaches the natural background.

Name	Units	GOOR	LMG 226-8	LMG 226-24	GOOR 1915
Sampling year		1996	1996	1996	1915
Screen depth	m BLS	17-27	8	24	17-27
EC	uS/cm	800	1030	490	180
TH[b]	mmol/L	4.0	5.1	2.3	0.9
pH		7.1	7.0	7.7	
Cl	mg/L	54	31	26	9.5
HCO_3	mg/L	404	384	166	104
NO_3	mg/L	0.1	27.5	<0.03	<0.03
SO_4	mg/L	90	166	65	7.8
Ca	mg/L	140	176	82	30
Mg	mg/L	11	17	6	3
Na	mg/L	31	29	11	
K	mg/L	5	9	1	
Fe	mg/L	4.90	0.34	0.27	0.25
Mn	mg/L	0.3	0.5	0.2	0.1
As	ug/L	4.5[a]	<0.1	1.6	
Cu	ug/L	5.5[a]	3	<0.7	
Ni	ug/L	1[a]	12	<0.7	
Zn	ug/L	8[a]	<6	<6	

[a] measured in 1992; [b] TH = Total Hardness.

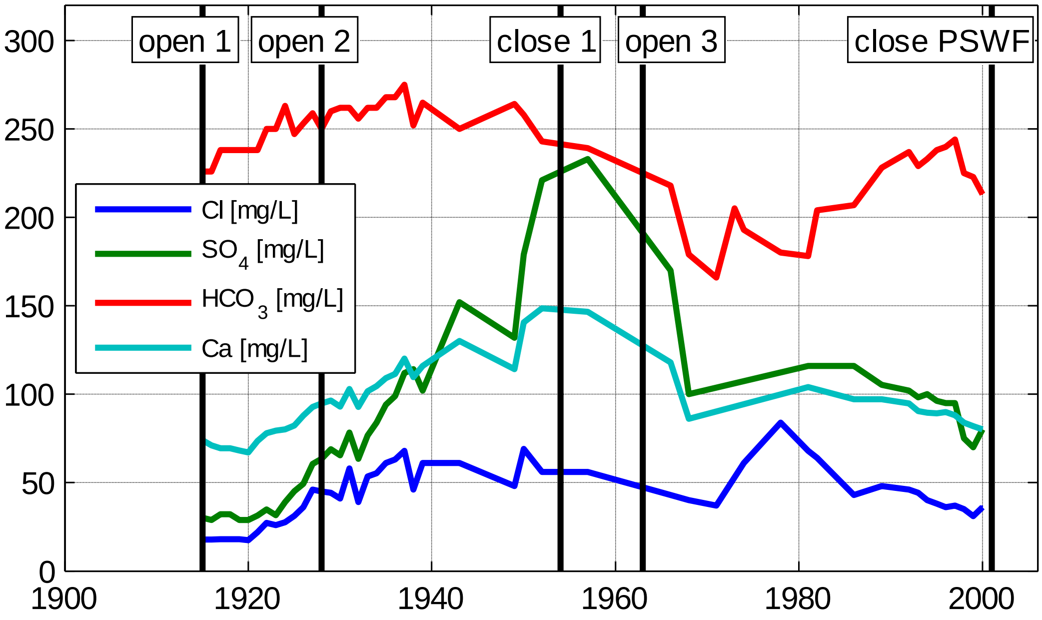


Fig 2.9: Concentration of major parameters in PSWF Oldenzaal from 1915 until closing down in 2001. The extension of the PSWF with new wells in 1928 and 1963 and the closing of the first location in 1954 are indicated by vertical lines.

SO_4 and Ca (and to a smaller extent Cl) present a similar pattern. SO_4 sources in the area are atmospheric deposition, pyrite oxidation caused by either NO_3 released from agriculture and/or O_2 due to lowering of water tables by groundwater abstraction. The NO_3 reduction capacity of the confining layer is also demonstrated by the absence of NO_3 in the pumped water, even though NO_3 concentrations above 200 mg/L are measured in shallow observation wells within the area. The acid released from the oxidation of pyrite is buffered by dissolution of calcite, which explains the Ca increase.

Hence the WFA-record, comprising 2 phases of expansion and reallocation in this case, is a clear indicator of groundwater quality deterioration in the area. The PSWF was definitively closed down in 2001.

2.9 Conclusions

PSWFs constitute a very valuable monitoring network of groundwater quality, capable to demonstrate pollution trends and to establish the natural background concentrations, due to their spatial distribution throughout the country and the long time series available, which in many cases cover the whole period of interest. In The Netherlands, PSWF water quality records are available since 1898, when groundwaters were hardly affected by anthropogenic influences and thus approximate the natural backgrounds. This forms a significant advantage over more recently installed national monitoring networks, where the natural background must be statistically inferred from data starting in the early 1980s. Other advantages of PSWFs are as follows: They are regularly sampled and analyzed for reasons of societal importance of drinking water production. The standard analytical package for PSWFs is much more extensive than for dedicated monitoring networks, by also addressing a long list of organic micropollutants that represent a hazard for human health. In addition, the water quality data can be considered representative for the relatively high volumes of water pumped, which are registered as well.

However, the mixed character of water samples obtained from PSWFs requires a more laborious interpretation than samples from conventional observation wells due to misleading effects resulting from variable pumping schemes during sampling and/or well field adaptation measures, which mask the effects of environmental problems by dilution, reallocation or changing the water sources. This problem can be counteracted by using quality records of unaltered wells or well fields, provided data are available or following the guidelines here presented otherwise.

Data obtained from PSWFs are biased towards good quality because they are drilled in specific areas of good groundwater, suitable for drinking water preparation, and because the water supply company may wish to retain negative quality data. Conventional monitoring networks are usually biased towards specific environmental hazards for which they are defined. In addition, PSWFs can be biased towards more oxidizing environments because of their local lowering of groundwater tables. The samples obtained from PSWFs are mixed groundwaters from different depths, geological formations, ages and origin, which are usually not in chemical equilibrium. The mixing of aerobic and anaerobic waters may result in samples containing O_2, NO_3 and Fe, which would rarely happen in an equilibrated water sample from a conventional observation well. The high, well-mixed volume is, however, also an advantage because of the large (sub)regional area a single sample represents.

2.10 Acknowledgements

This research was funded by the Joint Research Program of the Dutch Waterworks (BTO) and Delft Cluster, Project number CT05.30. Two anonymous reviewers are greatly acknowledged for their critical review on a previous version of this manuscript, which greatly improved the quality of this contribution.

Chapter 3

3 HyCA, the all in one approach for efficient spatial and temporal analysis of large water quality databases[2]

Abstract

A new methodology is presented for efficient spatial and temporal analysis of large groundwater quality databases. HyCA (HydroChemical Analysis) offers a systematic multidisciplinary approach that combines a database with numerous tools frequently used for the analysis of water quality data. The database is designed for the smooth acquisition, manipulation, control and verification of the data and for their hydrochemical, spatial, graphical and trend analysis. Integration of the database with the numerous analysis tools within a single user-friendly software package, minimizes the cumbersome data manipulation process with chance of errors, maximizes the time left for the analysis of the data and facilitates the connectivity and interactivity between tools. This brings the hydrochemical analysis of water quality databases to a higher level.

---

[2] This chapter is submitted for publication as Mendizabal, I., Stuyfzand, P.J., HyCA, the all in one approach for the efficient spatial and temporal analysis of large groundwater quality databases. Computers & Geosciences.

3.1 Introduction

Globalization and the development of ICT are causing a complete revolution in the way hydrologists and water quality specialists approach their work. Large amounts of water quality data are available via internet and experts are often involved in international research projects, with a number of partners and fieldwork sites. Furthermore, increasing legislative pressures such as The Water Framework Directive (2000; EU, 2008) and its daughter Groundwater Directive (EU, 2006b) enforce all EU member states to improve the chemical status of their waters, identify and reverse groundwater pollution trends and periodically report to the authorities. This requires extensive monitoring networks to be developed, not only in Europe, but also elsewhere.

Such an intensive monitoring effort yields a huge amount of data. The questions and procedures become more complicated, the hydrologic situation more complex and the labor costs and workloads increase. If we add the strict deadlines imposed, which require a fast analysis of the data, a situation is created, where the specialist needs a multidisciplinary tool, capable of dealing in an efficient way with numerous activities, such as data acquisition, control, analysis and reporting. There are various computer programs available on the market for this purpose (Table 3.1).

What is lacking, however, is a systematic multidisciplinary approach that combines relevant tools into a single user friendly software package, capable of dealing in an efficient way with all the activities required. This minimizes the cumbersome data manipulation process and maximizes the time left for the analysis of the data and to really understand the hydrochemical processes in the underground. In this contribution such a multidisciplinary tool is presented.

3.2 Capabilities

HyCA[3] (Hydro Chemical Analysis) is a powerful, efficient and user friendly computer program for the management, control, analysis and presentation of water quality data in four dimensions (X, Y, Z, t). Developed within a MATLAB© environment[4], which is used internationally by a wide range of institutions for complex technical calculations and software development. HyCA is a stand alone application that does not require a Matlab license and offers numerous tools for the activities to be performed by a water quality expert, from the moment a research project is defined until the final reporting of results. Such activities are summarized in Fig 3.1, together with the tools facilitated by HyCA for their efficient management.

The foundation of the program is a database, which can be easily filled with data from numerous formats with no size limitation, other than the memory of the computer. The database is complemented with numerous analytical tools for each compartment of the water quality assessment cycle, grouped into four categories: hydrochemical, spatial, graphical and trend analysis. All the capabilities of the program are accessed from the main screen (Fig 3.2), which is mainly based on a Geographical Information System (GIS) application that shows the spatial distribution of the sampling locations. The Map can be zoomed in/out, panned and used to select piezometers or wells by dragging a box or line transect. Sampling locations, chemical parameters and maps to be used as background are listed to the left. New maps can be added with a single mouse click. The graph under the map shows the time series and some basic statistics of the selected location/parameter combination. The map, graphs and statistics are immediately updated according to the selection in the listboxes. This provides a unique, extremely fast and convenient visual screening of the database.

3.2.1 Data acquisition – Insertion of new data

When a new dataset is added to a database, the integrity of the new data is automatically checked and corrected when required. Chemical parameters are recognized and their properties, such as parameter type, molecular weight and valence, are assigned from an internal database, which contains the properties of more than 2000 compounds, grouped in macro components, trace elements, isotopes and a wide range of organic micropollutants such as pesticides, pharmaceuticals and halogenated hydrocarbons. The program also accepts any parameter not yet available in the internal database, provided the user supplies the properties himself. Once defined, the new parameter is incorporated into the internal database and henceforth recognized in future sessions.

---

[3] www.hyca.nl/index.asp

[4] www. mathworks.com

Table 3.1: Tools available on the market for the storage, analysis and visualization of water quality data, with some of their capabilities (Inventory in Sept. 1010).

		Software name	HyCA	AquaChem	Hydro Geoanalyst	EnviroInsite	Enviro Data
		Price	2,000 $	1,495 $	5,495 $	399 $	4,000 $
Data Acquisition		Parameter recognition	+	+	-	-	-
		Unit homogeneization	+	+	-	-	+
		Chronological sorting	+	+	-	-	+
		Multiple value correction	+	+	-	-	-
		Censored data interpretation	+	+	-	-	-
Data Manipulation		GIS application	+	+	+	+	+
		Database	+	+	+	+	+
		Selection tools	+	+	+	+	+
		Universal unit conversion	+	+	-	-	-
		Parameter calculator	+	-	-	-	-
Data control and correction		Ionic balance	+	+	-	-	-
		Calculated EC	+	-	-	-	-
		Time series editor	+	+	-	-	-
Data analysis		Chemical watertype	+	-	-	-	-
		Sum parameters	+	+	-	-	-
		Frequently used ratios	+	+	-	-	-
		PhreeqC	+	+	-	-	-
		Norm exceedance test	+	+	-	-	+
		Trend analysis	+[1]	+	-	-	-
Data visualization	Spatial analysis	Mapping in plannar view	+	+	+	+	+
		Mapping in cross sections	+	-	+	+	-
		Three-dimensional mapping	+	-	+	+	-
		Geology in cross sections	-	-	+	+	-
	Graphical analysis	Time series plots	+	+	-	+	+
		Scatter plots (X/Y plots)	+	+	-	+	-
		Barplots	+	+	-	+	-
		Piper diagrams	+	+	-	+	-
		Stiff diagrams	+	+	-	+	-
		Box Whisker plots	+	+	-	+	-

[1] Only available for users with a valid license of Trendanalist.

New datasets are added to the original database in the corresponding place and are chronologically sorted. New data reported in different units than the original database are identified and converted to the standard units of the database. Measurements already available in the database that are repeated in the new dataset are checked on consistency. Double measurements with the same value are neglected. For each double measurement with differing value in the database and the new dataset, the user is given the option to choose either one of both values or their average. Multiple datasets can be simultaneously added in batch.

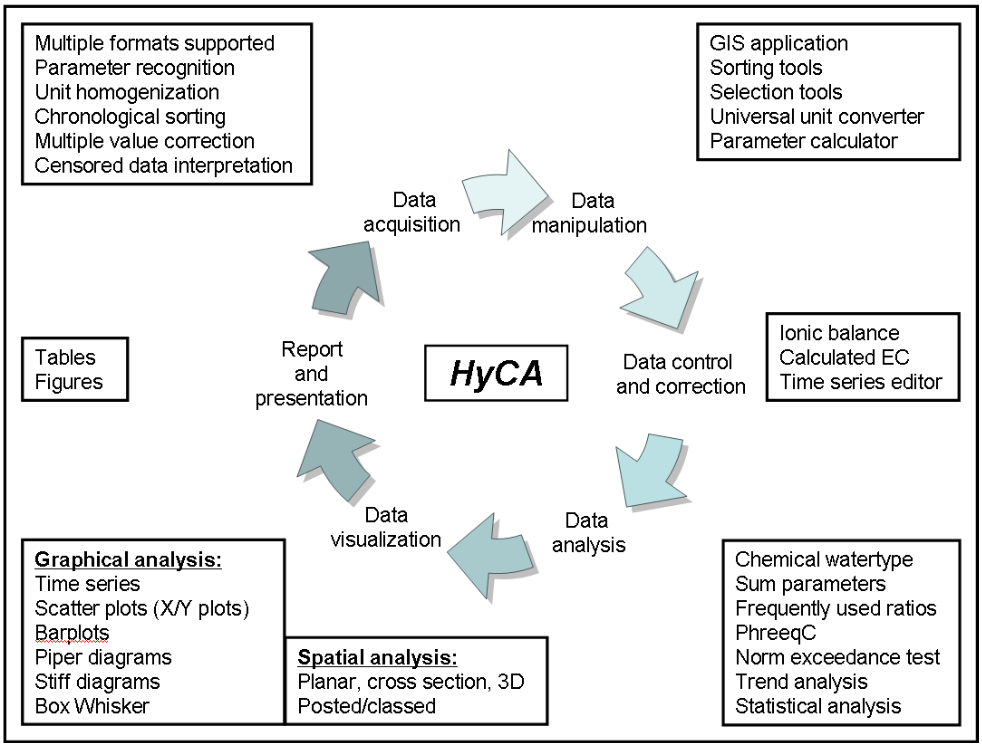
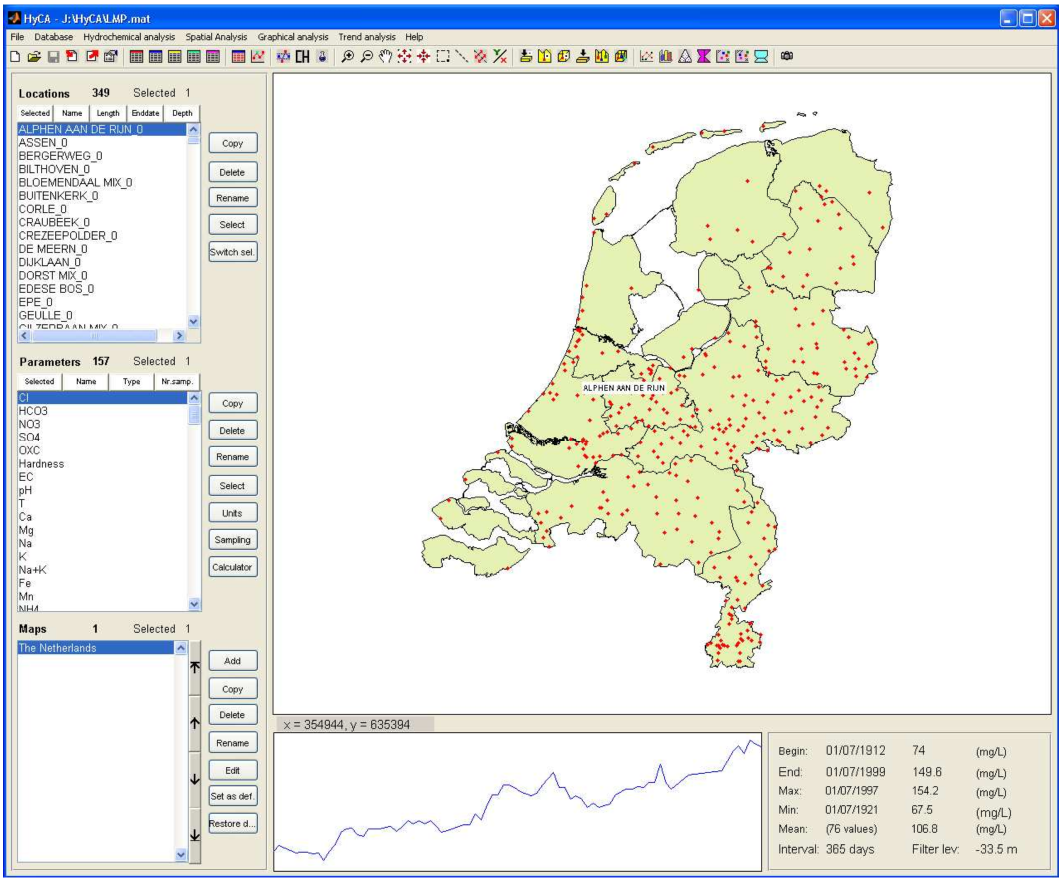


Fig 3.1: The water quality assessment cycle (WQAC) with the numerous tools facilitated by HyCA for the efficient performance of each activity.



Begin: 01/07/1912 74 (mg/L)
End: 01/07/1999 149.6 (mg/L)
Max: 01/07/1997 154.2 (mg/L)
Min: 01/07/1921 67.5 (mg/L)
Mean: (76 values) 106.8 (mg/L)
Interval: 365 days Filter lev: -33.5 m

Fig 3.2: Main screen of HyCA.

Censored data (values above or below a specific detection limit) are properly interpreted. Such data are very common in hydrochemistry, but not so easy to handle. Numerous computer programs replace them by simple substitution methods (<*x* by either 0, *x*/2 or *x*), which are widely used but have no theoretical basis and lead to undesirable and unnecessary errors when computing basic statistics (Helsel, 1990). HyCA applies such substitution methods in order to incorporate censored values to hydrochemical, graphical, spatial and trend analysis calculations, but maintains the original censored value for reporting purposes.

3.2.2 Data selection & manipulation

HyCA facilitates the screening of a database by means of numerous capabilities for a fast selection and sorting of both sampling locations and parameters, including a powerful GIS application. Locations can be selected according to numerous criteria such as the origin of the water, depth of well screen or any property defined by the user, either numerical (year of drilling, thickness of unsaturated zone, estimated travel time to well screen, etc.) or textual (location type, aquifer type, land use category, etc.). A selection of wells based on the range of a specific chemical parameter is also possible. New selection criteria can be used to refine a previous selection or to add/remove locations from it, which offers infinite selection flexibility. All parameters are classified, which facilitates the selection of a specific type of parameters, such as isotopes, macro constituents or trace elements.

A universal unit converter facilitates the recalculation of concentrations, temperature, electrical conductivity and total hardness to different units, either individually or in batch form. A parameter calculator is also available to define new parameters resulting from mathematical operations on existing parameters.

3.2.3 Data control and correction

The increasing number of hydrochemical parameters measured nowadays hinders our capacity to maintain an ordered and correct hydrochemical database. Errors and inconsistencies easily creep into databases, due to typing errors, decimal point errors, mixing of different units, etc. HyCA provides various tools to detect and correct these and other errors, and to check the accuracy of chemical analyses by calculating (a) the ionic balance of an analysis including the often neglected DOC, and (b) the electrical conductivity of water using the method of Stuyfzand (1983; 1987a), which yields an extremely high precision for waters ranging from rain water to brines.

The ionic balance (IB) is defined as

$$IB = 100 \times \frac{\sum cat - \sum an}{\sum cat + \sum an} \tag{3.1}$$

where: Σcat = sum of cations (meq/L); and Σan = sum of anions (meq/L).

The calculation of Σcat and Σan includes: (1) the often neglected transformation of H and OH activity as obtained by pH measurement into its concentration; (2) that part of orthophosphate that is not included in the determination of alkalinity; and (3) organic anions, according to a procedure presented by (Oliver et al., 1983). The balance is judged square, if: │IB│ < 2%, if Σan+Σcat > 8 meq/l; │IB│ < 3%, if Σan+Σcat = 2-8 meq/l; and │IB│ < 5%, if Σan+Σcat < 2 meq/l.

The electrical conductivity (EC) of water at a standard reference temperature (here $20^{o}C$) is a proxy for the total amount of dissolved solids (TDS) or rather the total amount of charged ions in solution. Vice versa the sum of all analyzed major constituents of water can be used to calculate the EC. This calculated EC is useful to check the accuracy of chemical analyses by comparing the calculated (EC_C) with the measured EC (EC_M; either in lab or field), according to

$$\delta_{EC} = 100 \times \frac{EC_M - EC_C}{EC_M} \tag{3.2}$$

The calculation of EC is not easy, because there are no simple relations in a natural mixed solution between concentrations or activities and EC, due to interactions of electrical and ionic nature. The rule stated by Appelo & Postma (2005) that EC = 50 (Σcat + Σan), is practical but too simple for the purpose of checking the accuracy of a water analysis, especially at higher concentration levels. HyCA calculates EC following the method presented by Stuyfzand (1983) with updates in Stuyfzand (1987a). The method consists essentially of a dialing system, which selects out of 6 transformed and adjusted methods described in literature (Blanquet, 1946; Dunlap and Hawthorne, 1951; Logan, 1961; McNeal et al., 1970; Rossum, 1975), the best for a given range of the sum of cations and anions, and for a certain anion-ratio. It is applicable to the range of 0.2-12,000 meq Σan+Σcat/L or an EC in between 10 and 200,000 µS/cm. An analysis will earn the mark "good", if the calculated EC approximates the accurately measured EC in such a way, that: $|\delta_{EC}| < 10\%$, if $\Sigma cat+\Sigma an < 8$ meq/l; $|\delta_{EC}| < 5\%$, if $8 < \Sigma cat+\Sigma an < 1{,}200$ meq/l; and $|\delta_{EC}| < 9\%$, if $\Sigma cat+\Sigma an > 1{,}200$ meq/l.

Errors and inconsistencies can also be detected by visual inspection of time series. Once identified, they can be easily corrected in a table or with the time series editor. The latter also facilitates the correction of individual values or a batch of them by a specific factor. This is extremely useful to correct datasets containing parameters measured in different units during a specific period, such as NO_3 as mg NO_3/L or mg N/L (Mendizabal and Stuyfzand, 2009, Chapter 2).

3.2.4 Hydrochemical analysis

HyCA performs a fully automatic norm exceeding test (NET) to identify and report water samples exceeding maximum or minimum permitted concentrations in groundwater, according to various legislations. HyCA also provides a routine to calculate the chemical watertype, hydrochemical facies (Stuyfzand, 1999) and various quality parameters and indices from standard chemical water analyses (Table 3.2).

Table 3.2: Summary of calculated parameters.

Category	Parameters involved
Data control	**IB, EC, missing values, (chemical inconsistency)**
Chemical watertype	**Chlorinity, Alkalinity, dominant cation and anion, BEX**
Hydrochemical facies	**SI-calcite or pH-class, redox index, BEX, WAPI, (POLIN)**
Sum parameters	**TDS, TIC, TIN**
Ca-CO2-H_2O system	**pH (if NA), CO_2, CO_3, TIC, SI**
Ratio's	**Wirdum-ratio (WIR), SAR, Exch Sodium Ratio (ESR), Cl/Br, Ca/Mg**
Correction for Sea salt	**Na, K, Ca, Mg, SO_4, TotH, B, Br, F, I, Li, Mo, Rb and Sr**
Capacities	**MOC, EC**

BEX = base exchange index; EC = electrical conductivity; IB = ionic balance; NA = not available; SI = saturation index; TDS = total dissolved solids; TIC = total inorganic carbon; TIN = total inorganic nitrogen ions; TotH = total hardness; WAPI = water pollution index; MOC = Modified oxidation capacity (Stuyfzand and Luers, 2000); WIR = Wirdum Ion Ratio (van Wirdum, 1980); SAR = Sodium Adsorption Ratio; ESR = Exchangeable Sodium Ratio (Appelo and Postma, 2005).

Such parameters are a valuable means to characterize groundwater resources, to delineate groundwater bodies (Mendizabal et al., 2011, Chapter 4) and to identify and understand hydrochemical processes governing the quality of the groundwater in general and the one delivered by public supply well fields (PSWFs) in particular. Some are briefly described in the following. A more detailed description is provided in the HyCA manual.

The chemical watertype is calculated on the basis of the main constituents of water, according to the method of Stuyfzand (1986b; 1989b; 1993). In one code (9 characters) the chlorinity, alkalinity, dominant cation and anion (including the support of geohydrochemical family members) and a base exchange index (BEX) are indicated (Fig 3.3). For example the watertype '$F_1CAHCO_3^{+}$' indicates fresh water (30-150 mg Cl/L), with alkalinity class 1 (61-122 mg HCO_3/L), calcium as the most important cation, HCO_3 as the most important anion, and a significantly positive base exchange index (+).

The redox level is deduced, as suggested by Berner (1981) and Stumm (1984), from most redox sensitive main components of water, i.e. O_2, NO_3, SO_4, H_2S, Fe, Mn, and CH_4, following the algorithm of Stuyfzand (1993; 2006). The reason is that on site determination of the redox potential runs into practical problems and is handicapped by unreliable results (Lindberg and Runnells, 1984) or difficulties in quantitative thermodynamic interpretation (Peiffer et al., 1992). Similar redox classifications were presented by Chapelle (2001), but these do not define the ‘mixed’ redox class and use different criteria. The mixed redox class is rather common in water samples obtained from PSWFs, due to the local mixing of waters from different origins and redox environments, which occurs within the pumped well (Mendizabal et al., 2011; Mendizabal and Stuyfzand, 2011(Chapters 4 and 5)).

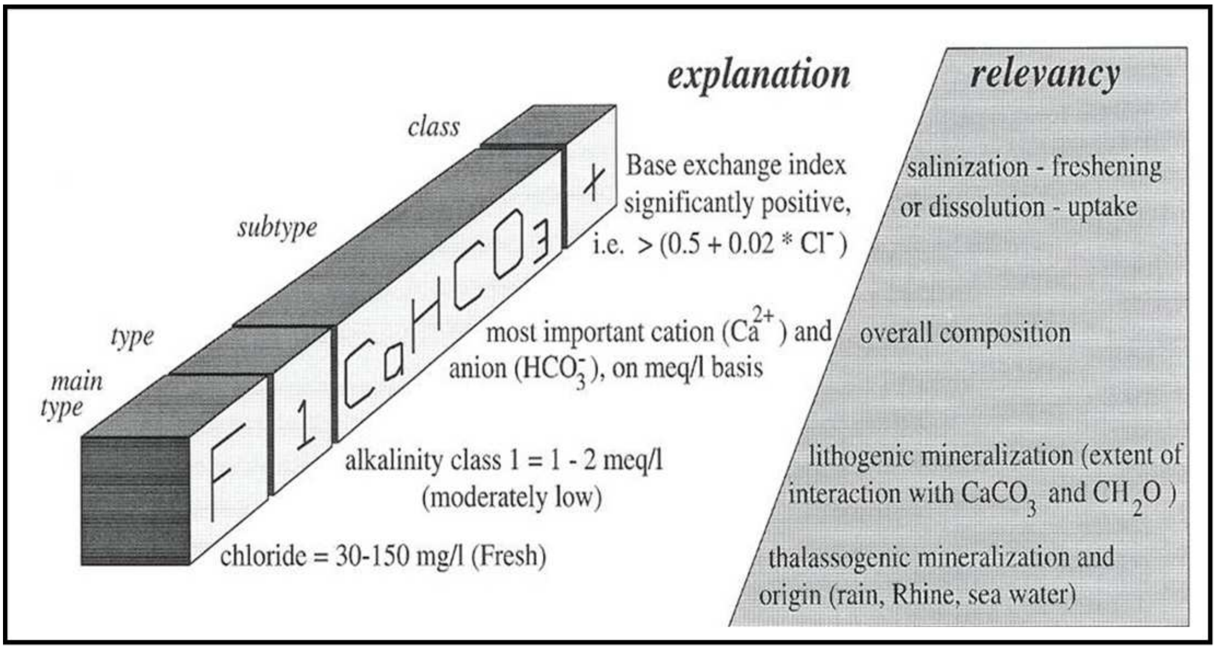


Fig 3.3: Coding and significance of the chemical watertype according to Stuyfzand's method (Stuyfzand, 1993).

MOC indicates the capacity of water to oxidize or reduce its environment. A positive value indicates oxidation capacity, and a negative value reduction capacity (Stuyfzand, 1989b). WIR is frequently used in ecohydrological research in the Netherlands, especially in combination with EC in a binary plot. A high value is often characteristic for lithotrophic water (for instance fresh groundwater that dissolved much calcite), and a low value for thalassocline water (for instance ocean water). SAR is frequently used to predict the degree to which irrigation water tends to provoke cation exchange reactions in the soil, notably the exchange of Ca and Mg for Na and thereby soil degradation. In the same way this also holds for artificial recharge or river bank infiltration during their initial phase, during and directly after displacement of the native groundwater. The Cl/Br-ratio on a mg/L basis is frequently used to determine the origin of water or its salinity (Alcalá and Custodio, 2005; Mendizabal and Stuyfzand, 2009 (Chapter 2); Stuyfzand, 1989a).

HyCA is also directly coupled to PHREEQC-2 (Parkhurst and Appelo, 1999), a very popular computer program for hydrogeochemical modeling. In connection with HyCA, PHREEQC-2 provides numerous direct options for hydrochemical calculations, such as equilibrating a sample or a batch of samples with a mineral, with or without temperature variations, before or after evaporation, with or without mixing, and much more. HyCA presents a graphical user interface to PHREEQC-2 for creating the input files, running the simulations and visualizing the results. A full working version of PHREEQC-2 is included with HyCA. It can be executed directly from the interface and the results added to the database as new parameters.

For more advanced hydrochemical modeling exercises, HyCA is also coupled to PHREEQC for Windows (Post, 1999) and PHREEQC Interactive (Parkhurst, 2005), open source graphical user interfaces (GUI) to PHREEQC-2. Input files of an unlimited number of samples for both GUIs are automatically created within a mouse click. The files can further be edited within the corresponding GUI and run, in order to calculate specific hydrochemical processes such as the change in water composition after heating to 95 ^{o}C, by evaporating 50% of the water, or by any other hydrochemical calculation supported by the GUI.

3.2.5 Trend analysis

In order to identify groundwater pollution trends in compliance with European legislation (EU, 2000; EU, 2006b; EU, 2008), HyCA is directly coupled to Trendanalist (Baggelaar and Van der Meulen, 2007), a computer program capable of performing a fully automatic trend analysis of a data series in a database. Each data series is tested for a monotonic trend (two-sided, with 95% confidence). The expert system of the program ensures that for each data series the trend test is used that best fits its relevant statistical characteristics, being the kind of probability distribution (normal or non-normal) and the occurrence or absence of autocorrelation and/or seasonality. Six trend tests are available, based on the parametric linear regression test and the distribution free Mann-Kendall test (Kendall, 1938; 1975; Mann, 1945). For both tests extensions are available to cope with autocorrelation and/or seasonality. The extensions of the linear regression test are dummy variables for the seasons and a first order autoregressive model for the noise (Box and Jenkins, 1976). See Hirsch et al. (1982) and Hirsch and Slack (1984) for the extensions of the Mann-Kendall test.

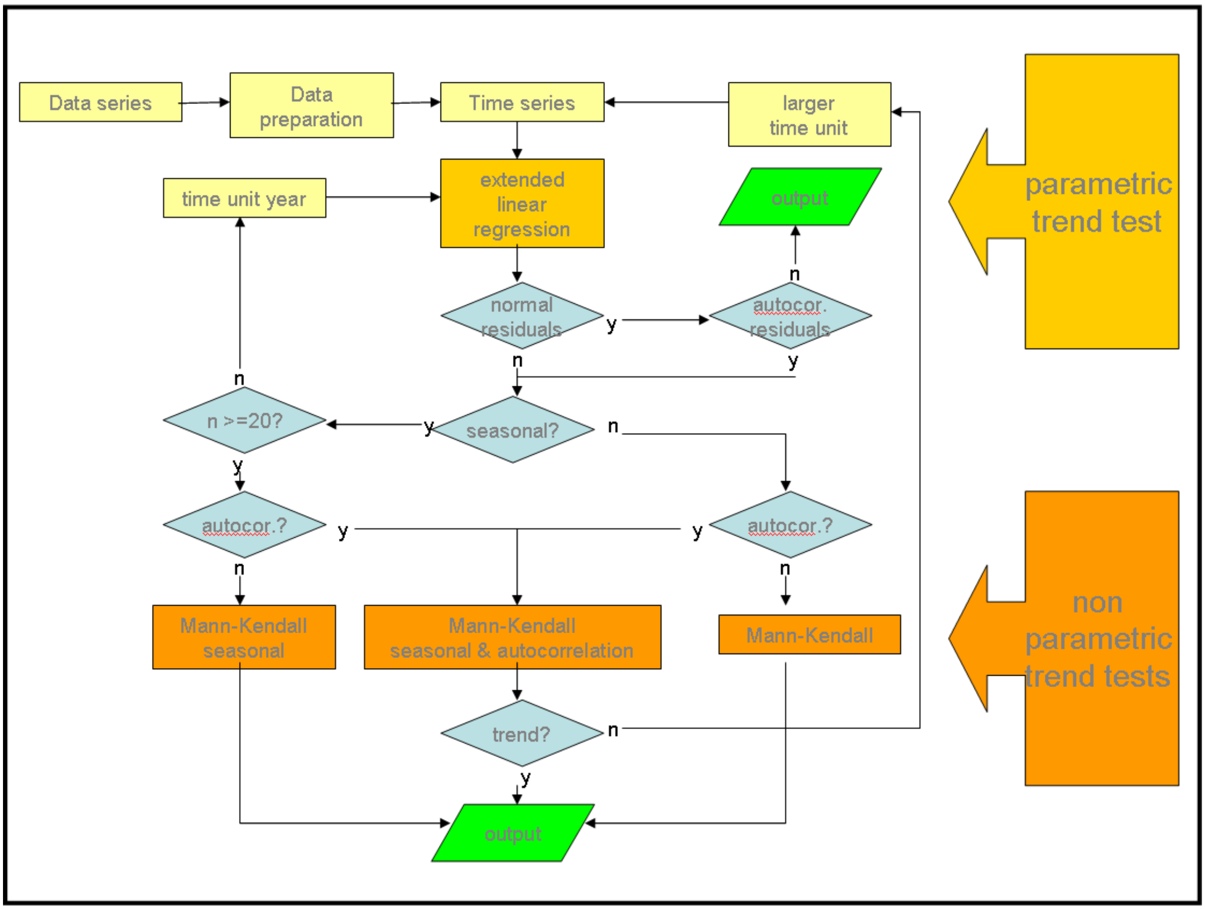


Fig 3.4: Automatic selection procedure for statistical trend analysis of groundwater quality data guaranteeing that the most appropriate trend test is selected for each separate data series.

The procedure that *Trendanalist* applies for each separate series is summarized in Fig 3.4. First, the extended linear regression model is estimated. If necessary, statistically non-significant model parameters for seasonality or autocorrelation are removed in successive iterations. Then the model residuals are tested for normality with the Kolmogorow-Smirnov test with Lilliefors correction (Lilliefors, 1967; 1969) and for autocorrelation with the Portmanteau test (Ljung and Box, 1978). If the model residuals come from a normal probability distribution and show no autocorrelation, the trend can be tested and quantified with the estimated slope parameter. Otherwise the procedure chooses one of the Mann-Kendall tests on trend, based upon the occurrence or absence of seasonality or autocorrelation in the time series (corrected for trend). Seasonality is tested with the Kruskal-Wallis test (Kruskal and Wallis, 1952) and autocorrelation with the runs test (Bradley, 1968), both distribution free tests. If the time series shows no seasonality, a trend is quantified as Theil's slope (Sen, 1968; Theil, 1950) and otherwise as Kendall's seasonal slope (Hirsch et al., 1982; Sen, 1968).

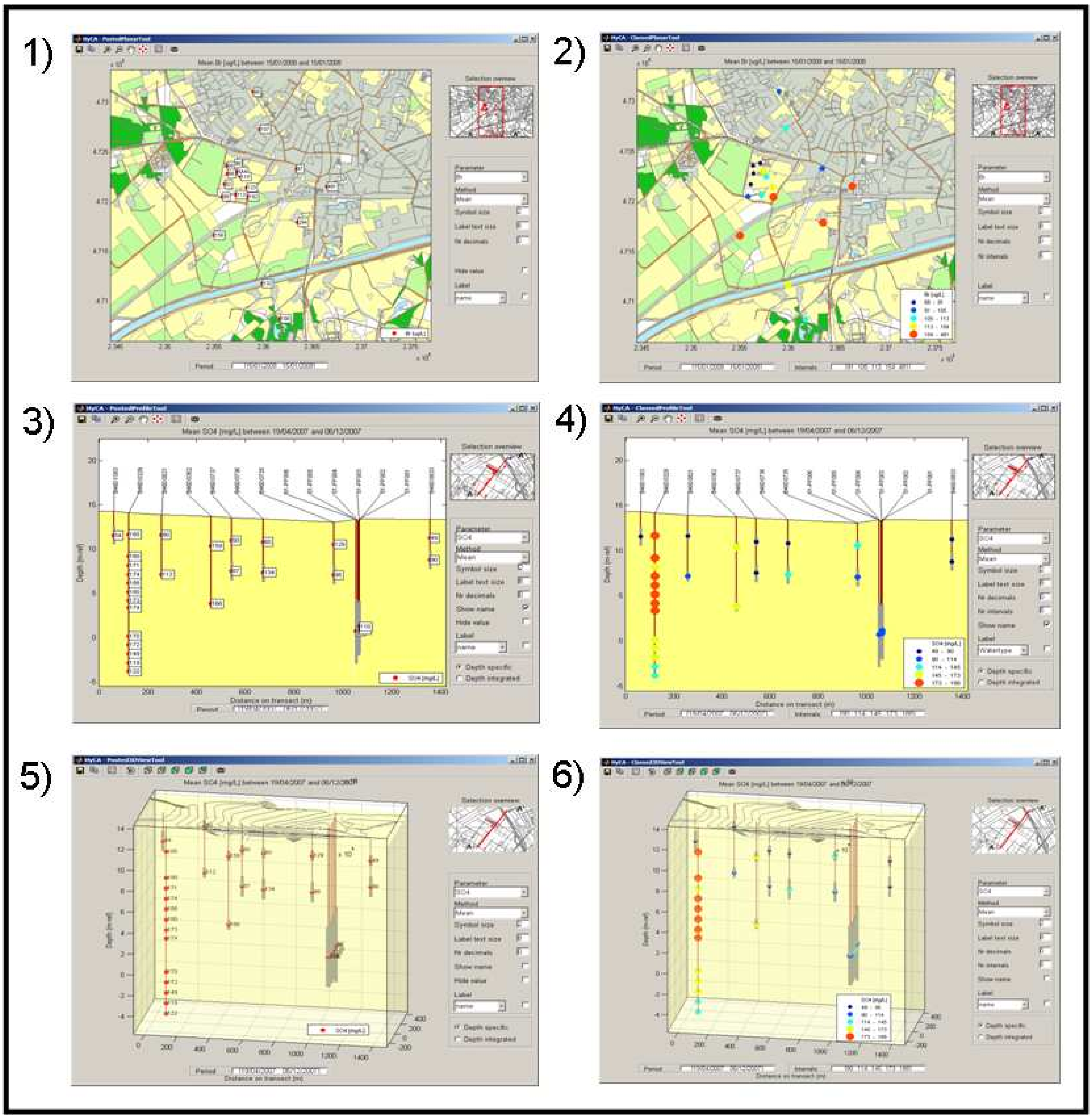


Fig 3.5: Mapping options offered by HyCA: 1) Posted planar view; 2) Classed planar view; 3) Posted profile view; 4) Classed profile view; 5) Posted 3D view and 6) Classed 3D view. They all hold for either parameter values or calculated trends.

3.2.6 Spatial analysis

HyCA offers fast and user friendly tools for the visualization of water quality data and the calculated trends. The spatial tool (Fig 3.5) presents numerous options to visualize the spatial distribution of specific water quality patterns either in planar view, cross section or three dimensions. For any parameter in the database, such maps are instantaneously created with a single mouse click, in two variants: 1) Classed maps, where measurements are plotted as a scaled circle of different color, according to a number of equidistant cutoff values automatically defined; and (2) Posted maps, where the measurement is labeled next to the sampling point. The period of interest, number and cutoff values of intervals, number of decimals, symbol size, etc. can be easily modified within a single mouse click.

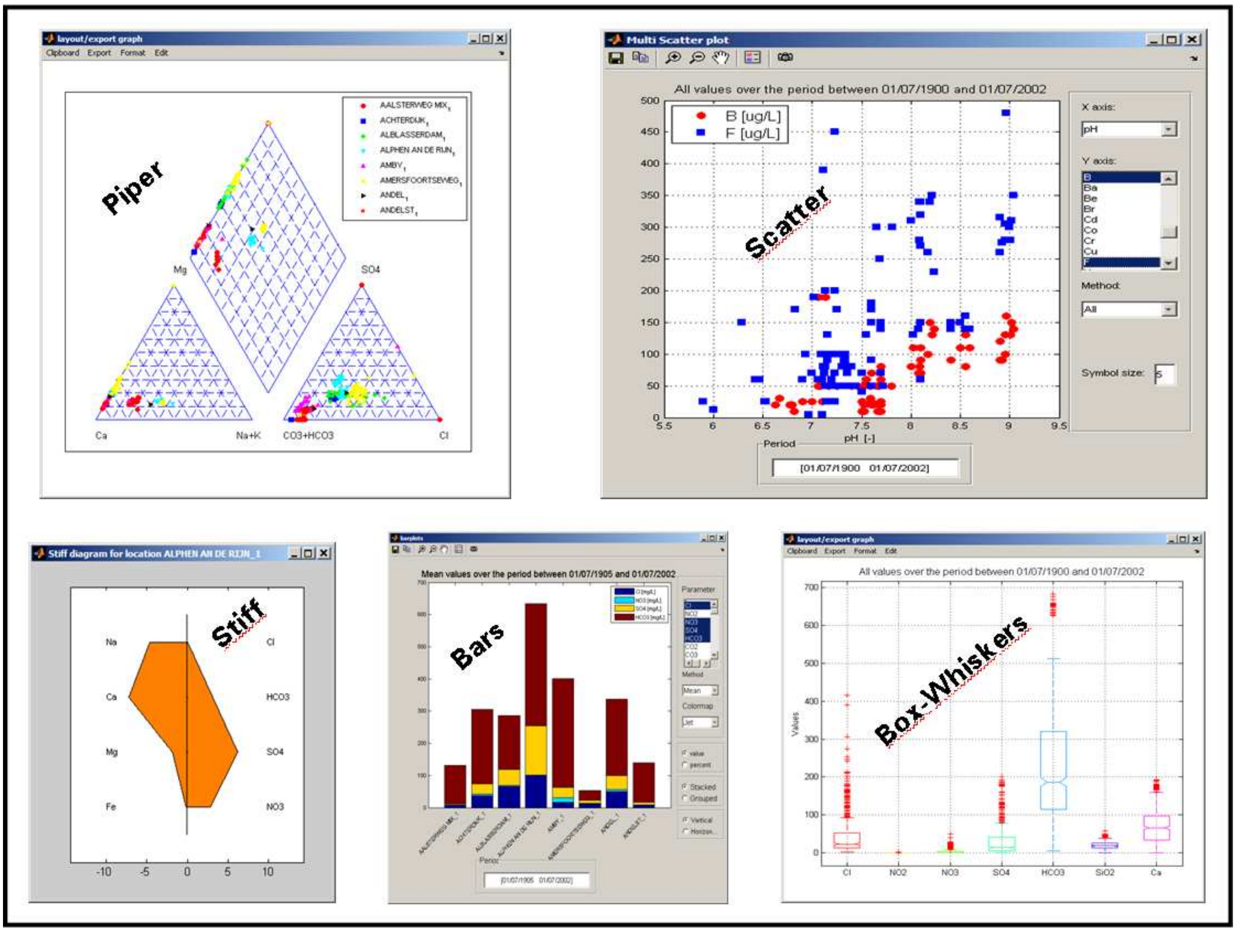


Fig 3.6: Graphical analysis tools offered by HyCA at the date of publication.

3.2.7 Graphical analysis

HyCA also offers a wide selection of tools for the graphical analysis of water quality parameters and comparison of hydrochemical properties of different observation locations. The graphical tools implemented cover time series graphs, bar plots, Stiff diagrams, Piper diagrams and scatter plots (Fig 3.6).

3.2.8 Report and presentation

Every figure and table produced within HyCA can be easily saved in different formats and directly used in reports. The ultimate layout of the figure can be edited before saving or exporting it.

3.3 Application

HyCA offers numerous tools that, in essence, cover a wide range of activities of the water quality assessment cycle (Fig 3.1). Such tools already facilitate the proper analysis of large databases by themselves and drastically reduce the time required for data manipulation. However, the most powerful feature of HyCA is the integration of the database and the numerous analytical tools within a single software package, increasing their interactivity and yielding a new generation of data analysis and visualization tools, capable of fully covering the demands of the water quality assessment cycle.

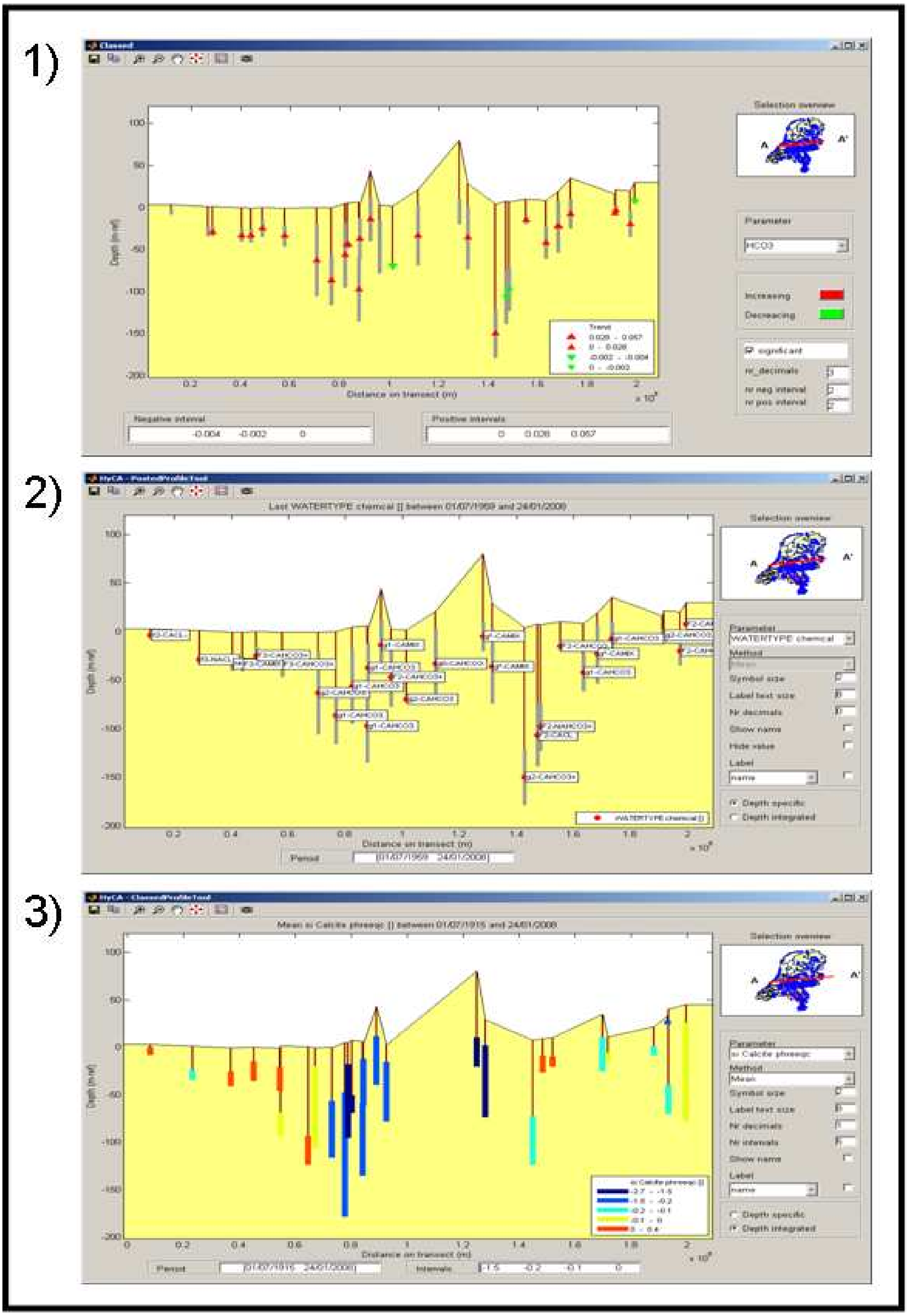


Fig 3.7: HyCA plots for public supply well fields along an East-West cross section over the Netherlands, show (1) trends in HCO_3 concentrations (mg/L/year); (2) watertype, as defined by Stuyfzand (1993); and (3) calcite saturation index of the raw water they deliver. PSWFs simplified to a single screen covering the entire depth of abstraction of individual pumping wells.

The capabilities of such tools are illustrated in Fig 3.7 by means of three examples. Example 1 is derived from the combination of the spatial analysis tool with the trend analysis tool; Examples 2 and 3 from the combination of the spatial analysis tool with the hydrochemical analysis tool. Fig 3.7.1 shows the results of the trend analysis exercise undertaken upon HCO_3 concentrations measured in public supply well fields along a West-East cross section over The Netherlands. Fig 3.7.2 and Fig 3.7.3 show respectively the water type, as defined by Stuyfzand (1993) and the Calcite saturation index over the same cross section.

The production of Fig 3.7.1 is usually a cumbersome procedure that would require the following steps: (1) gathering the proper data; (2) checking the consistency of the data by visual inspection; (3) manually recalculating the units to molarities; (4) calculating some basic parameters, such as the ionic balance; (5) rearranging the data into the proper format for a trend analysis software; (6) reading the data into the trend analysis software; (7) performing the trend analysis exercise for every time series; (8) rearranging the results into the proper format for a GIS; (9) making the proper map in the GIS. Note that most GIS systems are defined in two dimensions, so that horizontal maps and vertical cross sections cannot be easily simultaneously drawn.

Such a laborious procedure is simplified to 16 mouse clicks within HyCA: (1) open data file; (2) run Chemcal; (3-5) select Chemcal parameters; (6) open Measurements table for inspection of hydrochemical consistency; (7-9) sort rows by ionic balance, check that the ionic balances are acceptable and correct or discard data otherwise; (10) select every location and parameter; (11) run Trendanalist; (12) select HCO_3; (13-15) Select the line transect option and click start and end points on the map; (16) Draw a classed map of trends along the selected cross section.

Fig 3.7.2 and Fig 3.7.3 would require similar laborious procedures, which are reduced to a number of mouse clicks within HyCA. Such maps are valuable tools for the characterization and delineation of groundwater bodies. At present, it is not yet possible to add geological layers to the cross sections, in order to automatically produce cross sections such as the ones presented in (Mendizabal et al., 2011; Mendizabal and Stuyfzand, 2011; Mendizabal et al., 2012 (Chapters 4, 5 and 6)), but this feature will hopefully be implemented in a future version of the program.

3.4 Conclusions

HyCA is a computer program that combines already existing data analysis techniques into a user friendly computer program, which is suitable for both data storage and analysis. The combination of a database with numerous analysis tools provides a perfect environment to accomplish all the activities of the water quality assessment cycle within a single software package, minimizing the cumbersome data manipulation process and maximizing the time left for data analysis. Such combination also facilitates the connectivity and interactivity between tools, bringing the hydrochemical analysis of large water quality databases to a higher level. One of the main capabilities of HyCA that differentiates it from other products within the market is the extremely fast and convenient visual screening of the database, and the speed with which maps and figures are produced. These features cannot be illustrated within this contribution, but should be experienced while proving the demo version, available at www.hyca.nl.

3.5 Acknowledgements

This research was funded by the Joint Research Programme of the Dutch Waterworks (BTO) and by Delft Cluster, project number CT05.30. Jos von Asmuth, developer of Menyanthes, program for time series analysis of groundwater levels, is acknowledged for laying the foundation of the program around which HyCA was built. Inke Leunk and Luit Jan Slooten contributed to the code and Frans Lüers transcribed Stuyfzand's Chemcal program into visual basic. Paul Baggelaar and Eit van de Meulen collaborated in the coupling between HyCA and Trendanalist.

Chapter 4

4 Hydrochemical system analysis of public supply well fields, to reveal water quality patterns and define groundwater bodies: The Netherlands[5]

Abstract

Hydrochemical system analysis (HCSA) is used to better understand the individual state of and spatial patterns in groundwater quality, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones within each hydrosome (facies). The origin is determined by environmental tracers or geomorphological and potentiometric maps, the facies by combining age, redox and alkalinity indices. The HCSA method is applied to all 206 active public supply well fields (PSWFs) in The Netherlands, resulting in the distinction of nine hydrosomes and eleven facies parameters –age (young, intermediate, old), redox ((sub)oxic, anoxic, deep anoxic, mixed) and alkalinity (very low, low, intermediate and high). The resulting classification of PSWFs provides a means to (1) predict their vulnerability; (2) optimize groundwater quality monitoring programs; and (3) better delineate groundwater bodies, by considering groundwater origin and flow. The HCSA translates complex hydrochemical patterns into easily interpretable maps by showing PSWFs, groundwater bodies and hydrochemical facies. Such maps facilitate communication between researchers, water resources managers and policy makers and can help to solve complex groundwater resources management problems at different scales, ranging from a single well(field) or region to the national or European scale.

---

[5] This chapter was published as Mendizabal, I., Stuyfzand, P., Wiersma, A., 2011. Hydrochemical system analysis of public supply well fields, to reveal water-quality patterns and define groundwater bodies: The Netherlands. Hydrogeol. J., 19(1): 83-100.

4.1 Introduction

A public supply well field (PSWF) is defined as a coherent set of pumping wells delivering groundwater to be distributed to the public as drinking water, either without or after treatment. The chemical and microbiological composition of the raw (untreated) mixed groundwater from a PSWF is to be initially assessed or periodically monitored in compliance with the relevant national drinking water act (Safe Drinking Water Act, 1974; Water Framework Directive, 2000). Thereby PSWFs constitute an attractive (inter)national monitoring system for evaluating the chemical state of groundwater. Advantages may consist of long data records, extensive analytical programs, and representativity for the relatively large volumes of water pumped, which are registered as well. In Mendizabal and Stuyfzand (2009, Chapter 2) also the disadvantages are mentioned: (a) the chances on bias in using data from a well field, (b) historical changes in both the well field and the hydrochemical methods applied, and (c) the mixing of groundwater of different composition, origin and age.

The hydrochemical data resulting from PSWF monitoring are included in the regular reporting of European Union (EU) member states to the EU Commission, in compliance with the Groundwater Directive (2006), daughter of the Water Framework Directive (2000; 2008). The reason is that these data also supply very useful information on the groundwater environment, which in the opinion of the EU Commission should not degrade any further.

Thus, hydrochemical data from PSWFs are collected on a large scale and have been so for a long time. They have been extensively used in national groundwater surveys on for instance nitrate (Brooks and Cech, 1979; Goss et al., 1998; Kross et al., 1993; Rudolph et al., 1998; Stuart et al., 1995), fluoride (Lalumandier and Jones, 1999; Stas et al., 1937), bromide (Davis et al., 2004), iodine (Gezondheidsraad, 1932), arsenic (Stuyfzand et al., 2008), lanthanides (de Boer et al., 1996), carcinogens (Cech et al., 1988) and pesticides (Reed, 1987; Squillace et al., 2002). What is lacking, however, is a systematic approach that combines all relevant data into a clear typology of the raw groundwater pumped by a PSWF, so as to better understand the individual state of and spatial patterns in groundwater quality. This enables optimization of water quality monitoring programs, well head protection measures and well field adaptation procedures.

The aim of this contribution is to present such a systematic approach to combine all relevant data into a clear typology of PSWFs and to illustrate its capabilities by applying it to all 206 PSWFs active in The Netherlands in 2008. The method departs from the hydrochemical facies analysis (HyFA) introduced by Stuyfzand (1990; 1999) and renamed to hydrochemical system analysis (HCSA) by Stuyfzand (2005) as a means to map and diagnose all major factors accounting for regional variations in hydrochemistry, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The HCSA should not be confused with the well known groundwater flow systems analysis introduced by Toth (1963) and Engelen and Jones (1986). A groundwater flow system may transport various hydrosomes and a hydrosome may even exist, as palaeogroundwater, without flow (Stuyfzand, 1999).

The methodology presented here is a modified version of the original HCSA, in order to better address the mapping of PSWFs, by defining the hydrochemical facies as a combination of indices for the age, redox and alkalinity of the pumped water. The origin of the water is to be determined by environmental tracers and geomorphological and potentiometric maps. Here, the HCSA is also used to create a chemical typology of PSWFs. Although presented for The Netherlands, the HCSA can be applied to any network of PSWFs worldwide.

4.2 Setting and methods

4.2.1 Hydrogeological setting of The Netherlands

The major fresh groundwater resources in The Netherlands are contained in unconsolidated sediments of Tertiary and Quaternary age, composed of alternating layers of marine, eolian, fluvial, paludal and glacial origin. A unique, moderately large fresh groundwater body in consolidated rock is observed in Cretaceous limestone in the south-east of the country (Fig 4.1). These major groundwater bodies are recharged in the Holocene coastal dunes, the northern, eastern, central and southern Pleistocene uplands, and the Cretaceous limestone hills (inset of Fig 4.1).

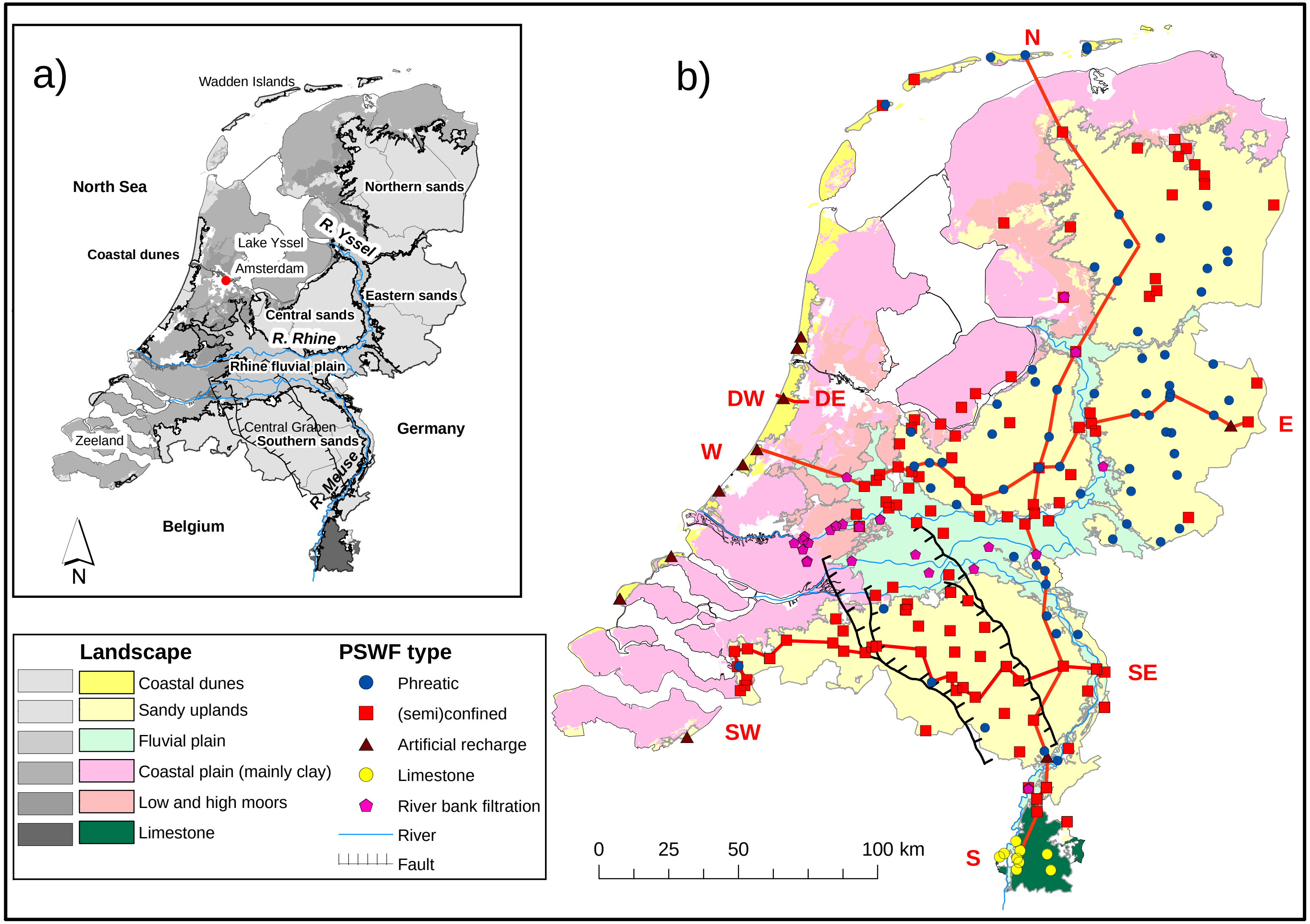


Fig 4.1: Location map of (a) The Netherlands and (b) the 206 PSWFs active in 2008, their hydrological type (according to Table 4.1) and the main recharge areas of groundwater pumped for public drinking water supply. The positions of the profiles depicted in Fig 4.2, 4 and 5 are indicated.

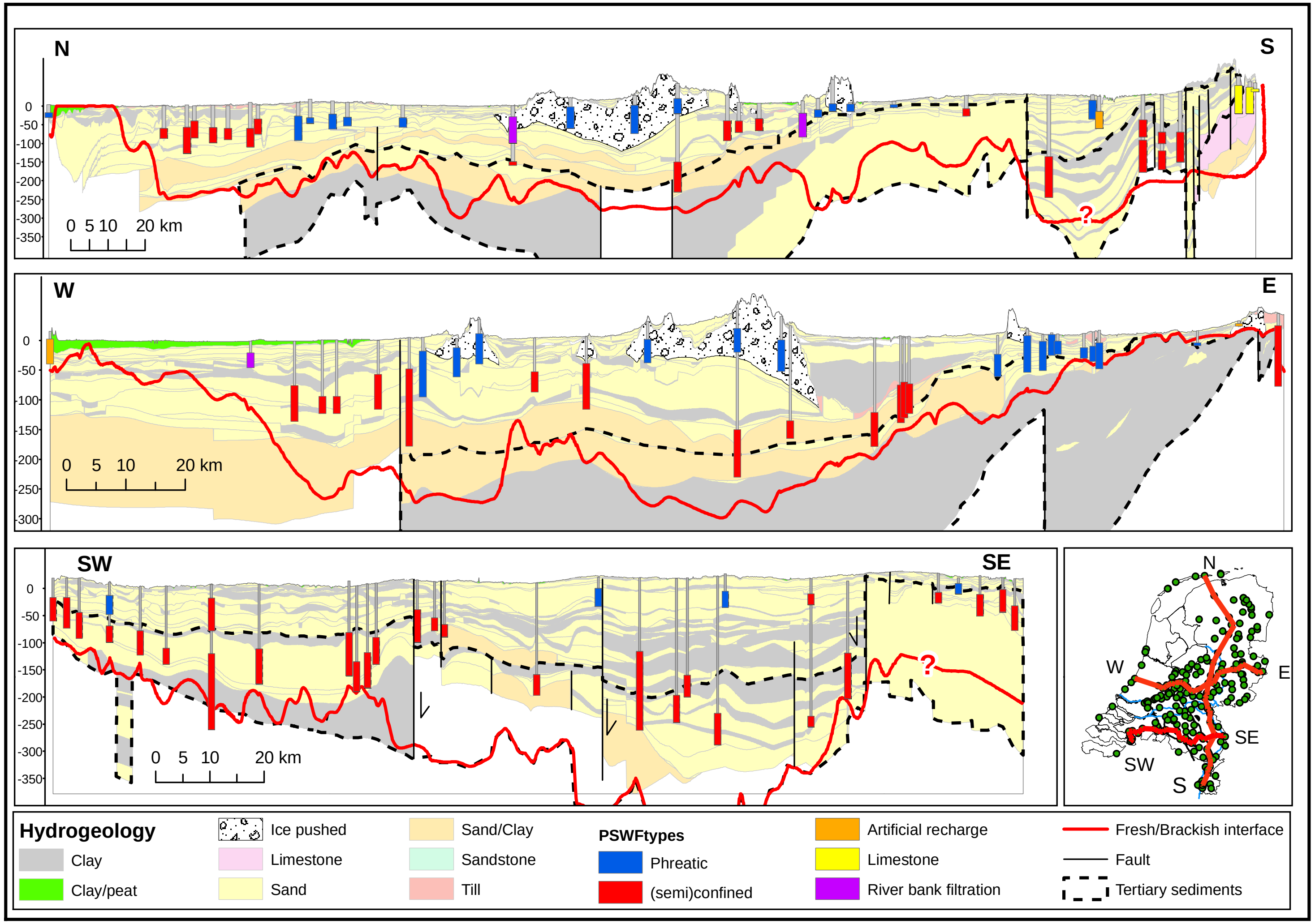


Fig 4.2: Hydrogeological cross sections over The Netherlands with the location and depth of abstraction (in m BSL) of PSWFs, in the directions N-S, W-E and SW-SE. PSWFs simplified to a single screen covering the entire depth of abstraction of individual pumping wells. The color of the well screen indicates the type of PSWF as defined in Table 4.1. The inset location map shows the position of the cross sections and active PSWFs in 2008. Hydrogeological data obtained from REGIS II.1 (Vernes and van Doorn, 2005).The fresh/brackish water interface (1000 mg/L Cl) is given by the red line (estimated by expert judgment around the question marks, due to lack of data). The dash line encloses sediments of Tertiary age.

The hydrogeological structure of The Netherlands and the depth to the fresh-brackish interface (here defined as 1000 mg Cl/L) are shown in three hydrogeological cross sections (Fig 4.2).

The fresh water resources in the coastal dune belt along the North Sea coast extend down to a maximum depth of 50-130 m BSL (below sea level). Those in the Pleistocene uplands reach depths of 100-250 m BSL in the Northern sands, 10-100 m BSL in the Eastern sands, 150-280 m BSL in the Central sands, and 100-500 m BSL in the Southern sands (Fig 4.2). The one in the Cretaceous hills has its base at 20-100 m BSL. The shallow position of the interface in the eastern uplands coincides with a shallow position of impermeable Tertiary clays. The deepest position of the interface in the southern uplands is tectonically determined by the Central Graben (Fig 4.1and 2), a deep tectonic graben structure in which coarse sands prevail down to a depth of 400-600 m BSL.

Groundwater resources have been supplemented by artificial recharge (AR) systems mainly in the coastal dunes and by river bank filtration (RBF) along the rivers Rhine and Meuse. Drinking water is also prepared by direct intake of surface water from these rivers and from Lake Yssel (19% of a total annual production of 1187 Mm^3 in 2004); those plants are not addressed in this study.

4.2.2 PSWFs and their data collection

The active 206 PSWFs in The Netherlands have initially been classified as indicated in Table 4.1, on the basis of the origin of the groundwater and the properties of the aquifer (Fig 4.1). Some further characteristics are mentioned in Table 4.1 as well. These data derive from the National Network of Public Supply Well Fields, an extensive database containing numerous properties of all Dutch PSWFs and the raw water quality and volumes pumped since 1898 (Mendizabal and Stuyfzand, 2009, Chapter 2). Most PSWFs consist of vertical PVC wells, with an average borehole diameter of around 60 cm (+/- 15 cm gravel pack) and an average screen length of 15-30 m. The use of PVC, which is advantageous because of insensitivity to corrosion, is quite unique worldwide as it was enhanced by the presence of a PVC manufacturer in The Netherlands (C. van Beek, KWR Watercycle Research Institute, personal communication, 2010). The wells within a PSWF are distributed following different geometrical patterns. PSWFs can either tap one or various aquifers, but every independent well is usually screened in a single aquifer. The water is mainly lifted by underwater pumps (positive displacement), but also by suction (both individually and in groups). Well technical details can be found in Makkink et al. (2000).

Table 4.1: Hydrological classification of PSWF-types in The Netherlands, with data referring to the year 2008. The number of PSWFs corresponds to the number of samples obtained during sampling (phreatic and confined parts of a PSWF pumping both aquifers are sampled separately and further considered as two PSWFs).

PSWF type	Sand and gravel				Limestone
	G		AR	RBF	
	Phreatic	(semi)confined			
Number of PSWFs	67	124	13	28	9
Mean raw water production per PSWF (Mm^3/y)[a]	2.7	3.7	14.8	2.6	2.6
Total amount of drinking water produced (Mm^3/y)[a]	182	441	193	74	23
% of total amount of drinking water produced[a]	20	48	21	8	3
Mean number of wells/collection points	10	12	124	18	7
Mean land surface (LS)(m ASL)	18	14	11	3	68
Mean abstraction level (m BLS)	26-61	83-135	11-29	21-55	24-74
Mean aquifer level (m BLS)	10-90	69-159	4-42	18-66	14-99
Mean aquifer thickness (m)	80	90	37	48	85
Mean depth to brackish water (m)	156	207	61	133	197
Age spectrum (y)	2-200	20-25000	0.1-0.3	1-50	2-200

[a] Water production in year 2004; G = fresh, autochthonous, actual groundwater; AR = artificially recharged water; RBF = river bank filtrate; LS = land surface; ASL = above sea level; BLS = below land surface.

During a national sampling campaign in the first trimester of 2008, all active PSWFs were sampled for chemical analysis. Samples were collected following the guidelines described in (Mendizabal and Stuyfzand, 2009, Chapter 2), in order to obtain the hydrochemically most representative samples for the well field. Samples were taken from faucets on the transport mains that discharge the water from various or all pumped wells, when these wells had been active for at least a couple of hours. In well fields where the storage capacity of the pumping station limited the number of wells that could simultaneously abstract water, the most representative selection of wells was switched on for obtaining a representative sample of the well field. In PSWFs tapping both phreatic and confined aquifers, two samples were collected, representative for each aquifer. Thus, a total of 241 samples was obtained from the 206 active PSWFs, including the ones obtained from a part of a PSWF.

Samples were analyzed for a wide package of parameters, including amongst others, macroparameters (cations, anions and nutrients), trace elements and the stable isotopes $\delta^{18}O$ and $\delta^{2}H$. Temperature, specific electrical conductivity (SEC), pH and dissolved oxygen were measured on site. Eh (electrode potential for redox state) was omitted because, unfortunately, it cannot be measured unambiguously in most natural waters (Appelo and Postma, 2005). On site determination of Eh runs into practical problems and is handicapped by unreliable results (Lindberg and Runnells, 1984) or difficulties in quantitative thermodynamic interpretation (Peiffer et al., 1992). Therefore, the suggestion by Stumm (1984) was followed to deduce the redox level from all redox sensitive main components of water. Samples for analysis of cations, PO_4, SiO_2 and trace elements were collected in 100 ml polypropylene bottles, after filtration in the field through a 0.45 µm millipore membrane filter, and acidified to pH<2 by addition of 0.7 ml HNO_3 Suprapur 65%. They were analyzed by inductively coupled plasma - mass and optical emission spectrometry (ICP-MS + ICP-OES). Samples for analysis of Cl, SO_4, HCO_3, NO_3, NO_2 and NH_4 were collected unfiltrated, in 100 ml polypropylene bottles and stored in a refrigerator for less than 3 days before analysis by spectrophotometry. Sulphide (HS^-) was not measured because of expected low concentration levels, expected problems with sample preservation and financial limitations. Samples for analysis of $\delta^{2}H$ and $\delta^{18}O$ were collected in 30 ml brown glass bottles without filtration and without any preservative. The bottles were fully filled and hermetically closed, to avoid atmospheric gas exchange. The samples were kept in the dark and at 4°C until analysis by mass spectrometry.

4.2.3 Hydrochemical system analysis

The hydrochemical system analysis (HCSA) developed by Stuyfzand (1990; 1999; 2006) yields a water typology and maps with the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome.

4.2.3.1 Hydrosomes

A hydrosome (also called hydrochemical groundwater system or groundwater body) is defined as a coherent, three-dimensional unit of groundwater with a specific origin. Its borders can be determined by geomorphological, land elevation and potentiometric maps and/or environmental tracers and geo-electrical soundings, provided enough observation wells are available.

A ‘hydrosome complex’ is composed of various adjacent hydrosomes with a very similar origin and recharge area. The complex members cannot be easily discerned from each other with environmental tracers. A ‘hydrosome type’ is characterized by a similar type of recharge water, like river water in case of RBF or AR hydrosomes. Hydrosomes belonging to the same type may have a totally different chemistry because of different source waters (for instance the Rhine River, Meuse River or Lake Yssel) and they do not need to be adjacent.

PSWFs may tap from different hydrosomes, mainly in the following cases: (1) AR and RBF well fields that inevitably also pump autochthonous groundwater; (2) salinizing well fields where minor quantities of, for instance intruding, recent seawater or upconing, saline palaeogroundwater mix with fresh groundwater; and (3) well fields abstracting from different aquifers in zones where different fresh water hydrosomes are interfingering. In these cases, for the sake of producing simple robust maps while using available hydrochemical and geo-electrical data, the boundaries for PSWF hydrosomes are defined as follows: (1) AR if >20% infiltrated, pretreated surface water; (2) RBF if >20% infiltrated river or lake water; and (3) autochthonous fresh groundwater if Cl < 1000 mg/L. The boundary of 1000 mg Cl/L is constrained to the availability of data.

In the following, an explanation of how to identify Rhine River bank filtrate and quantify its contribution to well fields in the Rhine fluvial plain by inorganic multitracing is given. The same environmental tracers are valid to identify pretreated Rhine water in AR systems. Meuse river water, either in AR or RBF systems, is more difficult to recognize and may require the simultaneous use of both inorganic tracers (other than those for Rhine water) and organic tracers (persistent micropollutants).

4.2.3.2 Identification and quantification of Rhine river bank filtrate

In Mendizabal and Stuyfzand (2009, Chapter 2) and Stuyfzand (1989a) Rhine RBF is identified amidst autochthonous groundwater in the Rhine fluvial plain of The Netherlands by means of δ^{18}O, Cl, the Cl/Br ratio and Mg. Of all the tracers, δ^{18}O is the best single tracer of Rhine RBF. Its use relies on the contrasting low δ^{18}O of Rhine water (on average δ^{18}O = -9.85 ‰; Mook 1968), as compared to autochthonous groundwater in The Netherlands with an average δ^{18}O of -7.6 ‰ (Stuyfzand, 1989a). The difference is related to the high contribution (ca. 70%) of the inland mountainous areas in Switzerland and Germany to the Rhine's discharge in The Netherlands, and the depletion of the heavier oxygen isotope δ^{18}O upon its preferential raining out from oceanic air when moving inland and uphill. δ^{18}O levels in autochthonous groundwater, however, may deviate from -7.6 ‰, especially when infiltrated during a glacial period (-9 ‰) or when infiltrated in swampy areas with high evaporation losses (-4 to -6 ‰), and due to differences in distance to the North Sea coastline (0.5 – 250 km), altitude (-7 to 321 m ASL) and/or land use. On the other hand, δ^{18}O levels in the Rhine may also deviate from -9.85 ‰ due to spatial and temporal variations. Higher values (up to -9.45 ‰) relate to smaller river branches with more evaporation and receiving exfiltrating groundwater. A recent trend of increasing δ^{18}O levels in the Rhine (-9.85 ‰ in the 1960-1970s, to -9.1 ‰ in the period 1997-2006) is noted as a result of climate change and various changes in water management in the Rhine catchment area (Stuyfzand, 2008b).

The second best tracer of Rhine RBF is the Cl/Br ratio. Rhine water has a significantly higher Cl/Br ratio (600-700, on a mg/L basis) than normal fresh and salt groundwater in The Netherlands (300). The anomaly is caused by the low Br content of salt waste from the salt mining industry in the Elzas region, which is discharged into the Moesel River, a tributary of the Rhine River. The ratio is less reliable than δ^{18}O, due to more complications. On the one hand, raised levels in autochthonous groundwater are encountered in urbanized areas, because of leaky sewer systems and/or road de-icing salt (Kelly, 2008). On the other hand, levels in RBF can be lower, mainly by the release of Br from organic rich muds that accumulate where river flow is reduced (Stuyfzand et al., 2005), and by abstraction of old RBF with a Cl/Br ratio ≤300 because it infiltrated before the salt mining industry started.

Other valid tracers for Rhine RBF, in addition to Cl and Mg, are molybdenum (Mo) and SEC, because their levels are significantly raised in the Rhine River due to various pollution inputs. Mo is present as the relatively mobile anion molybdate, which is sensitive to sorption and reductive precipitation. Thus, raised Mo concentrations are strong indicators of Rhine RBF, whereas low levels are less diagnostic because they may indicate either autochthonous groundwater or little-flushed, deep anoxic RBF systems. SEC, which is not conservative either, is a strong indicator of autochthonous groundwater from the central uplands, provided its value is very low (due to infiltration in the strongly leached sandy uplands) and the RBF is relatively young and polluted.

All these tracers can be individually used to quantify the percentage of RBF in the pumped water and the complications inherent to each of them can be reduced by combining them in a multitracing approach. The multitracing approach consists of the separate use of selected tracers, with due consideration of their boundary conditions, and averaging their results with a weighting factor W that depends on the tracer contrast (Table 4.2).

The percentage of RBF according to tracer *X* (*%RBF*$_X$) pumped by a PSWF is quantified by

$$\%RBF_X = 100\frac{C_M - C_G}{C_R - C_G} \tag{4.1}$$

where: C_M, = tracer concentration in sample, C_G = average concentration in autochthonous groundwater; C_R = tracer concentration in the river bank filtrate.

C_G and C_R are to be calculated as the average concentration of PSWFs (or preferably monitoring wells) that are a priori known (by potentiometric mapping, hydrological modeling and previous multitracing) to pump 100% groundwater and >90% RBF respectively. Concentrations in RBF are preferred among concentrations in river water, in order to take into account possible changes of non-conservative parameters during infiltration. Concentrations obtained for both end-member groups are listed in Table 4.2, together with their standard deviation (respectively S_G and S_R) and mean values of their recharge water.

The average %RBF resulting from multitracing (%RBF) then becomes:

$$\%RBF = \frac{\sum W_x \%RBF_x}{\sum W_X} \tag{4.2}$$

where the weighting factor W_X for tracer X is defined as follows:

$$W_X = \frac{\left\{ \left| C_R - C_G \right| \Big/ \sqrt{S_R S_G} \right\}_{TRACER\ X}}{Max \left\{ \left| C_R - C_G \right| \Big/ \sqrt{S_R S_G} \right\}_{ALL\ TRACERS}} \tag{4.3}$$

where S_R and S_G are the standard deviation of tracer X in, respectively, river bank filtrate and groundwater.

Eq. (4.3) is an intuitive equation, the results of which have been tested against the results of a student t-test. This test yielded a very similar ranking of tracers. However, the values obtained with Eq. (4.3) can be used directly, while those of the t-test can not. The absolute value of the difference in concentrations divided by the geometric mean of the standard deviations is a measure of the contrast of a tracer in both end members. The denominator is used to normalize the weights to values between 0 and 1. The weighting factor obtained is also a good indication of the performance of every independent tracer. Eq. (4.1) and (4.3) can be extended to account for situations where the raw water delivered by the PSWF is composed of a mixture of not just two waters (the usual case) but of three or more.

As already mentioned, every tracer has its own complications and its successful application is constrained to the conditions listed in Table 4.2. In all cases, waters should be younger than 5000-10000 years. All tracers except for $\delta^{18}O$ are constrained to the condition that (1) Rhine water should have infiltrated after ca. 1953, without contacting thick underwater muds; and (2) groundwater should be free of any significant urban, industrial or agricultural impact. Additionally, the % RBF calculated as based on Mo is always a minimum value, due to sorption and reductive precipitation.

4.2.3.3 Hydrochemical facies

Within a given hydrosome, the chemical composition of water varies in time and space, due to changes in recharge composition and in flow patterns, and due to chemical processes between water and its porous medium. Such variations in chemical character can be used to subdivide a hydrosome into characteristic zones or ‘hydrochemical facies’, a term introduced by Back (1960). The concept of geochemical facies and the use of geochemistry in determining groundwater origins, ages and flow systems is widely discussed by Glynn and Plummer (2005). In mapping a coastal aquifer system, Stuyfzand (1999) defined the facies on the basis of calcite saturation classes, and a redox, pollution and base exchange index. In mapping AR and RBF systems, Stuyfzand (2006) chose pH classes and the redox and pollution index. In the case of PSWFs, it is proposed to define the facies by combining age, redox and alkalinity indices.

Age index. The age index designates the possibility of relatively recent anthropogenic pollutants. It is derived from the percentage of ‘young’ groundwater (%Y) that infiltrated after 1953 (thus <55 years old in 2008): O (old) if %Y<5%, I (intermediate) if %Y = 5-50%, and Y (young) if %Y >50%. The year 1953 is chosen because it divides the ‘old’ period with negligible ^3H activities (at present) and relatively low pollution levels, from the ‘young’ period with relatively high ^3H activities and pollution levels. The %Y is obtained from the hydrological response curve of the well field as calculated by a calibrated groundwater model when available, or otherwise as approximated analytically in Mendizabal and Stuyfzand (2009, Chapter 2). Our method combines a calculation based on the depth to the water table, top and base of the well screen, average groundwater recharge rate and porosity, with a single tritium measurement of the raw water and the tritium record of the recharge water.

Redox index. The redox index determines the oxidation or reduction state of the groundwater and thereby the mobility of heavy metals and organic micropollutants (Chapelle, 2001; Stuyfzand, 1998a; Stuyfzand, 2006). Due to the practical problems of onsite measuring methods of Eh (Appelo and Postma, 2005) and difficulties in quantitative thermodynamic interpretation (Peiffer et al., 1992), the redox level was deduced, as suggested by Stumm (1984), from all redox sensitive main components of water, i.e. O_2, NO_3, SO_4, H_2S, Fe, Mn, NH_4 and CH_4 (Stuyfzand, 1993; 2006). Similar redox classifications were presented by Chapelle (2001), but these do not define the 'mixed' redox class, which is rather common in water samples obtained from PSWFs (10% of the samples obtained for this study), due to the local mixing of waters from different origins and redox environments, which occurs within the pumped well. The indicated redox clusters (sub)oxic (o), anoxic (a), deep anoxic (d) and mixed (m) are chosen here, because of limitations of data availability (especially regarding O_2, H_2S and CH_4) and the need to avoid maps that are too complex. The redox clusters (sub)oxic, anoxic and deep anoxic follow a logical succession within a hydrosome in the direction of groundwater flow. The redox cluster 'mixed' is assigned when samples contain antagonistic redox sensitive main components of water (like NO_3 and Fe^{2+}) above a specific threshold concentration (Table 4.3).

Alkalinity index. The alkalinity index is an excellent geochemical reaction progress variable, especially regarding the dissolution of carbonates and the oxidation of organic matter. It derives from alkalinity classes in a chemical watertype classification (Stuyfzand, 1989a). They are defined on a 2-log scale in meq (HCO_3+CO_3)/L: 0-0.5, 0.5-1, 1-2, 2-4 etc. Here, four alkalinity classes are defined: 0-1, 1-2, 2-4 and >4 meq/L (Table 4.4).

Facies coding. Each facies is denoted by a code consisting of the succession of the three indices. In order to reduce the number of facies codes on the map, those indices are not displayed which are considered 'standard state' of the hydrochemical system. The standard state is: intermediate age, anoxic, and high alkalinity. For instance, young, anoxic, low alkalinity groundwater is coded as Y2.

Table 4.2: Tracer concentrations used in Eq. (4.1) for quantifying the percentage of river bank filtrate pumped by PSWFs in the Rhine fluvial plain. W = weight assigned to each tracer; C_P = tracer concentration in precipitation. C_G = tracer concentration in autochthonous groundwater; C_F = tracer concentration in Rhine River water; C_R = tracer concentration in RBF. S_x = standard deviation of X. The number of PSWFs used to calculate average values of C_G and C_R are given in brackets.

Tracer application				Groundwater (100%)			Rhine water (>90%)		
Tracer	Units	Condition [a]	W	C_P	C_G (13)	S_G	C_F	C_R (12)	S_R
Cl	mg/L	B	1.00	5	13	4	120	105	7
Mo	µg/L	C	0.50	<0.1	0.2	0.1	1.5	1.3	0.2
$\delta^{18}O$	‰	A	0.47	-7.6	-7.1	0.5	-9.85	-9.6	0.2
Mg	mg/L	B	0.33	0.3	5	2	11	11	1
Cl/Br ratio	mg/L	B	0.29	293	292	48	650	485	35
EC	µS/cm 20°C	B	0.29	31	273	123	700	749	84
B	µg/L	B	0.23	<5	21	22	80	80	11

[a] Condition: A: waters should be younger than 5000-10000 years (condition fulfilled in all cases); B: as A, + Rhine water should have infiltrated after ca. 1953 without contacting thick underwater muds, and + groundwater should be without significant urban, industrial or agricultural impacts; C: as B, + calculated $\%RBF_{Mo}$ is always a minimum value.

4.3 Results

In The Netherlands, the spatial distribution of hydrosomes has been investigated by Engelen (1981), Stuyfzand (1989a; 1993), Griffioen and van der Aa (2002) and Beusen et al. (2008). From their work, the seven hydrosome complexes and two hydrosome types listed in Table 4.5 are considered relevant for PSWFs. All PSWFs are abstracting groundwater from these nine hydrosomes. The predominant hydrosome is indicated for each PSWF in Fig 4.3, together with the score for the three facies indices as derived from their water analysis.

Based on these data, three-dimensional maps of groundwater bodies and hydrochemical facies were produced on a national scale. Fig 4.4 shows the extension of hydrosomes with depth and the hydrochemical facies within every hydrosome in three cross sections over the country. The fresh-brackish interface (for practical reasons defined at

1000 mg Cl/L) was used as the lower boundary of hydrosome mapping. Brackish and salt hydrosomes are thus not further differentiated here, nor are those fresh hydrosomes that lack any abstraction by a PSWF.

Transboundary hydrosomes occur along the eastern and southern border of The Netherlands, with recharge areas in Germany and Belgium respectively. Those from Germany are incorporated into the adjacent Dutch hydrosome complex because of similar quality. Those from Flanders (northern Belgium) constitute a separate hydrosome due to clear quality deviations resulting from lithological differences of the outcropping Tertiary sediments.

Table 4.6 summarizes exploitation data for each hydrosome in 2008, regarding exclusively PSWFs.

Table 4.3: Practical criteria for the determination of the redox index –slightly modified after Stuyfzand (1993). Concentrations in mg/L.

Level	Environment	Criteria (mg/L)						
		O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S [a]	CH_4
0	Oxic	$O_2 \geq 0.9\ (O_2)_{sat}$		< 0.1	< 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.1
1	Penoxic (O_2 -reducing)	$1 \leq O_2 < 0.9\ (O_2)_{sat}$		< 0.1	< 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.1
2	Suboxic (NO_3 -red)	< 1	≥ 1	< 0.1	< 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.1
3	Transition (Mn -red)	< 0.5	< 1	≥ 0.1	< 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.1
4	Iron reducing	< 0.5	< 0.5		≥ 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.1
5	Sulphate reducing	< 0.5	< 0.5			A	yes	< 1
6	Methanogenic	< 0.5	< 0.5			B		≥ 1

Redox clusters:		Level	O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S [a]	CH_4
o	(sub)oxic	0-2	≥ 1 or	≥ 1	< 0.1	< 0.1		no	< 0.1
a	Anoxic	3-4	< 0.5	< 0.5		≥ 0.1	$\geq 0.9\ (SO_4)_O$	no	< 0.25
d	Deep anoxic	5-6	< 0.5	< 0.5			C	yes or	≥0.5
m	Mixed [b]	M	≥ 1 or	≥ 1	≥ 0.15 or ≥ 0.15			or	>0.1

[a] yes/no = yes/no clear H_2S-smell in field. [b] sample composed of a mix of water from different redox environments.
$[O_2]_{sat.} = 14.594–0.4\ t+0.0085\ t^2–97x10^{-6}\ t^3–10^{-5}\ (16.35+0.008\ t^2–5.32/t)Cl$, with t = temperature in ℃ and Cl in mg /L;
$A = 0.1[SO_4]_o < SO_4 < 0.9[SO_4]_o$, if $Cl \leq 300$ mg/L and else $0.5\ [SO_4]_o \leq SO_4 < 0.9[SO_4]_o$;
$B = SO_4 \leq 0.1[SO_4]_o$ or $SO_4 \leq 3$, if $Cl \leq 300$ mg/L or $SO_4 < 0.5\ [SO_4]_o$ if Cl>300 mg/L;
$C = SO_4 \leq 0.9[SO_4]_o$ or $SO_4 \leq 3$, if $Cl \leq 300$ mg/L; $[SO_4]_o$ = original SO_4 concentration in mg/L.

Table 4.4: Hydrochemical facies descriptors with their code and value. Standard state facies in italics. If standard state, then the facies code is omitted from the map for simplicity.

Index	Facies code	Facies descriptor	value	Standard state
Age	Y	Young	>50 %Y	no
	I	*Intermediate*	*5-50 %Y*	*yes*
	O	Old	<5 %Y	no
Redox	o	(sub)oxic	0-2	no
	a	*Anoxic*	*3-4*	*yes*
	d	Deep anoxic	5-6	no
	m	Mixed @	0-6	no
Alkalinity	1	Very low	0-1 meq/L	no
	2	Low	1-2 meq/L	no
	3	Moderate	2-4 meq/L	no
	4	*High*	*>4 meq/L*	*yes*

Well field managers should consider the individual quality of PSWFs in terms of the contributing hydrosome(s) and the hydrochemical facies within its catchment area (see section *Discussion*). In order to understand structural differences between well field types or hydrosomes, and for a compact reporting to water authorities, it does make sense to also show, in Table 4.7, the average water quality of the nine hydrosomes as pumped by PSWFs. In order to better differentiate between hydrosomes, some of them have been subdivided: hydrosomes I and U on the basis of a different origin of the infiltrating surface water – respectively Rhine (r), Meuse (m), Yssel (y) and other (o); and hydrosomes C, N and S on the basis of a different alkalinity and redox facies in deep PSWFs (alkalinity index 3 or 4 and redox index “a” or “d”) and shallow PSWFs were differentiated otherwise. The nine hydrosomes are briefly described in the following, in alphabetical order.

4.3.1 The Central hydrosome complex (C)

The largest and highest ice-pushed sandy hill area in The Netherlands constitutes the main recharge area of this hydrosome. The upper layers (roughly down to 50-70 m BSL) contain extremely low contents of reactive phases like calcite, pyrite or organic matter. This, in combination with a land use dominated by nature reserves, results in a high quality of the pumped water, which most frequently shows a young, (sub)oxic, low alkalinity facies (Fig 4.4; N-S and W-E). The composition is unique in The Netherlands with its low TDS, total hardness, alkalinity and concentrations of K, B, Ba, F and Li. Total hardness and alkalinity are often below drinking water standards of respectively 1 mmol/L and 60 mg/L (Water Supply Act, 2001). The lack of stronger acidification phenomena in most PSWFs is due to the slow advance of young, more acid water thanks to a relatively thick unsaturated zone (5-38 m) and low recharge rates due to the predominance of pine woods. Therefore, only a few PSWFs present raised concentrations of Al and lanthanides by dissolution of Al-silicate minerals at lowered pH (Table 4.7).

In the deeper, more reactive parts of the aquifer system, composed of calcareous marine sediments of Tertiary to early Pleistocene age, the dominant facies changes into old, deep anoxic water with high alkalinity.

4.3.2 The Coastal Dune hydrosome complex (D)

This hydrosome complex extends all along the North Sea coast of The Netherlands, including the Islands of Zeeland, the coastal mainland and the Wadden Islands. The fresh water lenses, up to 130 m BSL, are surrounded by intruded North Sea water and relict Holocene transgression waters (Stuyfzand, 1993). Numerous PSWFs pumped dune water during the late nineteenth and the twentieth centuries, but most of them have been closed down, or have been transformed in the 1950s into AR systems, due to severe salinization. Today, the only PSWFs abstracting 100% dune water are situated in the Wadden Islands. They mainly consist of nature reserves and yield groundwater of high quality, characterized by calcite equilibrium (high pH, Ca and HCO_3), high sea spray inputs (Cl, Br, Na, K, Mg and SO_4) and cation exchange due to a historical expansion of the fresh water lens (high K and Mg). They present the highest SiO_2 concentrations of all PSWFs, due to the leaching of biogenic opal (marine diatoms) from Holocene marine, fine-grained deposits below the dunes. All PSWFs are anoxic to deep anoxic and belong to alkalinity groups 3-4.

4.3.3 The Eastern hydrosome complex (E)

A shallow, calcareous and pyritiferous sandy aquifer on top of impervious Tertiary clay layers accommodates this thin hydrosome complex. PSWFs mainly pump young groundwater which on several sites is strongly affected by agricultural activities (high NO_3 SO_4, Cl and K). There, the high NO_3 loads and declining water tables triggered the oxidation of pyrite, which is reflected in the raised concentrations of SO_4, Fe, As, Co, Ni and Zn. The relatively high inputs of acidity via pyrite oxidation and atmospheric deposition are largely buffered by calcite dissolution. Consequently, pH, total hardness and HCO_3 are relatively high, necessitating the addition of an expensive water softening step to the purification system. In the central parts, groundwater is horizontally mixed with shallow oligomineral water (water with low TDS) from small ice-pushed ridges, poor in reactive phases such as calcite, pyrite or organic matter. This evening out of different qualities makes the averaged data in Table 4.7 less informative than the facies maps in Fig 4.3 and 4. The main facies within the Eastern hydrosome is, however, Ya4 (Fig 4.3).

Table 4.5: Hydrosome complexes (HC) and types (HT) in The Netherlands and their main characteristics.

Code	Hydrosome	Origin[a]	Source[b]	Aquifer material[c]	Sediment age[d]	Depositional environment[e]	% confined
C	Central sands (HC)	P	G	S	P	G / F	25
D	Coastal dunes (HC)	P	G	S	H	E / M	70
E	Eastern sands (HC)	P	G	S	P	G / F	0
F	Flanders (HC)	P	G*	S	T	M / F	100
I	Artificial recharge (HT)	R	AR	S	H	E / M	0
L	Limestone (HC)	P	G	L	C	L	20
N	Northern sands (HC)	P	G	S	P	G / F	90
S	Southern sands (HC)	P	G	S	P	F	30
U	River bank filtration (HT)	R	RBF	S	P	F	60

[a] Origin: P: Precipitation; R: River (or lake); [b] Source: G: Autochthonous groundwater <1000 years old, with local recharge; G*: Autochthonous groundwater >1000 years old; AR: Artificially recharged water; RBF: river bank filtrate; [c] Aquifer material: S: Sand and gravel; L: Limestone; [d] Sediment age: P: Pleistocene (+Tertiary); H: Holocene (+Pleistocene); T: Tertiary; C: Late Cretaceous; [e] Depositional environment: E: Eolian; F: Fluvial; G: Glacial; L: Lagunal; M: Marine.

4.3.4 The Flanders hydrosome complex (F)

In the south of The Netherlands, PSWFs abstract water from two different systems (Fig 4.4; N-S and SW-SE): deep, confined groundwater of Tertiary age, either infiltrated in Flanders (Belgium) or in the Dutch province of Brabant, and younger groundwater systems of local recharge belonging to the Southern hydrosome complex (discussed in the following).

PSWFs recharged in Flanders have been identified by their deep anoxic character (SO_4<1 mg/L), their age (0% water younger than 55 years), their low Cl concentration (about 6 mg/L when excluding PSWFs with salinization due to upconing) and their low Cl/Br ratio. PSWFs of this group abstract deep anoxic water from 50 to 250 m depth, with an estimated age in the order of 1,000 to 10,000 years. The normal modern δ^2H and δ^{18}O levels indicate that the water must have infiltrated after the last glacial period, whereas low ^{14}C activities (10-30 percent modern carbon (pmc); data not shown) point to an age >1000 years. Some of them might pump groundwater recharged in Germany or Limburg (in the southern part of The Netherlands). The presence of glauconite and apatite in several aquifer layers is suspected to be responsible for relatively high As, B and Li concentrations. Some PSWFs show salinization phenomena (raised concentrations of Cl, Br and Na), due to upconing of connate salt water from fine-grained marine deposits of early Pleistocene and late Tertiary age (Stuyfzand and Stuurman, 2008). The Cl/Br ratio is relatively low, especially in the samples without salinization, probably due to the more inland position of the recharge area which is known to reduce this ratio (Davis et al., 2004). All PSWFs in the Flanders hydrosome are old, deep anoxic waters of high alkalinity (Facies Od4).

4.3.5 Artificially recharged hydrosomes (I)

Most “I” hydrosomes are situated in the coastal dunes, in nature reserves. The chemical composition of every I hydrosome strongly reflects the quality of the pretreated surface water used for its artificial recharge. This means that there are large differences between the hydrosomes recharged by water from the Rhine River, Lake Yssel, Meuse River and a small brook in the south-west. On average, they yield groundwater in equilibrium with calcite, with high concentrations of Cl, Br, SO_4, Na, K, Ca, Mg, F, Mo and specific organic micropollutants (data not shown), and low concentrations of SiO_2. The infiltrated Rhine River water can be easily recognized in the coastal dunes by combination of its low δ^{18}O content and high Cl/Br ratio (Stuyfzand, 2008b). The tracer contrast between these water types is quite different from the one between Rhine river bank filtrate and autochthonous groundwater in the Rhine fluvial plain (Table 4.2).

Most I hydrosomes belong to alkalinity group 3 and present a (sub)oxic or mixed redox index. The mixed redox is due to the mixing of anoxic with (sub)oxic infiltrate and the admixing of both deep anoxic and (sub)oxic autochthonous groundwater in the recovery system, which occurs within the pumped well.

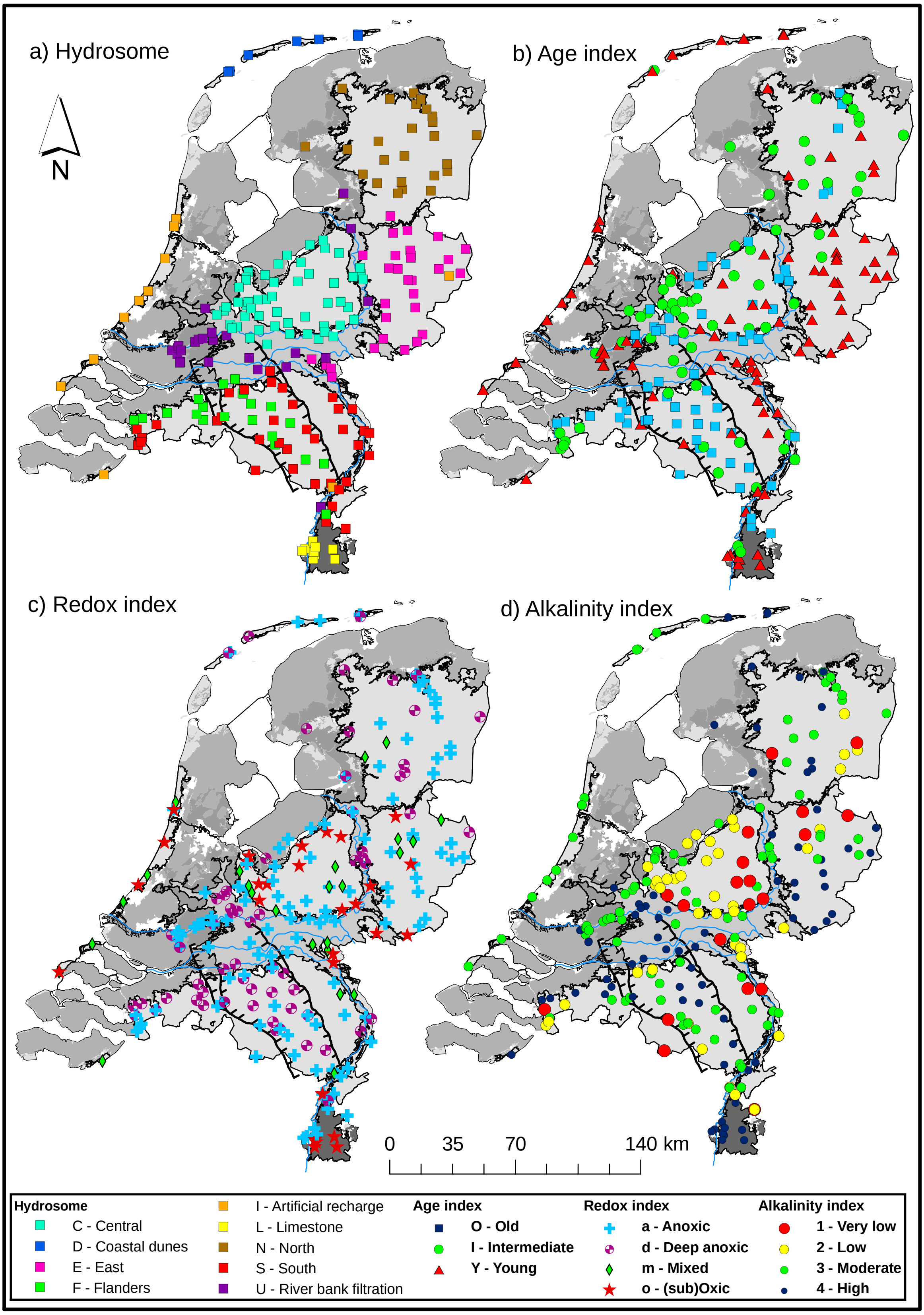


Fig 4.3: Spatial distribution of (a) hydrosomes assigned to all PSWFs active in The Netherlands in 2008 and the three hydrochemical facies indices – (b) age, (c) redox, (d) alkalinity.

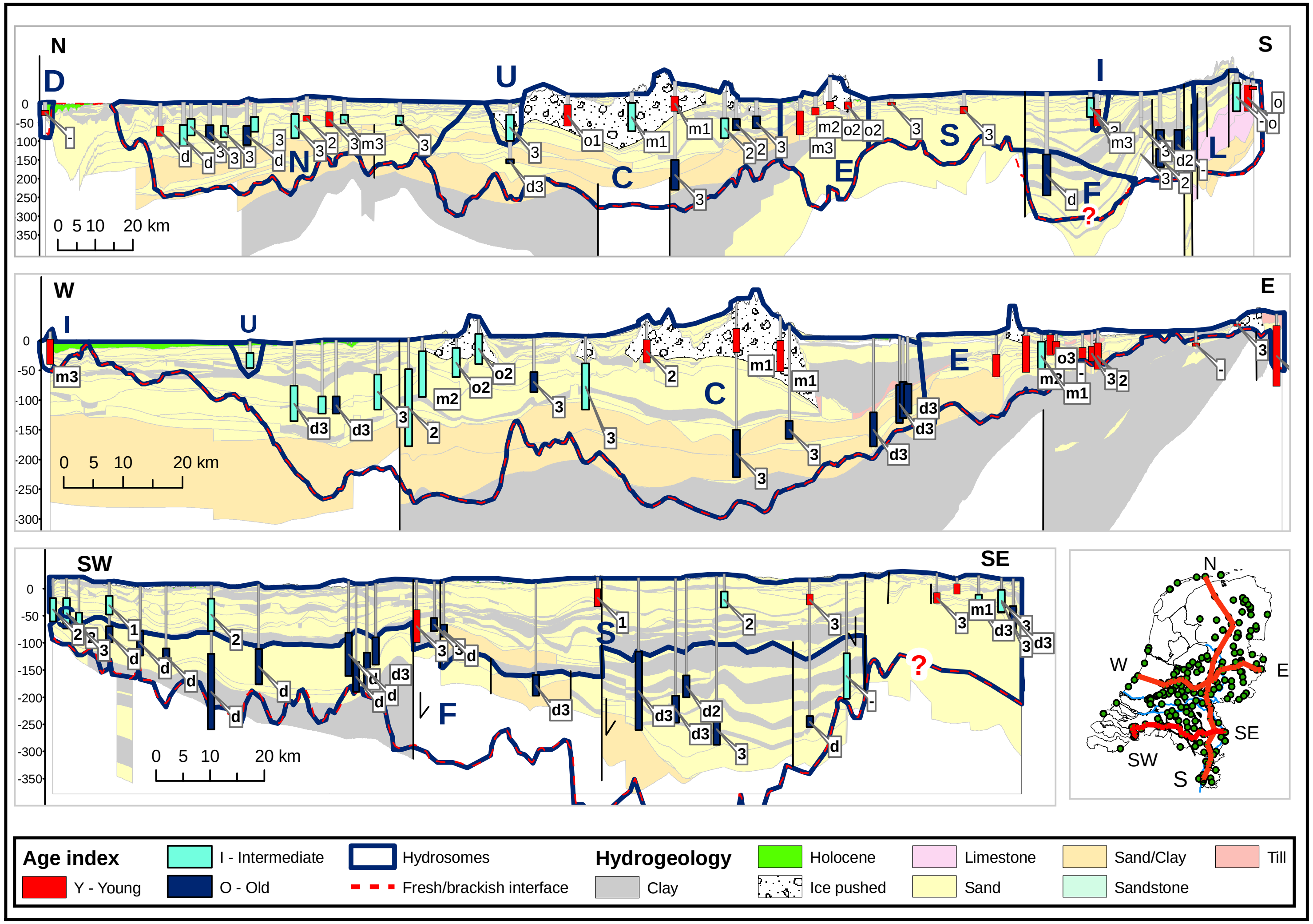


Fig 4.4: Hydrogeological cross sections N-S, W-E and SW-SE over The Netherlands with the spatial distribution of hydrosomes (groundwater bodies) and well screen position of public supply well fields (PSWFs). The color of the well screen indicates the age index. The labels show the hydrochemical facies assigned to each PSWF (legend in Table 4.5). The inset location map shows the location of the cross sections and all active PSWFs in 2008. Hydrogeological data obtained from REGIS II.1 (Vernes and van Doorn, 2005).

Table 4.6: Average exploitation data for the nine hydrosomes in The Netherlands in 2008, regarding exclusively PSWFs.

Hydrosome	C	D	E	F	L	N	S	I	U
Number of PSWFs	55	7	30	25	9	27	44	13	31
Mean water production per PSWF (Mm3/y)[a]	3.3	0.1	2.6	4.6	2.6	5.1	2.8	14.8	2.5
Total drinking water produced (Mm3/y)[a]	177	1	79	110	23	126	125	193	79
% of total drinking water produced[a]	19	0.1	9	12	3	14	14	21	9
Mean number of wells/collection points	9	10	11	13	7	18	9	124	18
Mean land surface (LS) (m ASL)	14	4	22	12	68	8	23	11	3
Mean abstraction level (m BLS)	64-114	21-33	24-54	131-195	24-74	53-94	64-114	11-29	26-58
Mean aquifer Level (m BLS)	44-153	10-36	7-74	121-215	14-99	33-134	56-127	4-42	23-69
Mean aquifer thickness (m)	110	27	67	94	85	101	71	37	45
Mean depth to brackish water (m)	222	59	100	236	197	164	210	61	139
% of PSWFs yielding specific age:									
Young water	16	86	93	0	78	22	20	100	55
Intermediate age water	40	14	7	0	22	56	32	0	35
Old water	44	0	0	100	0	22	43	0	10
% of PSWFs yielding specific redox:									
(sub)oxic	20	0	20	0	56	0	0	31	10
Anoxic	42	57	53	0	44	56	84	15	74
Deep anoxic	25	43	7	100	0	37	11	0	13
Mixed	13	0	20	0	0	7	5	54	3
% of PSWFs yielding specific alkalinity:									
Very low alkalinity	15	0	13	0	0	7	16	0	0
Low alkalinity	35	0	20	8	0	15	25	0	0
Moderate alkalinity	40	57	17	32	0	41	36	92	55
High alkalinity	11	43	50	60	100	37	23	8	45

[a] Water production in year 2004; LS = land surface; ASL = above sea level; BLS = below land surface

4.3.6 The Limestone hydrosome complex (L)

This hydrosome complex corresponds to a 100 m thick layer of karstified Cretaceous limestone covered by Pleistocene loess and fluvial gravels and underlain by Carboniferous shale (Fig 4.4; N-S and SW-SE). The groundwater has the highest concentrations of Ca and HCO_3, and the highest SEC, TDS and total hardness of all (Table 4.7). This obviously relates to the dissolution of calcite in an environment with high CO_2 pressures (in loess) and a high atmospheric deposition of acidifying SO_2 due to proximity of major industrial emission centers in Germany (Ruhr Gebiet), Belgium (Liege) and The Netherlands (DSM). Also highest are the NO_3 concentrations, which derive from agricultural immissions that meet insufficient reduction capacity in the fast circulating upper parts of the limestone aquifer. The concentrations of SO_4, Mg, F, Li, Mo and Sr as well as the Cl/Br ratio are remarkably high as compared to the other hydrosomes without AR and RBF. This may relate to high atmospheric inputs (SO_4 and F), high geochemical inputs (Mg, F and Sr from limestone), and contributions from urbanized areas or infiltrating surface waters (Li, Mo and Cl/Br ratio). The limestone hydrosome presents the facies Y and Yo (Fig 4.3).

4.3.7 The Northern hydrosome complex (N)

The Northern hydrosome complex is recharged on a sandy plateau largely composed of glacial till with few isolated terminal moraines and small ice-pushed hills, and with wide-spread occurrences of thin eolian cover sands. Originally much high-moor peat formed in areas where the glacial till aquitard hindered dewatering, but little peat remained after excavation for six centuries. The deeper groundwaters (older than 100 years) still present some characteristics of groundwater infiltrated through peat soils and with effects of open-water evaporation, showing high Fe, NH_4 and PO_4 concentrations and high δ^2H and $\delta^{18}O$ levels (column N_d in Table 4.7).

Table 4.7: Median water quality of PSWFs belonging to the nine hydrosomes defined.

		Recharged by local rain water										Recharged by river water						
Hydrosome [a]		C_d	C_s	D	E	F	L	N_d	N_s	S_d	S_s	I_m	I_r	I_y	I_o	U_m	U_r	U_o
Number of PSWFs		23	29	7	31	25	9	20	7	27	19	4	4	3	1	2	28	2
EC	μS/cm	324	196	556	526	392	774	471	294	455	252	482	613	700	616	525	701	730
pH	-	7.8	7.4	8.0	7.1	7.4	7.1	6.9	6.5	7.1	6.5	7.7	7.6	7.8	7.3	6.5	7.3	7.1
Temp	^oC	12.0	10.0	9.5	10.5	12.3	11.5	10.7	10.2	11.8	11.2	12.7	10.4		10.7	11.7	12.0	11.5
Cl	mg/L	12	15	77	28	9	26	27	24	18	11	42	81	105	33	34	100	64
HCO_3	mg/L	161	85	242	222	255	367	248	92	241	99	170	179	167	273	193	229	358
NO_3	mg/L	0.0	4	0	0	0	16	0	0.1	0	0	5	6	3.0	2.2	14	0	0.0
SO_4	mg/L	1	17	7	63	0.3	54	1	25	11	24	53	53	61	79	71	45	15
Ca	mg/L	50	34	76	90	65	136	78	37	78	38	70	79	73	114	89	83	109
Mg	mg/L	5	3	12	8	6	14	7	4	9	4	8	11	11	7	8	11	12
Na	mg/L	13	10	42	18	11	9	18	14	18	8	32	46	68	20	23	54	34
K	mg/L	1.3	1.0	3.5	2.4	3.7	2.3	1.8	1.7	3.8	1.8	5.9	5.0	5.5	12.4	3.9	4.9	3.7
Fe	mg/L	0.72	0.04	0.30	0.51	2.14	0.08	6.98	8.54	5.29	7.40	0.18	0.09	0.22	0.50	0.02	2.57	9.40
Mn	mg/L	0.09	0.04	0.10	0.19	0.07	0.00	0.25	0.35	0.18	0.10	0.07	0.03	0.07	0.32	0.00	0.52	0.47
NH_4	mg/L	0.3	0.01	0.5	0.2	0.6	0.0	0.4	0.1	0.5	0.1	0.11	0.1	0.1	0.32	0	1	3.2
PO_4	mg/L	0.5	0.2	1	0.3	0.8	0.2	1.0	0.8	0.9	0.4	0.3	0	0.2	0.1	0.1	0.9	1.8
SiO_2	mg/L	18	14	33	15	21	27	26	19	20	18	7	7	8	11	11	16	20
Al	μg/L	1	1	3	1	1	1	1	1	1	2	0.5	1	0.5	2	0.5	2	4
As	μg/L	0.3	1.2	0.3	0.9	1.3	0.3	0.3	1.3	0.9	0.3	3.4	2.8	1.5	1	0.3	1.3	1.5
B	μg/L	17	6	49	15	39	13	15	10	53	7	52	51	70	52	43	77	38
Ba	μg/L	18	10	2	42	12	40	58	42	51	39	50	23	91	82	81	92	99
Br	μg/L	44	44	222	62	32	50	71	51	52	36	118	192	179	144	87	201	160
Co	μg/L	0.02	0.0	0.02	0.03	0.01	0.02	0.0	0.9	0.0	0.0	0.35	0.20	0.2	0.52	0.07	0.08	0.11
Cu	μg/L	0.7	2.1	0.2	0.9	0.2	0.9	0.2	0.3	0.3	0.3	2.0	1.5	1.2	18.6	1.5	1.1	0.7
F [b]	μg/L	50	70	140	70	110	170	70	80	100	65	295	120	120	210		117	136
Li	μg/L	3.0	1.7	7.4	3.8	8.3	11.5	5.5	3.9	13.4	5.4	6.2	10.0	11.7	4.1	5.0	8.5	4.6
Mo	μg/L	0.2	0.2	0.2	0.2	0.1	0.8	0.1	0.1	0.1	0.1	2.0	1.7	1.6	1.0	0.1	0.8	0.2
Ni	μg/L	0	0	0.1	0.7	0.1	0.7	0	1.8	0.2	0.9	2.1	1.3	0.7	3.9	0.6	0.8	0
Sr	μg/L	165	92	352	261	247	379	210	107	344	114	272	445	427	419	191	456	359
Zn	μg/L	3	7	0.9	5	2	2	3	5	5	8	6	15	45	14	5	2	2
$\delta^{18}O$	$^o/_{oo}$	-7.2	-7.5	-6.7	-7.1	-6.9	-7.7	-6.0	-6.8	-6.9	-7.2	-6.2	-9.2[c]	-6.8	-6.4	-6.8	-9.4	-6.0
δ^2H	$^o/_{oo}$	-49	-48	-47	-47	-46	-52	-41	-46	-46	-47	-42	-64	-49	-45	-45	-66	-43
∑Lan	mg/L	0.08	0.08	0.09	0.1	0.08	0.07	0.1	0.07	0.09	0.18	0.12	0.12	0.11	0.21	0.11	0.11	0.22
Cl/Br	-	292	345	308	438	278	466	323	410	329	298	358	425	559	229	387	464	394
$SI_{calcite}$	-	0.1	-0.7	0.4	-0.1	0.1	0.1	-0.5	-1.6	-0.3	-1.5	0.1	0.1	0.2	0.1	-0.9	0	0.0
BEX	meq/L	0.58	0.26	1.05	0.61	0.81	0.89	0.44	0.37	0.92	0.43	0.92	0.595	0.81	0.77	0.75	0.6	0.61
TDS	mg/L	307	171	439	460	378	653	412	222	432	180	391	460	493	542	435	518	612
TH	mmol/L	1.4	1.0	2.4	2.6	2.0	3.9	2.2	1.1	2.3	1.1	2.1	2.4	2.3	3.1	2.5	2.5	3.2
TIC	mmol/L	2.9	1.5	4.0	4.7	4.6	7.4	5.7	2	4.6	2	2.9	3.1	2.8	5.0	5.5	4.2	7.2

[a] Hydrosomes subdivided in: d = deep; s = shallow; r = Rhine; m = Meuse; y = Yssel; o = other river;

[b] measured in 1992;

[c] Average value for infiltrated Rhine water deriving from tributary Lek;

ΣLan = sum of all lanthanides; SIcalcite = saturation index for calcite; BEX = base exchange index calculated as the meq-sum of the typically marine cations Na, K and Mg, corrected for a contribution of sea salt according to BEX=Na+K+Mg-1.0716 Cl, after Stuyfzand (1993)); TDS = total dissolved solids; TH = total hardness (Ca+Mg+Sr); TIC = total inorganic carbon (CO2+HCO3+CO3).

The low $CaCO_3$ contents of the upper sediments are responsible for the relatively low concentrations of Ca, Sr and HCO_3 and low pH and $SI_{calcite}$ in the shallow phreatic PSWFs (column N_s in Table 4.7). Most PSWFs deliver anoxic to deep anoxic water of Intermediate to old age.

4.3.8 The Southern hydrosome complex (S)

The Southern hydrosome complex comprises PSWFs pumping from Pleistocene and Tertiary sandy aquifers overlain by eolian fine sands (Fig 4.4). The spatial variability in reactive minerals of the locally deposited sediments yields a large heterogeneity within this hydrosome, which displays most of the discerned hydrochemical facies. The Southern hydrosome is divided in two groups in Table 4.7. Group S_d corresponds to PSWFs pumping deep confined Tertiary aquifers in the Central Graben (Fig 4.1 and Fig 4.4; N-S and W-E) that deliver old, unpolluted water of good quality, similar to the Flanders hydrosome. They also present high As, B and Li concentrations possibly released from glauconite, but they differ in higher Ba, Br, Cl, Sr, SO_4 and Zn concentrations. Group S_s corresponds to shallower PSWFs, some of them characterized by a low alkalinity (groups 1 and 2 in Fig 4.3). The ones with alkalinity <0.5 meq/L show high concentrations of Al, due to the dissolution of aluminum hydroxides. In these acidic environments trace elements are also mobilized, notably Be, Cd, Co, Cu, Lu, Y and Zn, together with all lanthanides. Most PSWFs to the east also present signs of pyrite oxidation, analogous to the Eastern hydrosome.

4.3.9 River bank filtrate hydrosomes (U)

This hydrosome type is composed of bank filtrate from the Rhine River (28 PSWFs), the Meuse River (2 PWSFs) and two lakes. The major occurrences are located in the western part of the Rhine fluvial plain (most PSWFs in the eastern part pump autochthonous groundwater because the Rhine drains the area there). Water quality is, like in the case of artificial recharge, mainly dictated by the influent river (or lake), which shows an increased pollution record until the 1970s, when sanitation measures in the drainage basins started to have significant effects (RIWA, 2002).

The hydrosomes composed of Rhine River bank filtrate present the highest B and Ba concentrations of all hydrosomes, and they contain more Cl, Br, Na, Mo and Sr but less $\delta^{18}O$ than the river bank filtrates from the Meuse and lakes. This is explained by a higher pollution load with B, Ba and Mo, the discharge of Br depleted salt waste into the Moesel River by salt mines in the Elzas area, and a large contribution of snow melt from the Alps.

The different types of RBF nicely range from (sub)oxic (Meuse) to (deep) anoxic (Rhine) to deep anoxic (lakes) in the global direction of surface water flow (Stuyfzand et al., 2006): a steep river gradient and coarse gravels along the Meuse are more conducive to maintaining (sub)oxic aquifer conditions, than where flow is more reduced and the sediments are finer-grained.

All PSWFs of the river bank filtrate hydrosome present moderate to high alkalinity. Most of them are anoxic, but all the redox classes are represented.

4.4 Discussion

4.4.1 Vulnerability of PSWFs

The HCSA offers direct insight into the vulnerability of PSWFs towards specific fluvial pollution hazards (if the hydrosome type is either ‘artificial recharge’ or ‘river bank filtration’), and towards those environmental pollution hazards that strongly depend on the three indices used to define the hydrochemical facies. How these indices relate to vulnerability is explained in the following.

The age index is a good indicator of vulnerability towards all hazardous compounds released at the surface. PSWFs delivering ‘young’ water are potentially vulnerable, while PSWFs delivering ‘old’ waters are much less vulnerable because of the longer travel time, which delays the pollution front and increases the chance of sorption and (bio)degradation or decay. PSWFs delivering old water are, however, often more vulnerable towards marine salinization from deeper layers, due to a shorter distance between the well screen and the fresh/brackish interface.

The alkalinity index gives an indication of the vulnerability towards acidifying processes. In calcareous aquifers (alkalinity index 3 or 4), the acid is very effectively buffered by calcite dissolution raising the concentrations of Ca and HCO_3 and, thus, hardening the raw water. Hardening is mainly a problem in the Limestone hydrosome and in the Eastern and Southern hydrosomes, where total hardness reaches values above 3 mmol/L. In non-calcareous aquifers (alkalinity index 1 or 2), the acidity is buffered by the soil and aquifer in a less desirable way, not by calcite dissolution, but by successively base exchange, the dissolution of silicate minerals, Al- and Fe-hydroxides. This results, when pH drops below 5-6 and alkalinity below about 1, in substantial concentration increases for Al and positively charged trace elements like Be, Cd, Co, Cu, Ni, Pb, Y, Zn and lanthanides.

The redox index is a measure of the capacity of the aquifer to reduce undesired oxidants like NO_3, SO_4, (per)chlorate and Cl_2, and to eliminate specific pollutants through by-products of reduction (like H_2S which triggers the precipitation of many metal sulfides), reductive dehalogenation (chlorinated hydrocarbons) or specific oxidation or reduction processes (many organic micropollutants including pesticides and pharmaceuticals).

(Sub)oxic PSWFs are more vulnerable than (deep) anoxic PSWFs, for example, to elevated NO_3 and SO_4 concentrations and those agrichemicals that resist biodegradation in a (sub)oxic environment. Anoxic or deep anoxic PSWFs are, on the other hand, more vulnerable than (sub)oxic PSWFs to As mobilizing from iron(hydr)oxides that reductively dissolve, and to those hydrophillic organic micropollutants in river water that resist biodegradation in a (deep) anoxic river bank but not in a (sub)oxic environment. A mixed redox PSWF is highly vulnerable to chemical well clogging, which is usually caused by precipitation of Fe and Mn hydroxides after mixing aerobic and anaerobic waters.

4.4.2 Optimizing the monitoring program

The PSWF typology resulting from the HCSA also constitutes a valuable tool for optimizing groundwater quality monitoring programs. The typology yields information on the origin of the water, the hydrogeochemical environment and the potential proximity of anthropogenic (modern) pollutants. This information helps to fine-tune the monitoring program to those parameters that are likely to be found in a specific water source and in a specific environment. Some guidelines to optimize the monitoring network are listed in Table 4.8.

PSWFs pumping young water should have a more frequent monitoring program with a wider analytical package than PSWFs pumping old water. PSWFs with a mixed redox index should analyze for a broader range of redox sensitive compounds because they receive inputs from both (sub)oxic and (deep) anoxic environments. Analogously, PSWFs with a specific redox index are likely to yield concentrations under the minimum detection limit (MDL) of the analytical method for a range of parameters, which could be monitored with a lower frequency. Following these guidelines based on the HCSA, costs are minimized and benefits maximized.

4.4.3 Reflections on ‘groundwater bodies’ as defined for EU

According to the Water Framework Directive (2000; 2008), EU state members must define and characterize bodies of water, based on stream basins (SB) for surface water and groundwater bodies (GWB) for groundwater. In order to facilitate the relation between surface and groundwater for ecological restoration purposes, the definition of GWBs is constrained to the previously defined SBs so that each GWB must fully lie within the boundaries of a SB. Following these guidelines, seven SBs and 23 GWBs were defined in The Netherlands (SGBP, 2009).

The resulting GWBs might be adequate from a European perspective, but present some inconsistencies on a national scale, because: (1) constraining the definition of GWBs to the boundaries of SBs may divide waters of the same origin and hydrogeological system into different GWBs; (2) a groundwater flow system can contain various hydrosomes, such as artificially recharged surface water and autochthonous groundwater; and (3) according to the Horizontal Guidance document on water bodies (EU, 2003), the delineation of GWBs should be based on geological boundaries to flow, so that any groundwater flow from one body to another is so minor that it can be ignored or can be estimated with adequate precision.

The HCSA overcomes these problems and yields more homogeneous GWBs, which are more logically delimited for water quality protection purposes and for answering international questions on transboundary aquifers. These GWBs are also better extrapolated in depth following the groundwater flow system, rather than a simple vertical extrapolation of the SB limits. Such vertical extrapolation introduces large errors, for example, in sandy aquifers overlain by clay and/or peat layers, where groundwater is mainly recharged through horizontal flow from neighboring sandy aquifers. In such areas (which are common in The Netherlands and elsewhere in Europe), the geographically established boundaries of the SBs are not consistent. The boundaries could be improved there by means of a HCSA, either applied to PSWFs as presented here, to observation wells, or both. Another urgent reason to apply the HCSA is the differentiation between groundwater *sensu stricto* and GWBs with AR and RBF, which are rapidly increasing in number and volume in many countries by the popularity of these methods for the production of clean safe drinking water. In the authors' opinion, such managed aquifer recharge systems and their effect on groundwater quality should be more thoroughly characterized within the Water Framework Directive, analogous to the effect of groundwater exfiltrating into surface water, which is considered a crucial cause of eutrophication of surface water ecosystems.

Regarding PSWFs, groundwater bodies used for the production of drinking water must be registered in the 'Register protected areas'. Such bodies are defined as (1) bodies of water used for the abstraction of water for human consumption which provide more than an average of 10 m^3/day in total, or which serve more than 50 persons, and (2) bodies of water intended for such level of use in the future (Water Framework Directive, 2000). Member states must guarantee the production of drinking water from the pumped water with the current purification methods and should even reduce their complexity in future. For this purpose and by order of the Ministry of Public Housing, Spatial Planning and the Environment (VROM), the Dutch National Institute of Public Health and Environment (RIVM) developed a protocol in order to compile all information relevant to water quality at the abstraction site in the so-called 'Dossiers for the area' (Wuijts et al., 2007). This information can be subsequently used to develop effective protection measures and will apparently be anchored in the National Drinking Water Act. The HCSA here presented could also be included in the 'Dossiers for the area', as a means to characterize PSWFs according to the groundwater origin and main hydrochemical facies, which indicates the processes affecting the quality of the water they deliver.

Table 4.8: Hydrogeochemical screening program for groundwater analysis, in sequential order –modified after Stuyfzand (1998b).

Origin (detection by Cl^-, Cl/Br, $\delta^{18}O$, EJ)	Analyze specific OMs and trace elements only in specific waters (Na-dikegulac in Rhine bank filtrate; Ag, Hg, Mo, Pb, Se, Sn, U in leachate of mine tailings).
Alkalinity index	If alkalinity index 3 or 4, do not analyze for Al, Be, lanthanides, Sc, Ti.
Redox index (by O_2, NO_3, SO_4, CH_4, EJ)	If deep anoxic, do not analyze for: Ag, Cd, Co, Cu, Hg, Ni, Pb, Se, Zn, AOX/VOX, chloro-alkanes and chloro-alkenes.
Age index (determined by either hydrological calculations or tracing methods (^3H, ^{14}C, Cl, CFCs, EJ)	If pre-industrial (>150 y), do not analyze for OMs; if pre-tritium (>55 y), do not analyze for recently developed OMs like CFCs and recently developed pesticides and pharmaceuticals.

EJ = by expert judgment; OMs = organic micro contaminants; AOX = absorbable organically-bound halogens; VOX = volatile organically-bound halogens; CFCs = chlorofluorocarbons.

4.4.4 Application for groundwater resources management

One of the major capabilities of the HCSA is the translation of complex hydrochemical patterns and processes into easily interpretable maps of groundwater bodies and hydrochemical facies, which can improve the communication between researchers, water resources managers and policy makers.

The HCSA can be the key to solving complex groundwater resources management problems at different scales. In regards to a single well, it can be applied to quantify its vulnerability, by identifying pollution sources and hydrochemical processes responsible for its water quality deterioration, and to optimize the monitoring program required to follow them up. On the scale of a PSWF, the HCSA reveals hydrochemical patterns within the well field that can be used to design a proper management strategy for the individual wells and optimize their pumping regime to guarantee the best quality of the raw water delivered by the PSWF. The results of the HCSA can also be used to decide the best location and screening depth of a new well when more capacity is required, or to choose the wells to close in order to reduce capacity or improve the quality of the whole well field.

Fig 4.5 shows the results of the HCSA in its original form, for a cross section in the coastal dunes of Amsterdam, which have been artificially recharged with pretreated Rhine water since 1957. The HCSA has been applied in The Netherlands to create detailed maps of the whole coastal area (Stuyfzand, 1993) and for AR and RBF systems in particular (Stuyfzand et al., 2006).

Fig 4.5 reveals the extent of five hydrosomes, in order of decreasing age: (M) connate, marine water, which was co-deposited with the Maassluis Formation at the beginning of the Pleistocene Epoch, about 2×10^6 years ago; (L) relic, Holocene transgression waters, which were formed between 8000 and 300 years ago during the various Holocene transgressions; (S) 'Actual' North Sea water, which infiltrated and still infiltrates through the actual sea floor, with a significant acceleration since the reclamation of lakes; (D) fresh, coastal dune water, which started to form about 5000 years ago when the first beach barriers were left behind an advancing shore line; and (P) polder water, which mainly consists of Rhine River water (flushing and irrigating the polders) and local rainwater, less than 500 years old.

Within each hydrosome, various facies were discerned by a combination of: (1) the redox level, determined as indicated in Table 4.3; (2) the calcite saturation index (calcite being the dominant dissolving mineral); (3) the pollution index POLIN, which is based on six equally weighted quality aspects; and (4) the base exchange index, BEX, which indicates (ancient) salt or fresh water intrusion (for details see Stuyfzand, 2008a).

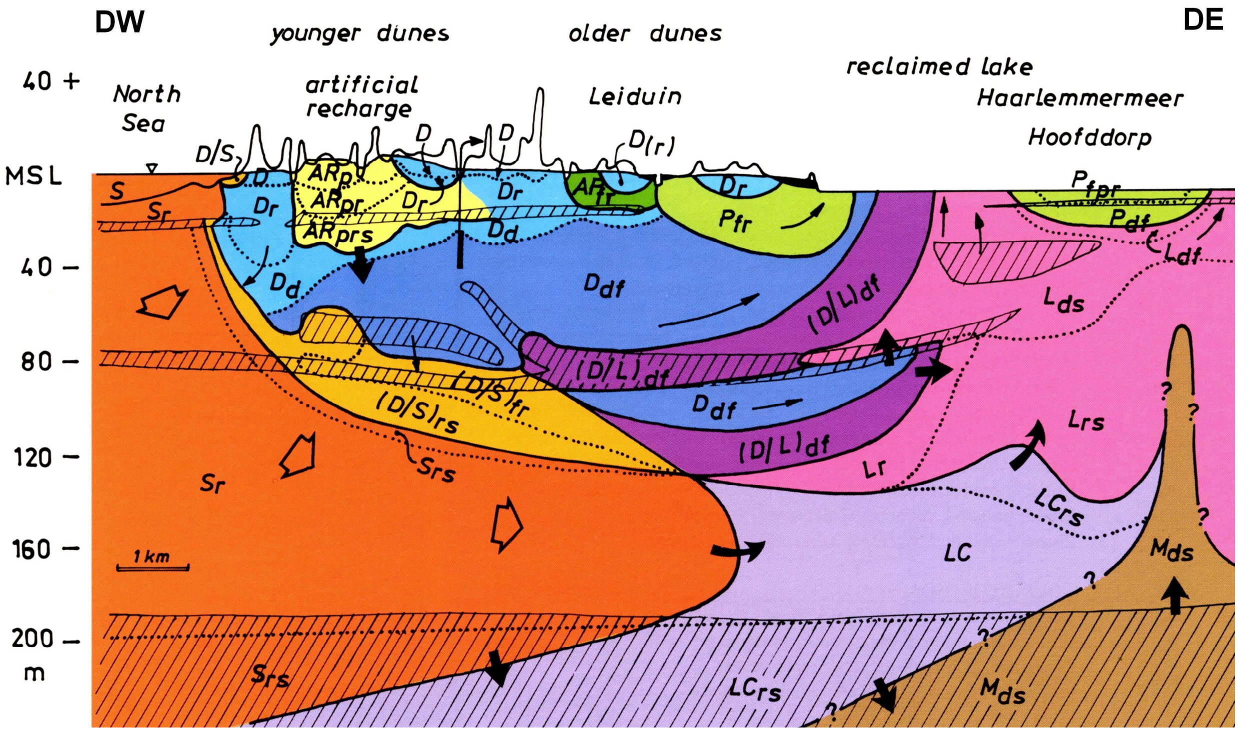


Fig 4.5: Cross section of the coastal dunes of Amsterdam, showing the areal distribution of hydrosomes with their hydrochemical facies as based on 200 well distributed samples (after Stuyfzand, 1993). Line of section DW-DE shown in Fig 4.1. Arrows indicate present groundwater flow. Codes are defined as follows: Hydrosomes: AP=artificially recharged polder; AR=River Rhine (artificially recharged); D=dune; L=relict Holocene transgression, marsh type; M=connate Maasluis; P=polder; S=North Sea; and (X/Y)=mixture of X and Y. Hydrochemical facies: a=acid; d=deep anoxic (methanogenic); f=freshened; p=polluted; r=reduced and s=salinized.

Fig 4.5 is presented here as an example of application of the HCSA to conventional observation wells. Further detailed interpretation of the hydrochemical patterns obtained from the HCSA is beyond the scope of this contribution, but a detailed analysis is available in Stuyfzand (1993).

The HCSA can easily be further upscaled to develop strategic plans on the availability of groundwater resources and their protection, on a regional scale. A water-supply company can use it to optimize the management of its groundwater resources by regulating production rates of individual PSWFs according to their vulnerability or quality, and also to decide which PSWFs to expand or close down, in order to guarantee their demands at the lowest purification costs or with reduced complexity of purification technology, in compliance with the Water Framework Directive. Further upscaling to a national or European level is also feasible. A three-dimensional map of groundwater bodies and hydrochemical facies on a European scale could serve as a means to (1) summarize the quality status of European groundwater resources, (2) visualize the extension of GWBs, also in transboundary aquifers; and (3) follow up their growth and size reduction, which is more difficult to achieve with many single value maps of specific parameters.

4.5 Conclusions

Public supply well fields (PSWFs) constitute an attractive (inter)national monitoring system for evaluating the chemical state of groundwater, in order to safeguard drinking water resources and monitor the environment. They are monitored on a regular basis as an integral part of the quality surveillance of national drinking water supply and they have been so for a long time. They have also been extensively used in national groundwater surveys on various indicator parameters, but what was lacking, however, was a systematic approach to combine all relevant data into a clear typology of PSWFs. The hydrochemical system analysis (HCSA) here presented is such an approach, which combines all relevant data in order to better understand the individual state of and spatial patterns in groundwater quality delivered by PSWFs, by addressing the spatial distribution of groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The origin is to be determined by environmental tracers, geomorphological and potentiometric maps, the facies by combining age, redox and alkalinity indices. The PSWF typology obtained provides a means to predict PSWF vulnerability, optimize groundwater quality monitoring programs and better delineate groundwater bodies, by considering groundwater origin and flow. The latter also covers the need to delineate groundwaters bodies with artificial recharge and river bank filtration, which are rapidly increasing in number and volume in many countries by the popularity of these methods for the production of clean safe drinking water and for storing surface water underground.

The HCSA translates complex hydrochemical patterns into easily interpretable maps by showing PSWFs, groundwater bodies and hydrochemical facies. Such maps can become a key to solve complex groundwater resources management problems at different scales, ranging from a single well(field) or region to the national or European scale. They facilitate communication between researchers, water resources managers and policy makers and show what is more difficult to achieve with single value maps of specific parameters.

The HCSA provides EU members with a means to redefine the boundaries of their GWBs as defined for the Water Framework Directive, in areas were the HCSA yields better results, with more homogeneous GWBs, more logically delimited for water quality protection purposes and better extrapolated in depth following groundwater flow. A three-dimensional map of such groundwater bodies and hydrochemical facies on a European scale could serve as a means to summarize the quality status of European groundwater resources, to visualize the extent of GWBs and to follow up their dynamics (growth and shrinking), which is not possible with single value maps of specific parameters. The HCSA has the potential to become the basis for consistent rationalization of water management strategies and of compliance with the EU Directives.

4.6 Acknowledgements

This research was funded by the Joint Research Programme of the Dutch Waterworks (BTO) and by Delft Cluster, project number CT05.30. R. Harting is acknowledged for his help during the production of the hydrogeological cross sections. V. Post, I. Cartwright, A. Bath and P. Glynn are greatly acknowledged for their constructive comments on an earlier version of this manuscript.

Chapter 5

5 Quantifying the vulnerability of well fields towards anthropogenic pollution: The Netherlands as an example[6]

Abstract

A new method is presented to asses the vulnerability of public supply well fields (PSWFs), other well fields or individual wells.

The Intrinsic Vulnerability Index towards Pollution (VIP) is based on the age, redox level, alkalinity (or acidity), and surface water fraction of the pumped water, resulting in a score ranging from 0 for old, deeply anoxic, high alkalinity ground water to 30 for young, (sub)oxic, acid ground water.

The Specific Vulnerability Index towards Pollutant X (VIP_X) combines VIP with four aspects: the current concentration of X in the pumped water; the mobility or mobilization potential of X in the hydrogeochemical environment as derived from the redox state and alkalinity of the raw water; the land use within the ground water catchment area; and the pollution risk for X, derived from its concentration in shallow groundwater and/or in the infiltrating surface water.

A national survey of all active PSWFs in the Netherlands revealed a low VIP in 50% and high VIP in 9% of them. Most PSWFs with a low VIP pump from very deep aquifers, and those with high VIP from either acidified, phreatic sandy aquifers, (sub)oxic, artificially recharged coastal dunes, (sub)oxic river banks or oxic limestone.

---

[6] This chapter was published as Mendizabal, I., Stuyfzand, P.J., 2011. Quantifying the vulnerability of well fields towards anthropogenic pollution: The Netherlands as an example. Journal of Hydrology, 398(3-4): 260-276.

5.1 Introduction

Groundwater is of major societal significance for many well-known reasons. One of the most important ones is that groundwater normally offers a direct and hygienically safe source of drinking water for public, agricultural, industrial and individual supply (Matthess, 1990). Groundwater resources, however, are becoming extremely vulnerable to a multitude of anthropogenic pollution sources (Appelo and Postma, 2005).

The concept of groundwater vulnerability was introduced by Albinet and Margat (1970), but has repeatedly been redefined (e.g. van Duijvenbooden, 1987; Vrba and Zaporozec, 1994). Nowadays, intrinsic vulnerability is defined as the general vulnerability of groundwater to any contaminant generated by human activities, while specific vulnerability is used to define the vulnerability of groundwater to a particular contaminant or group of contaminants (Daly et al., 2002). Both terms are equivalent to the terms aquifer sensitivity and groundwater vulnerability (USEPA, 1993).

Intrinsic vulnerability assessment is usually based on either hydro(geo)logical or hydrochemical criteria. The purpose is to produce vulnerability maps, which are used for: identification of areas susceptible to contamination, groundwater protection, environmental management, public information and education (Daly et al., 2002; Witkowski et al., 2004). Maps of the hydro(geo)logical type are mainly derived from a linear combination of a priori subjectively rated and weighted maps of different hydrological and lithological parameters (Aller et al., 1987; Civita and De Maio, 1997; Doerfliger et al., 1999; Foster, 1987; Goldscheider, 2005; Nguyet and Goldscheider, 2006; van Stempvoort et al., 1994; Vías et al., 2006). All these methods, like the frequently applied DRASTIC (Aller et al., 1987), have a predictive character and the system definition depends on the a priori selection of those parameters considered to be decisive for groundwater vulnerability assessment (Gogu and Dassargues, 2000). The hydrochemical approach is to compute a water quality index for all groundwater samples with sufficient analytical data, and map zones with distinct degrees of vulnerability on the basis of this index (Backman et al., 1998; Melloul and Collin, 1998; Saeedi et al., 2009; Stigter et al., 2006). However, this approach mostly is a hybrid of intrinsic and specific vulnerability, because the used water quality index is (also) based on specific contaminant levels.

The specific vulnerability is usually obtained by superimposing the actual pollution sources, which are subdivided on the basis of their pollution potential (urban areas, cultivated areas, waste dumps, industrial complexes etc.), on the intrinsic vulnerability map (Civita, 1994). Such methods have been especially applied to estimate the specific vulnerability to agricultural activities (Berkhoff, 2008; Boumans et al., 2005; 2008; Burkart and Feher, 1996; Burkart et al., 1999).

Assessment of both the intrinsic and specific vulnerability of public supply well fields (PSWFs), other well fields or wells, also requires the characteristics of the groundwater collection system, because characteristics like the depth of abstraction and the contribution of infiltrated surface water have a strong impact on the vulnerability, and may even change over time. Specific vulnerability determination of PSWFs requires the delineation of the well head protection area (WHPA) or water catchment area, and the mapping of land use within it. The delineation of such zones is considered the best way of dealing with the capacity of aquifers to transport contaminants, dilute and attenuate them in the saturated zone (Foster et al., 2002). Intrinsic vulnerability therefore not only depends on the hydrogeological and geological characteristics of the aquifer system but also on the characteristics of the well (field) itself, while remaining independent of the nature of and exposure to the contaminants. Specific vulnerability takes into account the properties of and the exposure to a particular contaminant (or group of contaminants) in addition to the intrinsic vulnerability of the well (field).

In this contribution, a new method of the hydrochemical type is presented to asses the vulnerability of groundwater towards anthropogenic inputs released at the surface, in particular for 'existing' well fields or wells. The added value of this method consists of using data from PSWFs and the structured hydrochemical approach, which departs from the Hydrochemical Facies Analysis (HyFA) introduced by Stuyfzand (1990; 1999) and renamed to Hydrochemical System Analysis (HCSA) by Stuyfzand (2006), as a means to map and diagnose all major factors accounting for regional variations in hydrochemistry. This is done by addressing the spatial distribution of groundwater bodies with a specific origin (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The method is modified in

Mendizabal et al. (2011, Chapter 4) in order to optimize it for mapping groundwater bodies (hydrosomes) contributing to PSWFs, by defining the hydrochemical facies as a combination of age, redox and alkalinity indices of the pumped water. These three indices are combined here into a single Intrinsic Vulnerability Index towards anthropogenic Pollution (VIP) and a Specific Vulnerability Index towards Pollutant X (VIP_X), with X being either a main constituent, trace element or organic compound.

Salinization of the pumped water due to upconing of natural, brackish groundwater is beyond the scope of this contribution, but it could be addressed in a similar way. The results of a national vulnerability assessment of all PSWFs in the Netherlands are discussed for some of the major water quality problems faced by the Dutch waterworks during drinking water production, i.e. raised levels of NO_3, SO_4, Al, Ni and bentazone (a herbicide).

5.2 Materials

5.2.1 Water quality data

The proposed method of vulnerability assessment of a well (field) requires water quality data from various sources: the raw water delivered, groundwater as sampled from shallow observation wells, and surface water, if the raw water delivered is composed of a significant fraction of surface water which infiltrated after for example artificial recharge (AR) or river bank filtration (RBF).

5.2.1.1 Raw water quality delivered by PSWFs

During a national sampling campaign in the first trimester of 2008, all active PSWFs in the Netherlands were sampled for chemical analysis. Samples were collected following the guidelines described in Mendizabal and Stuyfzand (2009, Chapter 2), in order to obtain the hydrochemically most representative sample for each well field. Samples of the mixed raw water were taken from faucets on the transport mains that discharge the water from various or all pumped wells, when these wells had been active for at least a couple of hours. In well fields where the storage capacity of the pumping station limited the number of wells that could simultaneously abstract water, the most representative selection of wells was switched on for obtaining a representative sample of the well field. Variances in water quality between different wells within a PSWF were not addressed in this national survey, except for 35 PSWFs known to tap both a phreatic and confined aquifer. For those PSWFs a separate sample was collected from each aquifer. Thus, a total of 241 samples was obtained from 206 active PSWFs.

Samples were analyzed for a wide set of parameters, including amongst others, macroparameters (main cations and anions, and nutrients), trace elements and the stable isotopes $\delta^{18}O$ and $\delta^{2}H$. Temperature, specific electrical conductivity (SEC), pH and dissolved oxygen were measured on site. Samples for analysis of cations, PO_4, SiO_2 and trace elements were collected in 100 ml polypropylene bottles, after filtration in the field through a 0.45 µm Millipore membrane filter, and acidified to $pH < 2$ by addition of 0.7 ml HNO_3 Suprapur 65%. They were analyzed by ICP-MS + ICP-OES. Samples for analysis of Cl, SO_4, HCO_3, NO_3, NO_2 and NH_4 were collected unfiltrated, in 100 ml polypropylene bottles and stored in a refrigerator for less than 3 days before analysis by spectrophotometry. Sulphide (HS^-) was not measured because of expected low concentration levels, expected problems with sample preservation and financial limitations. Samples for analysis of $\delta^{2}H$ and $\delta^{18}O$ were collected in 30 ml brown glass bottles without filtration and without any preservative. The bottles were fully filled and hermetically closed, to avoid atmospheric gas exchange. The samples were kept in the dark and at $4^{o}C$ until analysis by mass spectrometry.

Data on pesticides were obtained from the national PSWF data bank, an extensive database containing numerous properties of all Dutch PSWFs, annual means of their raw water quality as analyzed by the individual water utilities on a routine basis, and the annual total volumes pumped since 1898 (Mendizabal and Stuyfzand, 2009, Chapter 2).

5.2.1.2 Dutch national groundwater quality monitoring network

Groundwater quality is regularly monitored in The Netherlands by means of the Dutch national groundwater quality monitoring network (LMG). LMG was established in 1979 by the Dutch National Institute for Public Health and the Environment (RIVM) in order to quantify human impacts on groundwater quality in space and time. The network comprises 400 piezometer nests evenly distributed throughout the country, with a higher density in areas relevant for drinking water production (Reijnders et al., 1998; van Duijvenbooden, 1987).

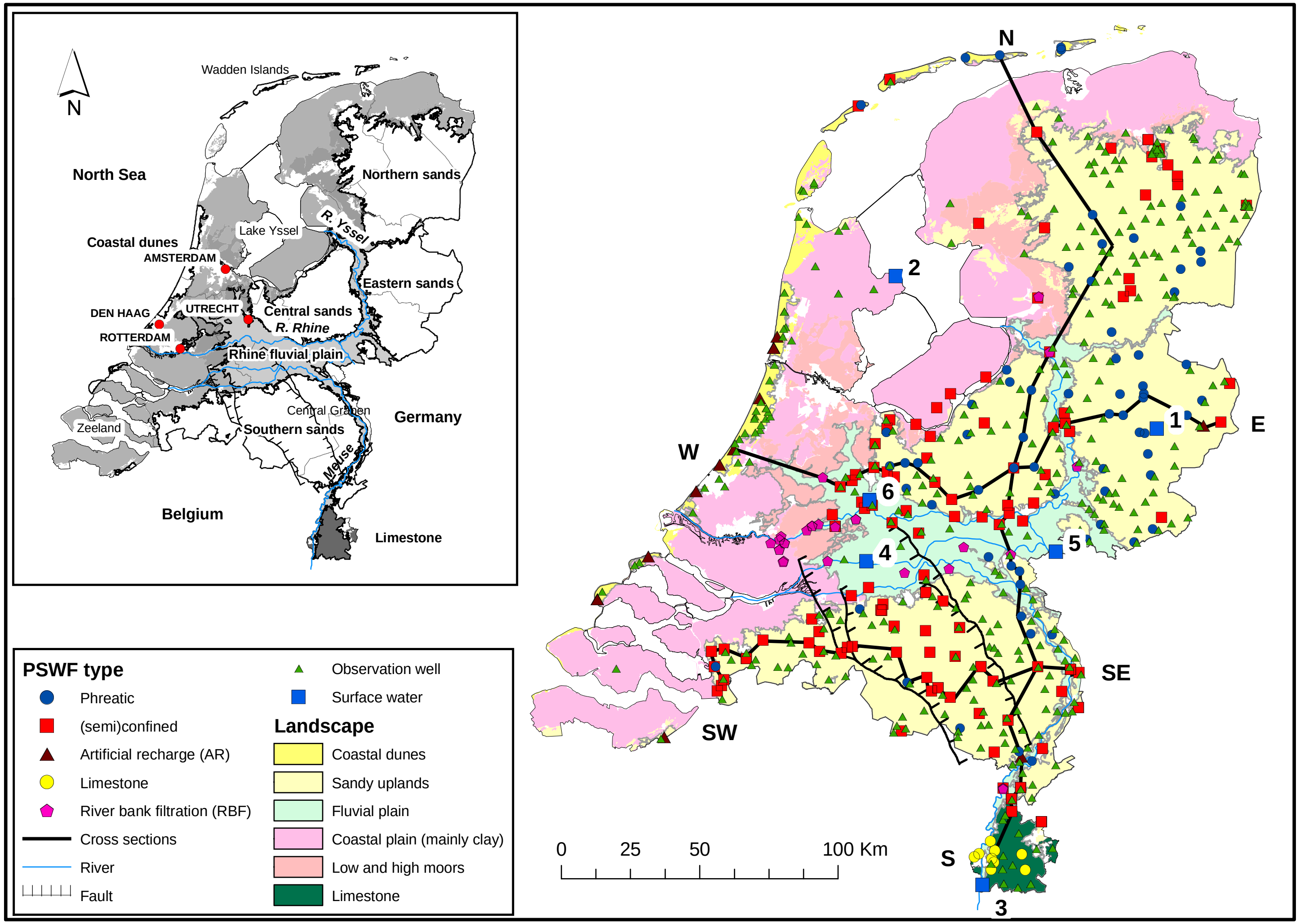


Fig 5.1: Spatial distribution of the National Network of PSWFs projected on top of a landscape map of The Netherlands. PSWFs are classified according to source water and aquifer type into: phreatic, (semi)confined, artificial recharge (AR), river bank filtration (RBF) and limestone. Also shown: observation wells of the Dutch national and provincial groundwater quality monitoring networks (LMG), important surface water sampling points and the location of the cross sections depicted in Fig 5.8.

All wells were constructed using a standardized drilling method, dimensions and well completion, with 2 m long screens at about 9, 15 and 24 m BS (below surface). The land use around every well is well documented. The upper (9 m BS) and lower piezometers (24 m BS) are sampled and analyzed for macro and micro constituents every 1 -4 years, depending on the vulnerability of the groundwater (Wever, 1998). The other piezometer is sampled occasionally. LMG is a valuable network that has been used in numerous studies to determine shallow groundwater quality on a national scale (Frapporti, 1994; Meinardi et al., 2003; Reijnders et al., 1998; van den Brink et al., 2007). Since 1989, the network has been enlarged with 12 provincial groundwater quality monitoring networks (PMG), which follow the same construction and sampling protocol for optimal integration. PMG fulfills additional purposes, like groundwater quality surveillance of specific nature reserves. In this contribution, LMG and PMG will be addressed together as LMG.

A total of 533 piezometers was selected for the risk assessment, after removing the ones in peat or marine clay areas or with brackish waters, because no drinking water is produced in such areas. Wells with AR or RBF waters or upward flow (seepage) were also discarded. Their spatial distribution is shown in Fig 5.1.

In 2006, 771 piezometers from both networks were sampled and analyzed for more than 50 pesticides and organic micro pollutants (Van der Linden et al., 2007). In 207 piezometers at least one pesticide was detected, 87 of which exceeded the norm of 0.1 µg/L (Dutch Ministry of Environment, 2001). The herbicides bentazone and mecoprop (MCPP) and fungicide carbendazim were the most frequently found compounds.

5.2.1.3 National surface water quality monitoring network

Quantification of the specific vulnerability of PSWFs delivering more than 20 % of surface water, (AR and RBF in Fig 5.1) requires quality data of the surface water prior to infiltration. For this purpose, data from the River Waterworks Association (RIWA) were used, a cooperative of Dutch water supply companies that use surface water for the production of drinking water. The most relevant monitoring stations are indicated in Fig 5.1.

5.2.2 Well head protection areas (WHPAs)

The well head protection area (WHPA) is the surface and subsurface area surrounding a water well or well field supplying a public water system, through which contaminants are likely to move toward and reach such water well or well field (USEPA, 1997). The surface area is identical to the water catchment area of the well field. When interpreting water quality data from well fields, the land use within the catchment area and the changes in both the area and the land use should be known.

WHPAs are delineated by several methods, ranging from simple analytical approaches to complex computer models. USEPA (1998) provides a detailed literature review on methods used until 1998. Numerous analytical approaches have also been developed for selected ideal cases (Broers and van Geer, 2005; Ceric and Haitjema, 2005; van Ommen, 1986). The simplest one is a fixed-radius WHPA (Ceric and Haitjema, 2005), which applies to a fully penetrating, single extraction well, screened in a confined aquifer of infinite areal extent without regional flow component. The most elaborate option is to obtain the WHPA from a numerical groundwater model, which is more appropriate in complex geohydrological settings (Franke et al., 1998). The optimal method is usually the one that simplifies the flow system as much as possible while still preserving its geological and hydrologic characteristics (Paradis et al., 2007). In Portugal, for example, WHPAs are defined based on analytical solutions and on groundwater flow and particle tracking, assuming that groundwater flow into the well is radial by means of an axisymmetric flow model (Lobo Ferreira and Oliveira, 2004).

In order to guarantee the sustainability and safety of drinking water, the entire WHPA should be protected against any kind of contamination. In practice, however, due to the impossibility of protecting such large areas, authorities are forced to define smaller areas where specific activities are to be banned. In the Netherlands, such areas are defined according to the travel time of water (t_{H2O}) within the pumped aquifer (CBW, 1980; TCB, 1988; 1989), resulting in three protection areas: (1) the groundwater protection area (GPA), defined as the area within the 25 year contour (of t_{H2O}) taking into account both vertical and horizontal flow in the aquifer (thus excluding the unsaturated zone); (2) the no drilling area (NDA), defined for confined aquifers as the area within the 25 year contour based only on horizontal flow within the pumped aquifer; and (3) the microbiological protection area (MPA), defined as the area within the 60 day contour, in the aquifer at the depth of the well screen. A schematic representation of the protection areas for a phreatic and confined PSWF is shown in Fig 5.2, where the well field has been condensed into a single abstraction well.

The GPA aims at protecting the area within the 25 year contour against persistent compounds, so as to offer sufficient time for research and legislative procedures to remediate or restart pumping at an alternative site in case of a calamity. The NDA is needed to preserve the groundwater protection capacity of confining layers by prohibiting any drilling within it. The MPA should protect against pathogens, because 60 days are assumed to be sufficient for die-off of pathogenic micro-organisms in contaminated groundwater, to the extent that health risks have been eliminated (Knorr, 1937). The minimal extension of the MPA is 30 m and depending on the distribution of individual wells within the PSWF, various MPAs can be defined, one for each well or group of wells. Analogously, any of the protection areas of a PSWF can also be formed by a number of polygons, depending on the groundwater flow system. In some regions, the 10 and 100 year contours are also used to ban specific activities.

The spatial extension of the WHPAs in the Netherlands is summarized in Table 5.1. Note that although all WHPAs together cover 7.6% of the Netherlands, only 2-2.8% of the country is actually protected because WHPAs are not entirely protected.

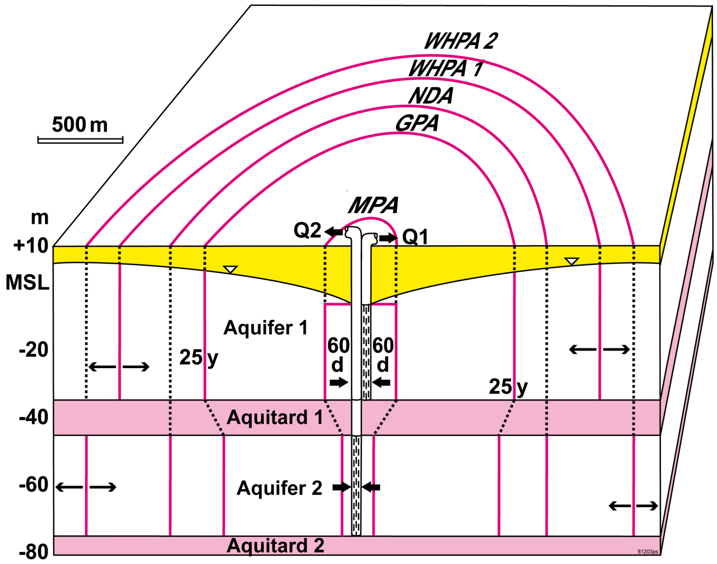


Fig 5.2: Groundwater protection areas as defined in the Netherlands for PSWFs in phreatic and confined aquifers. WHPA: Well head protection area, GPA: Groundwater protection area, NDA: No drilling area and MPA: Microbiological protection area. Q1 >> Q2.

Table 5.1: Groundwater protection areas for PSWFs in the Netherlands with their extension.

Area	Name	t_{H2O} contour	Nr defined	Area [Km^2]				% of Netherlands
				Min	Mean	Max	Total	
WHPA	Well Head Protection Area	Inf.	213	0.1	12	68	2562	7.56
NDA	No Drilling Area	25 years [a]	60	0.5	11	342	685	2.02
GPA	Groundwater Protection Area	25 years	191	7.7E-05	5	26	941	2.78
MPA	Microbiological Protection Area	60 days	233	7.7E-05	0.7	40	165	0.49

[a] Only taking into account horizontal flow within the pumped, confined aquifer.

Nowadays, as stated by Dutch legislation (Dutch Government, 1979; 1986), the protection areas and the activities prohibited within them are regulated by the provincial authorities in their own Provincial Environmental Plans. In practice, the extension of the protection areas is not only based on the contours of t_{H2O} (in the Netherlands mainly derived from numerical groundwater models), but also on the proximity of main infrastructures, like roads and surface water bodies. All protection areas defined in the Netherlands (Wuijts et al., 2008) are shown in Fig 5.3.

5.2.3 Land use

The land use within all WHPAs was calculated from the LGN database, a product of the Centre for Geo-Information of Wageningen University, containing a raster database with 25 m × 25 m resolution covering the entire Dutch territory. LGN is based on a combination of geodata and satellite images that is updated every 3-5 years since 1986. In the most recent version available, LGN5 (Hazeu, 2006), land use is divided in 38 classes, which were aggregated for this study in nine main land use categories (Table 5.2).

The resulting land use map (Fig 5.4) is clearly predominated by agriculture. The main nature areas are found in the Central sands and in the coastal dunes, where numerous PSWFs pump groundwater of high quality. The main urbanized areas are the cities of Amsterdam, Rotterdam, The Hague and Utrecht, located within the western clay/peat areas. They pose a large pollution source, but the effect on drinking water resources is limited by the lack of PSWFs in these areas of unfavorable hydrogeological conditions, with low yields and shallow brackish water.

Table 5.2: Land use types in the Netherlands as defined in the grid LGN5, and categories resulting from their aggregation for the risk assessment. Percentage of total areal extension of categories: Intensive agriculture (24); extensive agriculture (30); intensive urbanization (7); extensive urbanization (8); salt marshes (0.2); nature (4); forest (8), fresh water (8) and North Sea (10).

ID	Land use	Category	ID	Land use	Category
2	Maize	Intensive agriculture	31	Beaches and dunes	Nature
3	Potatoes	Intensive agriculture	32	Scarcely vegetated dunes	Nature
4	Beets	Intensive agriculture	33	Vegetated dunes	Nature
5	Cereals	Intensive agriculture	34	Heathlands in dune areas	Nature
6	Other agricultural crops	Intensive agriculture	35	Shifting sands	Nature
8	Greenhouses	Intensive agriculture	36	Heathlands	Nature
9	Orchards	Intensive agriculture	37	Heathlands with minor grass influence	Nature
10	Bulb cultivation	Intensive agriculture	38	Heathlands with major grass influence	Nature
1	Grass	Extensive agriculture [a]	39	Raised bogs	Nature
44	Swampy pastures in peat areas	Extensive agriculture	41	Miscellaneous swamp vegetation	Nature
18	Continuous urban area	Intensive urbanization	42	Reed swamp	Nature
19	Built-up in rural area	Extensive urbanization	45	Herbaceous vegetation	Nature
21	Coniferous forest in urban area	Extensive urbanization	46	Bare soil in natural areas	Nature
22	Built-up area with dense forest	Extensive urbanization	11	Deciduous forest	Forest
23	Grass in built-up area	Extensive urbanization	12	Coniferous forest	Forest
24	Bare soil in built-up area	Extensive urbanization	40	Forest in raised bogs	Forest
25	Main roads and railways	Extensive urbanization	43	Forest in swamp areas	Forest
26	Buildings in rural area	Extensive urbanization	16	Fresh surface water	Fresh water
30	Salt marshes	Salt marshes	17	Salt surface water	North Sea

[a] The aggregation of grassland into the category extensive agriculture is currently under discussion, because the net N-surplus on grassland is as high as on most arable land use types (mainly because in many areas grassland corresponds to a spatial mixture or temporal alternation of grassland and arable land, and because various grasslands present high N-mineralization and high atmospheric N inputs). Yet, grassland was aggregated to the category extensive agriculture, because aggregating it into the category intensive agriculture would only be justified for NO3 but not for the other pollutants considered.

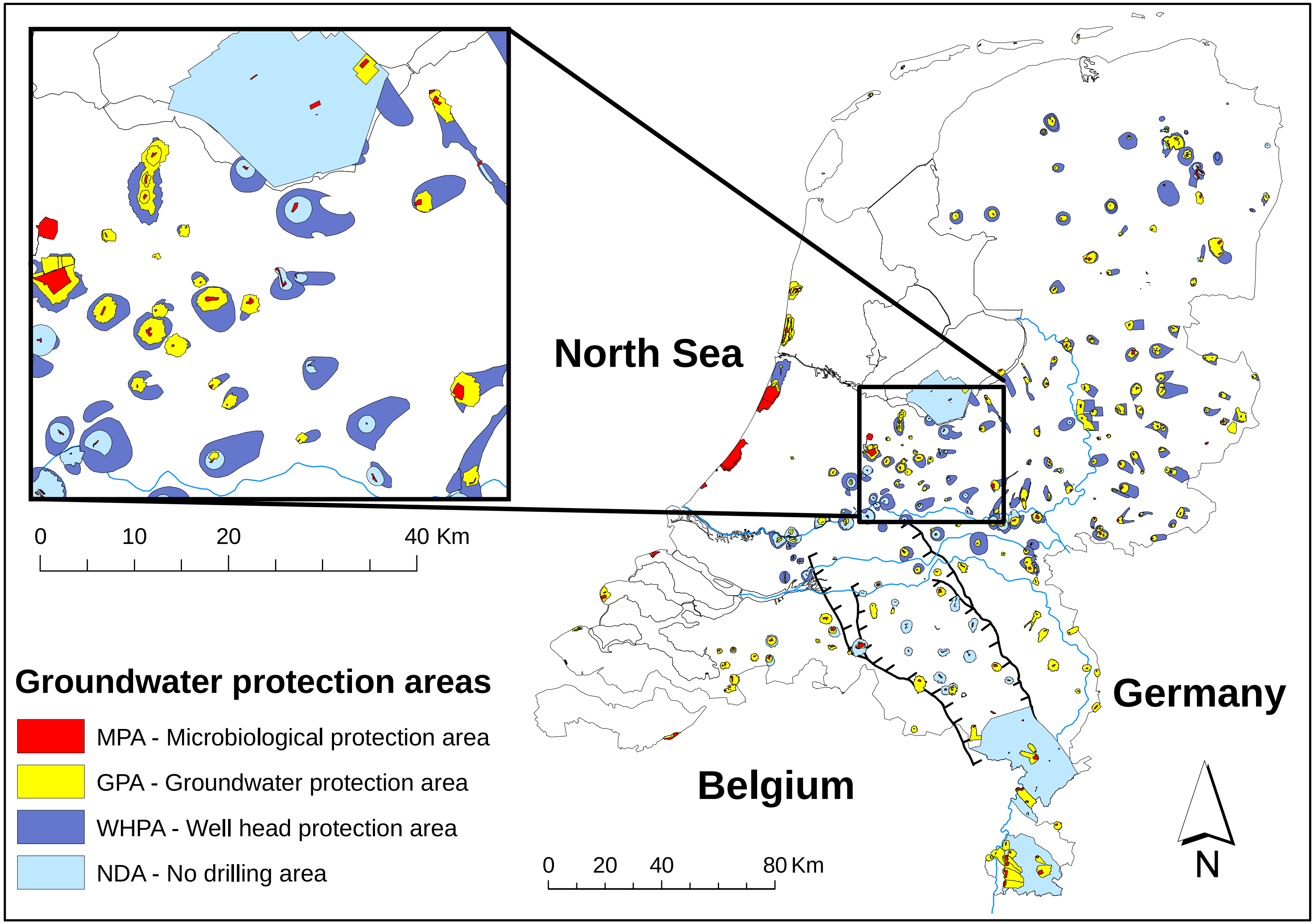


Fig 5.3: Spatial distribution of groundwater protection areas in the Netherlands as defined in Table 5.1, based on data from Wuijts et al. (2008). WHPA = well head protection area; NDA = no drilling area; GPA = groundwater protection area; MPA = microbiological protection area.

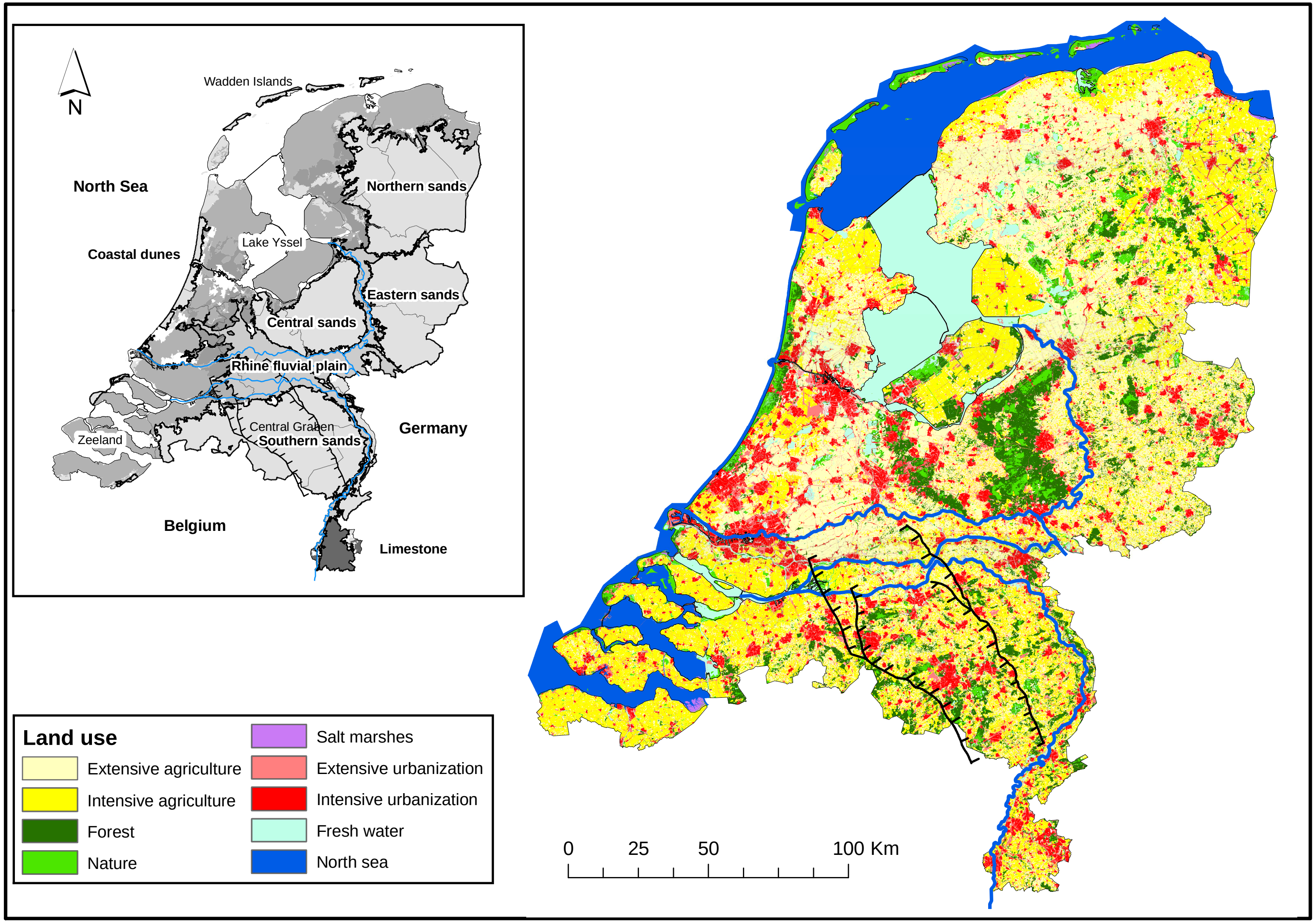


Fig 5.4: Land use map of the Netherlands aggregated in nine land use categories for the risk assessment. Data from LGN5, a land use database of the Centre for Geo-Information of the Wageningen University.

For every PSWF, the fraction of every land use category within the WHPAs was calculated by intersecting the categorized land use map (Fig 5.4) with the WHPAs (Fig 5.3) using a Geographical Information System (GIS).

5.2.4 Drinking water standards

Several parameters which are strongly related to anthropogenic activities and also cumbersome for drinking water production were selected for their specific groundwater vulnerability assessment. They are listed in Table 5.5, together with their drinking water standards according to Dutch legislation (Government, 2001).

5.3 Methods

5.3.1 Intrinsic vulnerability

Intrinsic vulnerability assessment of groundwater resources is usually based on aquifers, which are steady units that can be characterized by steady hydraulic properties that describe the recharge and flow regime within them. Especially well fields and wells are, on the contrary, dynamic units for at least three reasons: (i) their discharge is regulated by man and normally not constant; (ii) water quality or quantity problems frequently force the owners to change the depth, the number of wells or the management; and (iii) drilling and pumping may alter the hydraulic and hydrogeochemical characteristics of the aquifer system. The first two reasons form part of the so-called 'well field adaptation', which is defined in Mendizabal and Stuyfzand (2009, Chapter 2) as *"The capacity of a PSWF to adapt to the environment in order to produce enough water volume to fulfill the drinking water demand, with sufficient quality for preparation of drinking water at the lowest cost while avoiding expensive treatment".* In this contribution an overview of common adaptation measures and their implications are also given.

A well (field) therefore requires a dynamic vulnerability index, covering both aquifer and well properties in order to be able to evolve with well field adaptation measures. Two factors are required for this purpose, a facies factor (*F*) to cover changes in water composition, and a source factor (*S*) to cope with the fraction of groundwater and/or surface water delivered, which may even change over time.

The following dimensionless Intrinsic Vulnerability Index to Pollution (VIP) for a well (field) is therefore proposed:

$$VIP = S \times F \qquad [-] \qquad (5.1)$$

The introduction in VIP of a not strictly intrinsic parameter such as the source water is justified for a well (field), because a mixture of groundwaters from different sources and origins may be pumped. The quality of the water delivered is strongly determined by the source water, and therefore also the well's vulnerability.

The source factor S is defined as follows:

$$S = f_G + 1.5 f_{AR} + 2 f_{RBF} \qquad [-] \qquad (5.2)$$

where f_G = fraction of groundwater; f_{AR} = fraction of artificially recharged surface water; f_{RBF}= fraction of river bank filtrate. The terms f_{AR} and f_{RBF} are to be estimated by multitracing techniques as described in Mendizabal and Stuyfzand (2009, Chapter 2) and elsewhere (Clark and Fritz, 1997; Kass, 1998).

S thereby accounts for the higher vulnerability of PSWFs delivering surface water, which is generally more polluted, mostly not passing a favorable unsaturated zone, and showing shorter travel times which result in less sorption and (bio)degradation. The AR fraction is assigned less weight than the RBF fraction, to account for the beneficial effect of (1) pretreatment of the source water, frequently by coagulation and sedimentation prior to infiltration and (2) the option to temporarily close the inlet during high pollution peaks in the river. Note that when infiltrated surface water does not contribute, S equals 1 and VIP equals *F*.

The dimensionless facies factor in Eq. (5.1) is defined as:

$$F = \frac{\sqrt{\%Y + 21}}{\mathrm{Re}d} \times \sqrt{\frac{1 + 10Acid}{Alk + 0.1}} \qquad [-] \qquad (5.3)$$

where *%Y* = percentage of 'young' groundwater, infiltrated after 1953 (thus <55 years old in 2008); Red = redox level; Alk = alkalinity, as HCO_3 + CO_3 (meq/L); Acid = the mineral acidity, as H^+ (mmol/L).

The factors 21, 1, 10 and 0.1 in Eq. (5.3) have been inserted to prevent F from becoming either 0 or infinite when *%Y*, Acid or Alk are zero, and to create a vulnerability scale ranging from close to 0 for very old, deeply anoxic groundwater with an alkalinity of 10 meq/L, to ca. 50 for very young, oxic pH=4 groundwater with zero alkalinity. F is to be considered dimensionless, which is only true when replacing Red by Red √1% and when calculating alkalinity in mmol/L as $HCO_3 + 2CO_3$.

F covers the aquifer and well (field) characteristics indeed, because the term *%Y* (indicating the potential proximity of modern pollutants) is mainly determined by the well or well field (rate and depth of abstraction) and aquifer (porosity and recharge rate), whereas the redox level and alkalinity (or acidity) indicate how the aquifer system is digesting the input of oxidants and acids.

Table 5.3: Practical criteria for the determination of the redox level in unmixed redox environments (above; slightly modified after Stuyfzand (1993)), and mixed redox environments (below). Concentrations in mg/L.

Level	Unmixed redox environment	Redox cluster	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
1	Oxic		$O_2 \geq 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
2	O2-reducing	(sub)oxic	$1 \leq O_2 < 0.8\ (O_2)_{SAT}$		< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
3	NO_3-reducing		< 1	≥ 1	< 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
4	Mn-reducing	anoxic	< 1	< 1	≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
5	Iron reducing		< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.2
6	Sulphate reducing	deeply anoxic	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	0.2 - 0.5
7	Methanogenic		< 1	< 1			< 0.2 $(SO4)_O$		≥ 0.5

Level	Mixed redox environment	Mix of levels	Criteria [mg/L]						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	H_2S #	CH_4
3.0	O2 – Mn	2 + 4	≥ 1		≥ 0.1	< 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
3.5	O2 – Fe	2 + 5	≥ 1			≥ 0.1	≥ 0.8 $(SO_4)_O$	no	< 0.1
4.0	O2 – H2S	2 + 6	≥ 1				0.2-0.8 $(SO4)_O$	yes	< 0.1
4.5	O2 – CH4	2 + 7	≥ 1				< 0.2 $(SO4)_O$		> 0.1
4.0	NO3 – Fe	3 + 5	< 1	≥ 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	no	<0.1
4.5	NO3 – H2S	3 + 6	< 1	≥ 1			0.2-0.8 $(SO4)_O$	yes	< 0.1
5.0	NO3 – CH4	3 + 7	< 1	≥ 1			< 0.2 $(SO4)_O$		<0.1
5.0	NO3 – CH4	3 + 7	< 1	≥ 1					> 0.1
5.5	Fe – H2S	5 + 6	< 1	< 1		≥ 0.1	0.2-0.8 $(SO4)_O$	yes	< 0.1
5.5	Fe – H2S	5 + 6	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$	yes	0.2 - 0.5
6.0	Fe – CH4	5 + 7	< 1	< 1		≥ 0.1	≥ 0.8 $(SO_4)_O$		≥ 0.5
6.5	H2S – CH4	6 + 7	< 1	< 1			< 0.2 $(SO4)_O$	yes	< 0.5
6.5	H2S – CH4	6 + 7	< 1	< 1			0.2-0.8 $(SO4)_O$	yes	≥ 0.5

yes/no = yes/no clear H_2S-smell in field; not a solid but soft criterion; $(SO_4)_O$ = original SO_4 concentration [mg/L], see text; $[O_2]_{sat.} = 14.594–0.4\ t+0.0085\ t^2–97x10^{-6}\ t^3–10^{-5}\ (16.35+0.008\ t^2–5.32/t)Cl$, with t = temperature in ℃ and Cl in mg/L.

The *%Y* is obtained from the hydrological response curve (HRC) of the well (field) as calculated by a calibrated groundwater model when available, or otherwise as approximated analytically in Mendizabal and Stuyfzand (2009, Chapter 2). The year 1953 is chosen, because it divides the 'old' period with negligible ^3H activities (at present) and relatively low pollution levels, from the 'young' period with relatively high ^3H activities and raised pollution levels. A low value for *%Y* reduces *F*, because a long detention time in the aquifer system strongly delays the arrival of pollutants, raises the chance of retardation by sorption and of biodegradation along a longer flow path, and is frequently associated with the presence of aquitards with a higher sorption capacity. The factor 21 is added to prevent that water with *%Y* = 0 would always yield a zero value for *F*, which is not realistic because a significant but smaller pollution load existed prior to 1953. This factor could be changed into for example 21 –0.21%O, with %O being the percentage of 'very old' water, older than 200 or 1000 years.

A positive alkalinity combines with practically zero mineral acidity and reduces F when Alk >0.9 meq/L, while an acidity >0.03 mmol/L (pH < 4.5) combines with zero alkalinity and increases F by at least a factor of 3.

The redox level is deduced, as suggested by Berner (1981) and Stumm (1984), from most redox sensitive main components of water, i.e. O_2, NO_3, SO_4, H_2S, Fe, Mn, and CH_4, following the algorithm of Stuyfzand (1993; 2006) given in Table 5.3. The reason is that on site determination of the redox potential runs into practical problems and is handicapped by unreliable results (Lindberg and Runnells, 1984) or difficulties in quantitative thermodynamic interpretation (Peiffer et al., 1992). Redox assessment systems similar to Table 5.3 were presented by a.o. Chapelle (2001), but these use (somewhat) different criteria and do not define the 'mixed' redox classes shown in Table 5.3. Mixed redox classes are very common in water samples from PSWFs (50% of the PSWF samples in this study), due to the inherent mixing of waters from different origins and redox environments, when long well screens are pumped.

The assessment of SO_4-reducing conditions is mainly based on estimates of the original SO_4 concentrations $(SO_4)_0$ rather than on scarce information regarding H_2S smell during sampling or H_2S data from laboratory measurements (normally <0.1 mg/L). In case of AR or RBF systems the concentration of $(SO_4)_0$ was easily determined by using the excellent linear positive relation between SO_4 and Cl concentrations in many Dutch surface waters (Stuyfzand, 1986a). Thereby the following is assumed: conservative behavior of Cl during and after infiltration, negligible SO_4 mobilization by pyrite oxidation and no SO_4 mobilization by dissolution of gypsum. The presence of gypsum can indeed be ignored in all aquifers used for fresh water supply in the Netherlands.

For water with a limited surface water contribution (with $f_{AR} + f_{RBF} < 0.2$), the following, less accurate approach was chosen to estimate $(SO_4)_0$ assuming that the SO_4 contribution by upconing of brackish groundwater starts to become important only when Cl > 20 mg/L and when the upconing potential (UP) ≥ 1. UP is defined as follows in mg/L/m:

$$\left.\begin{array}{lll} UP = Cl/\Delta Z & if & Cl > 20 \\ UP = 0 & if & Cl \leq 20 \end{array}\right\} \qquad (5.4)$$

where Cl (mg/L) = chloride concentration in pumped water; *ΔZ* (m) = vertical distance between lower well screen level and the fresh brackish interface set at 150 mg Cl/L.

Depending on UP, $(SO_4)_0$ is now calculated by

$$\left.\begin{array}{lll} (SO_4)_O = 0.14\times(Cl-20)+ & & \\ (0.5+\%Y/200)\times 20 & if & UP \geq 1 \\ & & \\ (SO_4)_O = (0.5+\%Y/200)\times Cl & if & UP < 1 \end{array}\right\} \qquad (5.5)$$

The factor 0.14 equals the SO_4/Cl ratio in ocean water; all concentrations in mg/L.

The resulting estimate of $(SO_4)_0$ is in all cases on the conservative, i.e. low side, thus resulting in a bias towards SO_4 reducing conditions. This applies in particular to PSWFs that show pyrite oxidation by either excessive fertilizer loads or declining water tables. In order to reduce this error, a second criterion was added for assigning SO_4 reduction, namely that methane should be 0.2–0.5 mg/L.

The facies parameters of Eq. (5.3) are further described in Mendizabal et al. (2011, Chapter 4), as part of a hydrochemical system analysis (HCSA), to define a PSWF typology based on the specific origin of the pumped water (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome. The spatial distribution of the facies parameters is shown for all PSWFs in the Netherlands in Fig 5.5, together with the hydrosomes defined in Mendizabal et al. (2011, Chapter 4).

5.3.2 Specific vulnerability

The assessment of the Specific Vulnerability Index to Pollutant X (VIP_X) of a well (field) follows an approach comparable to the assessment of VIP (Eq. (5.1)), by tailoring facies factor (*F*) and source factor (*S*) to the pollutant considered, while adding another factor, namely the normalized concentration of pollutant X (C_X/N_X) in the raw water of the well (field). Thus VIP_X becomes:

$$VIP_X = (S_X + C_X / N_X)\times F_X \qquad [-] \qquad (5.6)$$

where S_X = source factor for pollutant X (-); F_X = facies factor for pollutant X (-); C_X = concentration of pollutant X in raw water of well (field) (mg/L); N_X = maximum permissible concentration of pollutant X in drinking water, or if not existing, the baseline concentration (mg/L).

The calculation procedure is elucidated in Fig 5.6.

5.3.2.1 Determination of S_X

The following dimensionless specific source factor (S_X) is proposed:

$$S_X = f_G \times \frac{\sum\left(A_{WHPA}^{Y} \times w_Y \times R_X^Y\right)}{\sum\left(A_{WHPA}^{Y} \times w_Y\right)} + \sum\left(f_Z \times w_Z \times \mathrm{R}_X^Z\right) \quad [-] \qquad (5.7)$$

where f_G = fraction of ground water (-); f_z = fraction of surface water infiltrated from surface water body Z (-); w_Y = recharge rate on area covered by land use category Y (m/year); w_Z = weighting factor depending on type of surface water (1.5 if AR; 2 if RBF); A^Y_{WHPA} = part of WHPA or water catchment area covered by land use category Y (m^2); R^Y_X = risk factor for pollutant X from land use category Y (-); R^Z_X = risk factor for pollutant X from surface water body Z (-).

The dimensionless risk factors are calculated by taking:

$$R_X^Y = \frac{P90_X^Y}{N_X} \quad [-] \qquad (5.8)$$

$$\mathrm{R}_X^Z = \frac{P90_X^Z}{N_X} \quad [-] \qquad (5.9)$$

where $P90^Y_x$ = 90th percentile of concentration of pollutant *X* in shallow groundwater under land use category *Y* in a recent period (here 1979-2003) (mg/L); $P90^Z_x$ = 90th percentile of concentration of pollutant X in infiltrating surface water body *Z* in a recent period (here 1990-2008) (mg/L).

In our survey of 241 PSWFs in the Netherlands, the risk factor for the groundwater fraction is based on shallow groundwater quality data from a selection of 533 shallow piezometers of LMG, excluding piezometers in the coastal plain with brackish waters (no PSWFs present there) and in areas under influence of AR, RBF or upward seepage. The upper piezometers (at 9 m BS) were used to establish the cumulative frequency distribution including P90 for selected pollutants under a specific land use type. Land use types were aggregated into land use categories according to Table 5.2. In areas where the specific land use around a PSWF was not documented, this could be assigned by intersecting the categorized land use map (Fig 5.4) with LMG (Fig 5.1) using a Geographical Information System (GIS). The intersection method was structurally applied only to distinguish between intensive and extensive urbanization areas.

For the Netherlands, the weighting factor w_Y in Eq. (5.7) and the P90 concentrations in shallow groundwater for six land use categories and in six surface water bodies are summarized in Table 5.4. The recharge rate as a function of land use (weighting factor w_Y) refers to a mean gross precipitation of 0.82 m/year and data in Stuyfzand (1993). Note that the data for constituents that also occur in suspended state in the surface water, like Al, As and Ni, should refer to samples analyzed after filtration through a 0.45 µm millipore membrane filter.

Normalized risk factors obtained with Eq. (5.8) for every land use category and with Eq. (5.9) for the main surface water bodies, are listed in Table 5.5.

5.3.2.2 Determination of F_X

The Facies factor for pollutant X (F_X) has been adjusted, in order to cope with the different mobility or mobilization potential of pollutants, depending on alkalinity and the redox environment (Table 5.6). Many anthropogenic pollutants are most mobile or become mobilized in oxic, low alkalinity environments, and immobilized in deeply anoxic, high alkalinity environments (as happens to Ni and U). This is called, for convenience, the normal situation, which does not require any adjustment of Eq. (5.3). However, many other pollutants are mobilized or mobile in (deeply) anoxic environments (Fe, As, NH_4, benzene and mecoprop) or in high alkalinity environments (oxy-anions, As and NH_4) and some are mobilized regardless of the redox conditions (Al, Ca and Ti) or alkalinity (carbendazim, tetra, NO_3, benzene and mecoprop). Combination of the different dependencies of pollutant behavior on alkalinity and the redox level yields 14 options (Table 5.6). The score of alkalinity and redox level can thus be normal (as in Eq. (5.3)), reverse, minimum or maximum as shown in Table 5.6.

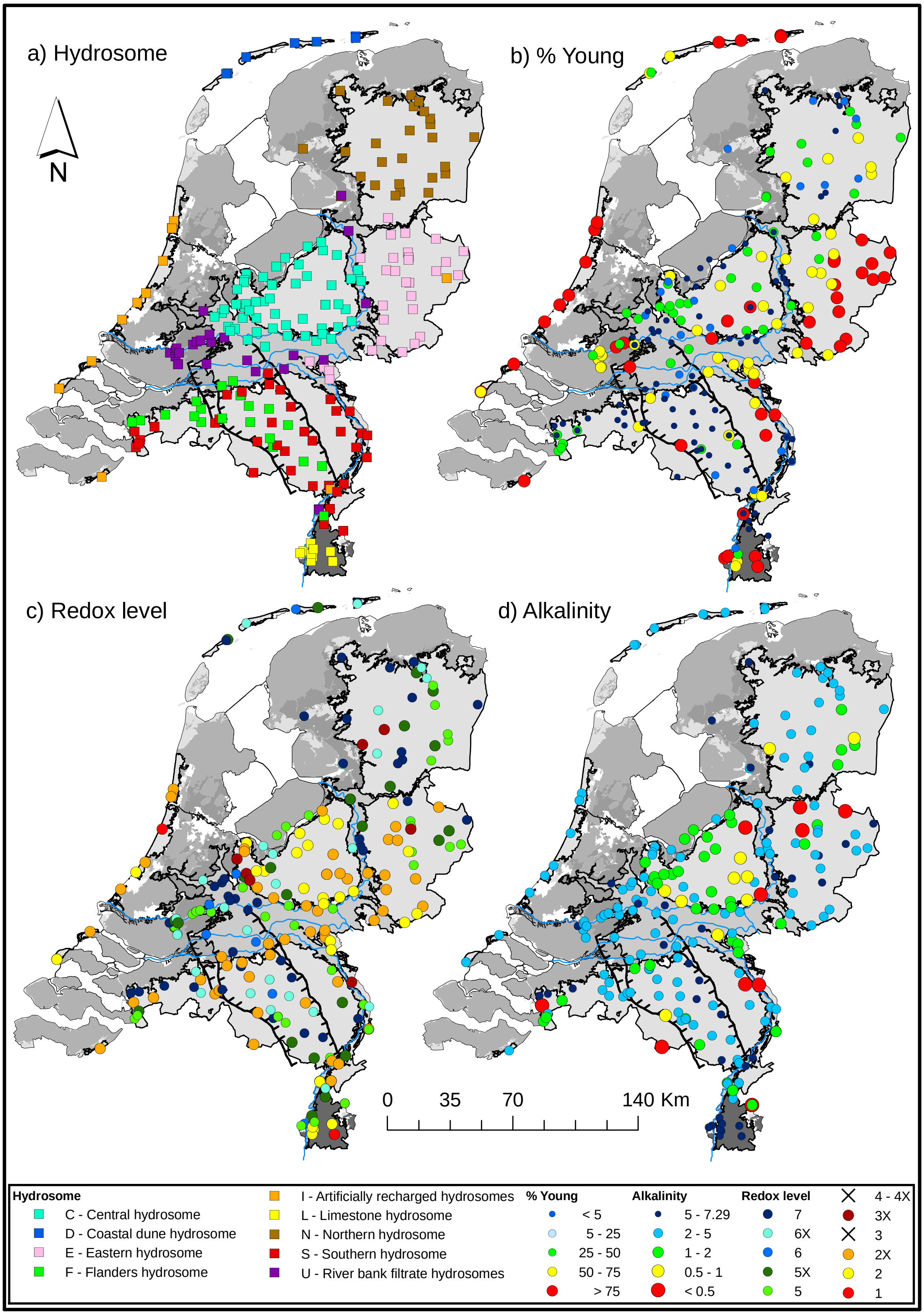


Fig 5.5: Spatial distribution of 4 intrinsic vulnerability parameters for all 241 active PSWFs in The Netherlands in 2008: the various ground water bodies (hydrosomes), % of young groundwater, redox level and alkalinity (meq/L). Mixed redox levels are coded as for instance 3X (= mix of redox level 3 with any higher level).

Table 5.4: The 90th percentile of (a) groundwater quality at 9 m BS for each land use category, as based on LMG data in period 1979-2003, and (b) surface water quality in period 1990-2008 at monitoring points 1-6 (see Fig 5.1 for location). Bent = Bentazone; Carb = Carbendazim; MCPP = Mecoprop.

	W_Y	Cl	NO3	SO4	Al	As	Ni	Bent	Carb	MCPP
	m/year	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Land use categories										
Intensive agriculture (Ai)	0.20	147	283	198	3033	9.7	73	0.39	0.070	3.39
Extensive agriculture (Ae)	0.30	159	155	259	1293	11.8	38	0.29	0.050	2.53
Intensive urbanization (Ui)	0.20	183	125	185	252	19.2	31	0.15	< 0.05	< 0.05
Extensive urbanization (Ue)	0.35	194	92	137	195	24.9	9	0.06	0.090	0.21
Forest (F)	0.20	108	71	132	6738	7.0	55	0.07	0.040	< 0.05
Nature (N)	0.45	166	14	148	65	6.4	3	0.03	< 0.05	< 0.05
Surface water										
Enschede Canal (1)	-	110	39	62	38[b]	0.5[b]	2.6[b]	0.03	< 0.05	0.13
Lake Yssel, Andijk (2)	-	223	19	91	44[b]	1.0[b]	2.0	0.03	0.047	0.10
Meuse, Eijsden (3)	-	64	17	62	51[b]	0.9[b]	1.9[b]	0.03	0.023	0.08
Meuse, Brakel (4)	-	71	19	68	18[b]	0.8[b]	1.5[b]	0.04	0.093	0.05
Rhine, Lobith (5)	-	202	17	81	61[b]	1.4	1.7	0.03	0.034	0.07
Rhine, Nieuwegein (6)	-	165	21	79	65[b]	2.6	1.7	0.05	0.050	0.03

[b] measured without filtration and estimated from relationship between filtrated and unfiltrated: $Al_{filtrated} = Al/10$; $As_{filtrated}=As/2$; $Ni_{filtrated}=Ni/3.5$.

Table 5.5: Pollution risk factors for each land use category and surface water type, after normalization to the drinking water norm (Eq. (5.8) and Eq. (5.9)). The data used are derived from Table 5.4. Bent = Bentazone; Carb = Carbendazim; MCPP = Mecoprop.

Parameter	Cl	NO3	SO4	Al	As	Ni	Bent	Carb	MCPP
Units	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Drinking water norm	150	50	150	200	10	20	0.1	0.1	0.1
Land use categories									
Intensive agriculture (Ai)	0.98	5.66	1.32	15.17	0.97	3.65	3.85	0.70	33.86
Extensive agriculture (Ae)	1.06	3.10	1.73	6.46	1.18	1.90	2.92	0.50	25.31
Intensive urbanization (Ui)	1.22	2.49	1.23	1.26	1.92	1.53	1.50	<0.50	<0.50
Extensive urbanization (Ue)	1.30	1.83	0.91	0.97	2.49	0.46	0.60	0.90	2.10
Forest (F)	0.72	1.42	0.88	33.69	0.70	2.77	0.70	0.40	0.00
Nature (N)	1.11	0.29	0.99	0.33	0.64	0.70	0.30	<0.50	<0.50
Surface water									
Enschede Canal (1)	0.73	0.78	0.42	0.19	0.05	0.13	0.25	<0.50	1.26
Lake Yssel, Andijk (2)	1.49	0.38	0.61	0.22	0.10	0.10	0.25	0.47	1.00
Meuse, Eijsden (3)	0.43	0.35	0.41	0.25	0.09	0.09	0.25	0.23	0.80
Meuse, Brakel (4)	0.47	0.38	0.45	0.09	0.08	0.08	0.36	0.93	0.50
Rhine, Lobith (5)	1.35	0.35	0.54	0.30	0.14	0.09	0.25	0.34	0.70
Rhine, Nieuwegein (6)	1.10	0.42	0.53	0.32	0.26	0.09	0.50	0.50	0.32

When required, the reversal is performed according to

$$\mathrm{Re}\,d_X = \mathrm{Re}\,d_{Max} - \mathrm{Re}\,d + 1 = 8 - \mathrm{Re}\,d \tag{5.10}$$

$$Alk_X = Alk_{MAX} - Alk = 10 - Alk \tag{5.11}$$

where Red_X = reversed specific redox level; Red = redox level of sample (see Table 5.3); Red_{Max} = maximum redox level (=7); Alk_X = reversed alkalinity; Alk = alkalinity of sample (as HCO_3 + CO_3 in meq/L); Alk_{Max} = maximum alkalinity (=10).

The minimum or maximum is used for pollutants with respectively a high or low mobilization regardless of the redox level or alkalinity. Minima for both Red and Alk are used for pollutants that are mobile or mobilized in any environment (bentazone and Cl). Maxima for both Red and Alk pertain to immobile pollutants under any circumstances, such as PCB.

Substitution of the specific facies parameters for pollutant *X* in Eq. (5.3) (or the original facies parameters when no reversal is required) yields the specific facies factor for pollutant *X* (F_X).

Table 5.6: Water quality parameters selected for the specific groundwater vulnerability assessment, with their mobility, mobilization or occurrence in selected redox and alkalinity environments. Partly based on data in Stuyfzand (1998a) and Stuyfzand et al. (2007).

Redox	Low mobility / low mobilization			High mobility / high mobilization		
	Low Alk	High Alk	Alk Indiff	Low Alk	High Alk	Alk Indiff
Oxic	As, NH4	Fe	benzene	Ni, U	oxy-anions	carbendazim, tetra, NO3,SO4
Deeply Anoxic	oxy-anions	Ni, U	carbendazim, tetra, NO3,SO4	Fe	As, NH4	benzene, mecoprop
Redox Indifferent	Ca	Al, Ti	PCB	Al, Ti	Ca	bentazone, Cl
Setting of Alkalinity (top) and Redox (bottom)						
Oxic	reverse reverse	normal reverse	max reverse	normal normal	reverse normal	min normal
Deeply Anoxic	reverse normal	normal normal	max normal	normal reverse	reverse reverse	min reverse
Redox Indifferent	reverse max	normal max	max max	normal min	reverse min	min min
Scoring of Alkalinity and Redox with settings						
	normal		reverse		min	max
Alk	0-10 = 0-10; >10 = 10		0-10 = 10-0; >10 = 0		0	10
Redox unmixed	1-7 = 1-7		1-7 = 7-1		1	7
Redox mixed	1-7 = 1-7		3 = 5 3.5 = 4.5 4 = 4 4.5 = 3.5	5 = 3 5.5 = 2.5 6 = 2 6.5 = 1.5	3	6.5

5.4 Results

5.4.1 Presentation of results

VIP and VIP_X were calculated for 241 active PSWFs in the Netherlands in 2008. The spatial distribution of VIP and of VIP_X for NO_3, SO_4, Ni and Bentazone is shown in Fig 5.7. In the 35 PSWFs with two samples obtained from different aquifers, the more protected sample (lower VIP, smaller dot) is plotted on top of the more vulnerable one (larger dot), in order to facilitate the visualization of both symbols. Note that the black stars in Fig 5.7 represent PSWFs for which no WHPA has been defined. In most cases, certainly in the area within the Central Graben (see Fig 5.7), these PSWFs pump from deep, confined aquifers delivering water older than 1000 years. This makes them highly protected against any pollutant released at the surface, and yields a VIP_X close to 0. The spatial distribution of VIP is also shown in three cross sections over the country (Fig 5.8).

Table 5.7 shows seven intrinsic vulnerability classes with the linked average specific vulnerability scores for nine pollutants, and how VIP is distributed in the Netherlands over the 241 PSWFs and the nine hydrosomes mapped in Fig 5.5. Results for these nine main groundwater bodies, with further subdivision where useful, are summarized in Table 5.8.

5.4.2 Intrinsic vulnerability of PSWFs

Our national survey of the intrinsic vulnerability of 241 PSWFs towards pollution in 2008 yields the skewed distribution of VIP shown in Table 5.7.

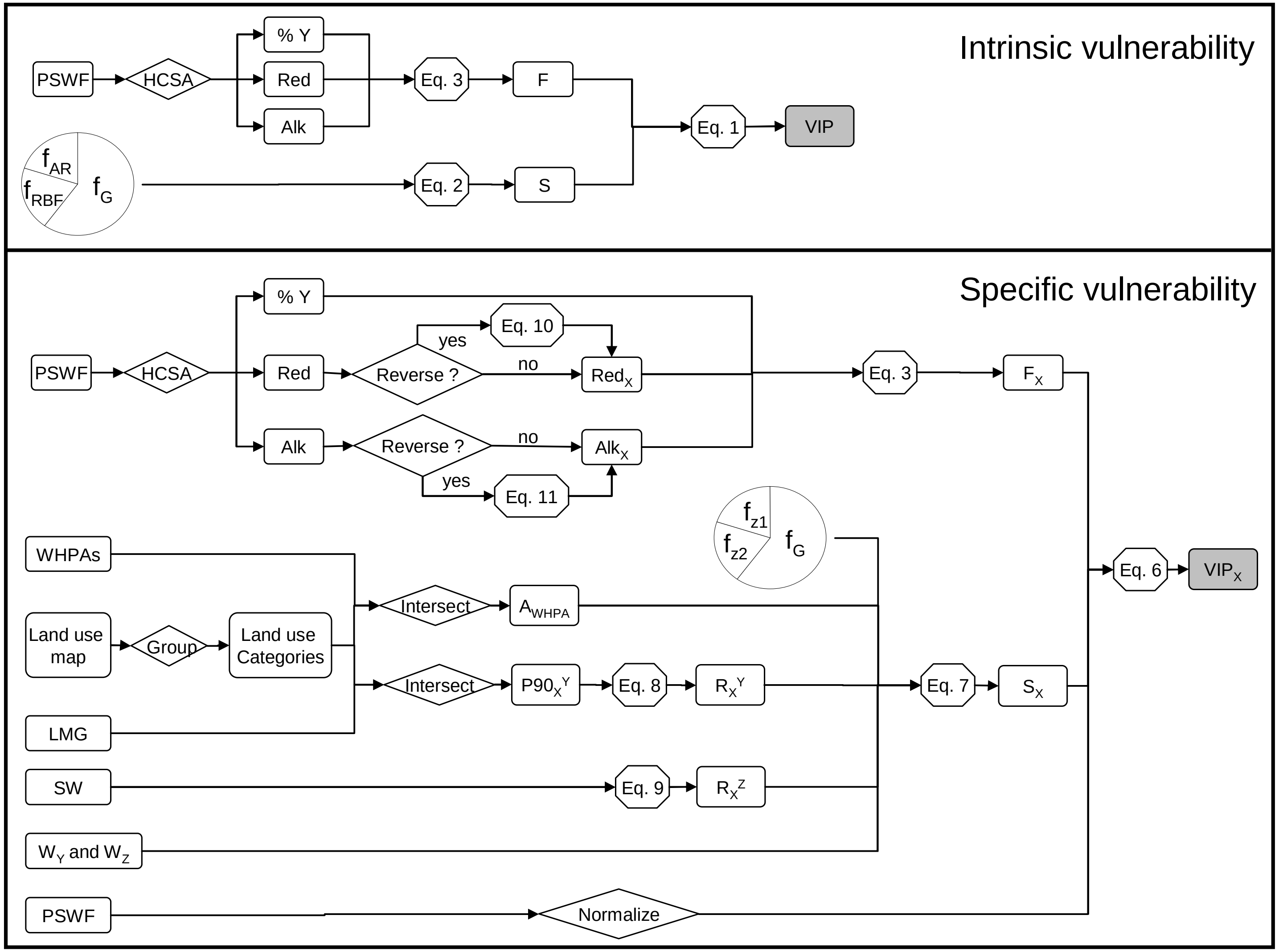


Fig 5.6: Procedure to calculate the intrinsic and specific vulnerability of PSWFs (respectively above and below). SW = Surface water quality. Other acronyms are explained in text.

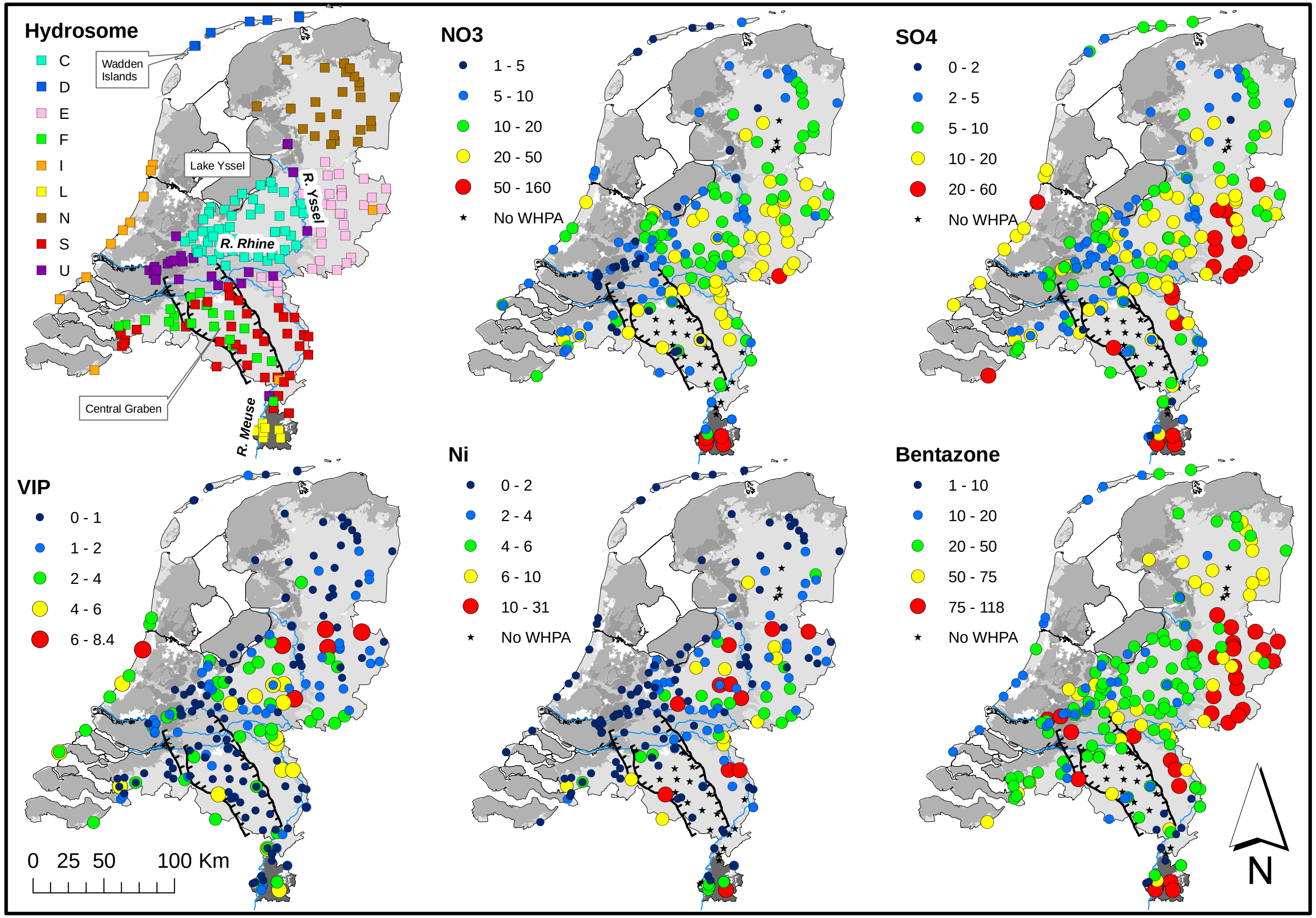


Fig 5.7: Intrinsic (VIP) and specific (VIP_X) vulnerability of groundwater resources at the depth of abstraction, for 241 water samples obtained from the 206 active PSWFs in the Netherlands in 2008, together with the 9 hydrosomes. The black stars represent PSWFs with no WHPA defined, which in most cases (certainly in the area within the faults) are deeply confined PSWFs delivering water older than 1000 years and therefore, highly protected against pollutants released at the surface.

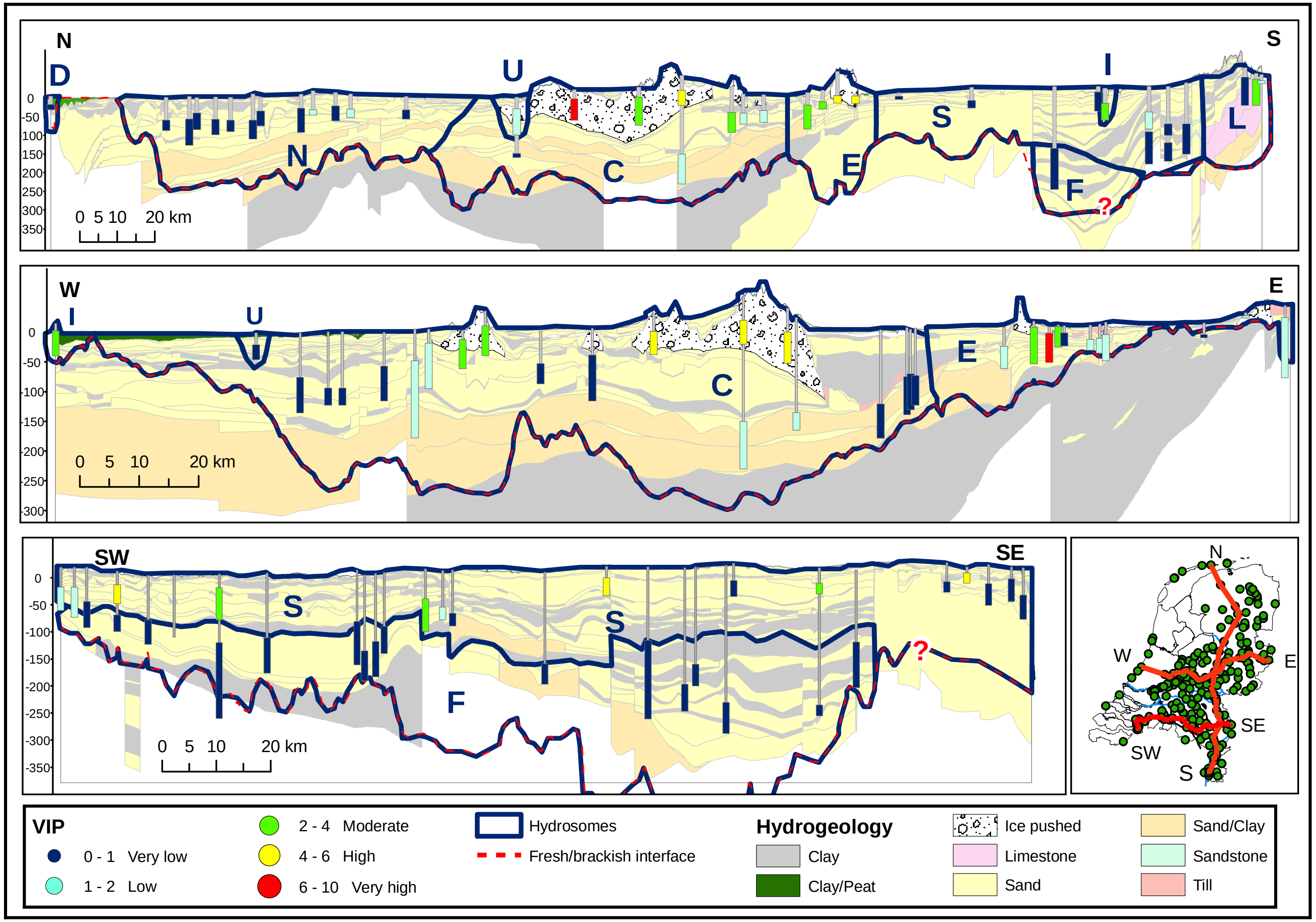


Fig 5.8: Hydrogeological cross sections over the Netherlands in the directions NS (upper), WE (middle) and SW-SE (lower), with the location and depth of abstraction (in m ASL) of PSWFs, simplified to a single screen covering the entire depth of abstraction of individually pumped wells. Geological data obtained from REGIS II.1 (Vernes and van Doorn, 2005). The color of the well screen indicates the VIP score. The inset location map shows the position of the cross sections and active PSWFs in 2008. Hydrosomes (groundwater bodies) are delimited by dark blue lines and the fresh/brackish water interface (1000 mg/L Cl) is given by the red line.

Table 5.7: Intrinsic vulnerability classes, with the score of Dutch Public Supply Well Fields (PSWFs) and Dutch hydrosomes, and with the average specific vulnerability for 9 pollutants. Ben = Bentazone; Car = Carbendazim. Shallow = mostly <70 m BS and/or in phreatic aquifer; Deep = mostly >70 m BS and/or in semiconfined aquifer.

Intrinsic	Vulnerability	PSWF	Average Specific Vulnerability of PSWFs ($^{S}VIP_{X}$)									Hydrosomes (see Fig.7+8)	
^{I}VIP	Class	%	Cl	NO3	SO4	NH4	Al	As	Ni	Ben	Car	shallow #	deep
<0.5	Extremely low	24.5	14.3	4	2	40.6	13	1.9	0.4	22.3	0.0	D^{1}	C, F, L, N, S
0.5-1.0	Very low	25.7	27.8	9	5	51.4	28	1.9	1.0	39.5	0.2		
1-2	low	24.9	43.8	15	10	25.5	39	1.1	2.0	41.8	0.8	C, D, E, I, L, N, S, U	none
2-4	Moderately high	16.2	42.1	24	17	15.0	63	0.7	3.8	43.1	2.4		
4-6	high	6.2	32.5	33	20	14.6	140	0.6	8.4	42.2	2.0	C^{2}, E^{2}, I^{3}, L^{4}, S2	none
6-10	Very high	2.5	35.9	28	20	10.5	210	0.5	14.8	41.7	3.5		
>10	Extremely high	0	-	-	-	-	-	-	-	-	-	none	none

1 = shallow but below anoxic calcareous aquitard; 2 = acidified aquifer; 3 = open recovery or low reduction capacity; 4 = oxic system.

About 50% of all PSWFs shows an extremely low to very low VIP (<1). These PSWFs are mainly observed at greater depth or in the exfiltration zones of hydrosomes C, F, L, N and S (frequently within a confined aquifer), and in hydrosome D (Fig 5.7 and 5.8 and Table 5.7 and 5.8). They combine a (sufficiently) long travel time with a high redox level, high alkalinity and low to zero percentage of infiltrated surface water (<20%). The water has a deeply anoxic, high alkalinity character due to prolonged contact with reactive sediments in calcareous and reducing deeper parts of the aquifer system. Hydrosome F scores best (VIP = 0.3) due to the lowest average percentage of young groundwater (0%) and highest average percentage of deeply anoxic water (97%) of all 241 PSWFs (Mendizabal et al., 2011, Chapter 4). It is situated in a deep, very reactive, (semi)confined aquifer largely composed of glauconitic sands of Tertiary age (section *SW-SE* in Fig 5.8).

Low to moderately high scores (1-4) are found in 41% of all PSWFs, notably in the relatively shallow hydrosomes I (with AR), U (with RBF) and E, and at shallow depth in the infiltration area of hydrosomes C, L, N and S (Fig 5.7 and Table 5.7 and 5.8).

The remaining 9% of all PSWFs has a (very) high VIP (4-10). These very vulnerable PSWFs have shallow well screens and are pumping from: (a) acidified, phreatic sandy aquifers in either Pleistocene, ice pushed hills (hydrosomes C and E) or eolian Pleistocene hills (hydrosome S); (b) (sub)oxic artificially recharged coastal dunes (hydrosome I); or (c) oxic limestone (hydrosome L).

The acidified upper tens of meters of Pleistocene sandy aquifers also show a low organic matter content, and therefore yield a very low alkalinity and redox level. Both aspects are due to natural leaching for many millennia in combination with anthropogenic impacts especially since the early 1900s. The latter consist of a lowering of groundwater tables due to drainage and groundwater pumping, and increased acid inputs by atmospheric deposition.

Only those AR systems score a VIP >4, which have a very high fraction of AR (>80%) and a relatively low redox level (≤2). These (sub)oxic systems are exclusively situated in the coastal dunes where large scale AR started in 1955. They show a low reduction capacity due to a high level of pretreatment, prolonged flushing with oxic surface water, relatively short travel times and a low reduction capacity of dune sand. One system has an open recollection system (composed of canals instead of wells or drains) where reaeration reduces the redox level to level 1 and thereby contributes to the highest VIP score of all (8.4).

Just one PSWF in limestone also presents a high VIP (4.4), namely the only one with redox level 1 (compare Fig 5.5 and 5.7). All other PSWFs in limestone show a surprisingly low VIP (0.4-2.1), notwithstanding a rather young age (*%Y* = 13-86%) and, in the shallow PSWFs, a rather low redox level (2). This is mainly due to (a) the high acid buffering capacity of the limestone aquifer, resulting in a high alkalinity of the pumped water (Fig 5.5.d), and (b) a rather high redox level (5-6) in the deeper PSWFS.

PSWFs with bank filtration of Rhine River water present a lower VIP as compared to PSWFs with artificial recharge using the same source water (compare I_R and U_R in Table 5.8). This is due to longer travel times and a more anoxic character after passage through reducing clay and peat layers in the fluvial plain. There is no difference in VIP between AR and RBF systems using Meuse River water (compare I_M and U_M in Table 5.8), because of comparable travel times and redox levels. Contrary to most Rhine RBF systems in a semiconfined sandy aquifer, the RBF systems along the Meuse River pump from a phreatic gravel aquifer without interaction with clay and peat layers.

5.4.3 Specific vulnerability of PSWFs

The specific vulnerability of PSWFs towards selected pollutants (VIP_X) shows spatial patterns that deviate from VIP (Fig 5.7), when the mobility or mobilization of the specific pollutant does not show a ‘normal’ relation with the redox level and alkalinity (Table 5.6), or when the land use within the WHPA leads to an associated risk factor which is either very low (nature) or very high (intensive agriculture) while VIP is respectively very high or very low. Thus, PSWFs with high intrinsic vulnerability in areas of limited contaminant load may have a low specific vulnerability, and PSWFs with low intrinsic vulnerability in areas of high contaminant load may have a high specific vulnerability. A good example of this inverse relation is formed by the artificially recharged PSWFs in the coastal dunes with moderately high to very high VIP, but in most cases a (very) low VIP_X regarding NO_3, Ni and bentazone (Fig 5.7). This is due to the relatively low concentrations in the pretreated surface waters and also in the admixed local groundwater, which is derived from the dune nature reserve, where anthropogenic activities with a negative impact on groundwater quality are strictly forbidden. In addition, the high alkalinity of the river water prevents Ni to be mobilized from the aquifer matrix.

On the contrary, many PSWFs in limestone present a relatively low VIP but (much) higher VIP_X towards most pollutants depicted in Fig 5.7, due to the intensive agriculture in the area (Fig 5.4) and the short travel times within the aquifer (Fig 5.5b).

Table 5.8: Mean VIP and VIP_X for all PSWFs in the Netherlands, subdivided into the 9 hydrosomes shown in Fig 5.5 (C, D, E, F, I, L, N, S, U), with further subdivision according to depth (d = deep; s = shallow) or surface water type (m = Meuse; o = other; r = Rhine; y = Lake Yssel).

Hydrosome	Nr of PSWFs	F	S	VIP	VIP_X						
					Cl	NO_3	SO_4	Al	As	Ni	Bent[a]
C_d	26	0.5	1.0	0.5	20	7	4	19	1.9	0.8	36
C_s	29	3.2	1.0	3.2	27	16	10	75	0.6	3.7	27
D	7	0.7	1.0	0.7	43	3	6	11	1.5	0.5	12
E	30	1.8	1.0	1.8	37	30	18	52	1.1	3.8	80
F	25	0.3	1.0	0.3	15	4	2	15	2.1	0.5	17
I_m	4	2.6	1.4	3.7	34	12	15	4	0.4	0.8	18
I_o	2	1.6	1.4	2.2	56	14	14	15	0.6	1.3	42
I_r	4	2.8	1.4	3.9	41	10	16	10	0.4	0.9	13
I_y	3	2.4	1.3	3.2	84	9	17	21	0.4	1.1	14
L_d	4	0.6	1.0	0.6	20	5	4	11	1.0	0.4	24
L_s	5	2.0	1.0	2.0	38	73	27	44[b]	1.0	5.2[b]	94
N_d	20	0.5	1.0	0.5	23	7	4	16	2.3	0.6	37
N_s	7	1.4	1.0	1.4	33	18	10	62	1.3	3.2	63
S_d	26	0.7	1.0	0.7	12	3	2	10	0.6	0.3	16
S_s	18	1.4	1.0	1.4	23	10	7	88	0.6	2.9	26
U_m	2	3.1	1.2	3.7	14	7	11	1	0.0	0.2	4
U_o	2	0.5	1.4	0.7	54	6	5	9	3.0	0.4	38
U_r	27	0.8	1.8	1.4	89	5	7	5	1.0	0.3	25
Minimum		0.25	1	0.25	0.4	0	0	0	0	0	0
Mean		1.45	1.11	1.59	31.3	14	9	44	1.4	2.4	37
Maximum		7.96	1.99	8.35	117	160	59	347	8.5	30.9	118

[a] Bent = Bentazone; [b] Values too high because the national P90 concentrations are too high for limestone.

The level of VIP_X differs for the pollutants considered in Fig 5.7 and Table 5.8, because of differences not only in their pollution load and actual concentration, but also in their maximum permissible concentration in drinking water. Overall high values in Table 5.8 are obtained for Cl and bentazone, which behave conservatively (redox and alkalinity indifferent). Infiltrated Lake Yssel and Rhine River water score highest in Cl (I_Y and I_R in Table 5.8), but show a relatively low score for bentazone. This is completely dictated by the concentrations in the infiltrating surface water. The highest bentazone vulnerability is observed in the shallow parts of hydrosomes E, L and N (Table 5.8) where intensive agriculture constitutes a very strong source and where bentazone already reached the wells.

Other PSWFs with a low bentazone vulnerability are the ones pumping water without bentazone from either hydrosomes F and S_d, which are 100% composed of very old water, or hydrosome D which is located in the coastal dune nature reserve.

Al and Ni show a similar spatial distribution (Table 5.8 and Fig 5.7), with high vulnerabilities for low alkalinity PSWFs especially when situated in areas with intensive agriculture and forests (Table 5.6). The source of Al mainly consists of Al (hydr)oxides that dissolve at low pH (roughly <5.4), whereas the main source of Ni is the oxidation of pyrite and the dissolution of Al-silicates, both in an acidic environment as well. Table 5.8 and Fig 5.7 show, however, an erroneously high vulnerability of limestone PSWFs for Ni and Al, because limestone should protect best against acidification. The error crept in by taking for their risk factor, the 90th percentile of the whole national monitoring network, which includes acidified sandy regions without limestone. The solution of this problem is to use the shallow local monitoring network for the limestone aquifer. This recommendation to use the local shallow network, if available, pertains to all PSWFs.

NO_3 and SO_4 are both mobile or mobilized in (sub)oxic environments, regardless of the alkalinity, and are reduced in respectively anoxic and deeply anoxic environments. They show indeed similar vulnerability patterns (Fig 5.7). However, VIP_{NO3} is higher than VIP_{SO4} in PSWFs without AR or RBF, due to a higher risk factor for groundwater in areas with intensive agriculture and urbanization (Table 5.5). Shallow PSWFs in areas of intensive agriculture show the highest NO_3 vulnerability. PSWFs with AR or RBF show a relatively high VIP_{SO4}, as a result of relatively high concentrations in the infiltrated surface water. PSWFs in the coastal dunes present low VIP_{NO3} due to the lack of agriculture in the WHPA, and by NO_3 reduction in a marine aquitard. Their VIP_{SO4} is higher, because of less SO_4 reduction in this aquitard and higher atmospheric inputs.

Arsenic vulnerability of PSWFs shows a completely different pattern (Table 5.8). It is high in deeply anoxic, high alkalinity environments, which predominate in hydrosome F, the deeper parts of hydrosomes C and N and in specific RBF systems (U_O).

5.5 Discussion

VIP and VIPx belong to the hydrochemical type of vulnerability assessment methods which are tailor made for PSWFs but can also be applied to monitor wells. VIP is more retrospective than the hydrogeological methods, because VIP addresses aquifers that are already pumped. The advantage of VIP is that the data are easily accessible and offer a broad hydrochemical scan.

It should be realized that both intrinsic and specific vulnerability are not constant properties of PSWFs. This is not a surprise for the specific vulnerability, because the land use within the WHPA, the pollution load connected to various types of land use, and the current concentration of pollutant X will certainly change over time. In addition, the size of the WHPA (or rather ground water catchment area) may vary due to changes in natural recharge or pumping.

It is more surprising that the intrinsic vulnerability should also often be considered a dynamic property of PSWFs, even though it will be more constant than the specific vulnerability. The reason is that normally inevitable changes in PSWFs take place, which bear a direct impact on VIP. Such changes are grouped under the term well field adaptation measures, defined in Mendizabal and Stuyfzand (2009, Chapter 2) as measures taken in order to produce enough water volume to fulfill the drinking water demand, with sufficient quality for preparation of drinking water at the lowest cost and avoiding expensive treatment. They include among others the drilling of new wells, changes in pumping rate, abandoning polluted wells (shallow ones to escape from pollutants emitted at land surface, or deeper ones when salt groundwater is upconing) or switching from groundwater to either AR or RBF systems. These measures rapidly influence the hydrological response curve (and thus *%Y*) and the source factor (if modifying the AR or RBF fraction), and, normally with a delay, also the redox level or alkalinity of the water pumped.

PSWFs with high intrinsic vulnerability in areas of limited contaminant load may have a low specific vulnerability, and PSWFs with low intrinsic vulnerability in areas of high contaminant load may have a high specific vulnerability. Such conditions are quite common in the Netherlands. Most important is to identify those PSWFs with high VIP and low VIP_X in order to preserve their water quality in time by additional protection measures (if still needed). For PSWFs where both VIP and VIP_X are high, it may be too late for protection but early enough to program mitigative and curative measures.

VIP strongly depends on the estimation of the percentage of young water (*%Y*). In most cases, *%Y* was obtained from the hydrological response curve (HRC) computed with a calibrated groundwater model. For PSWFs lacking a calibrated groundwater model, the HRC was estimated following the method introduced in Mendizabal and Stuyfzand (2009, Chapter 2). This method consists of a simple analytical approximation, which is corrected on the basis of a single tritium analysis of the raw water in year x and a known tritium input function for the aquifer. It may have overestimated *%Y* in case tritium data are lacking for relatively shallow PSWFs pumping from a confined aquifer. This situation which would yield an overestimation of VIP was very rare. On the other hand, the HRC of a PSWF obtained from a calibrated groundwater model is usually calculated for the maximum abstraction capacity of the PSWF as stated in its exploitation license. Real pumping rates, however, are usually smaller, which may change the *%Y* as well.

A limitation of the method is perhaps that application of VIP_X to any pollutant X requires a definite setting of the pollutant's behavior in dependency of the redox level and alkalinity according to Table 5.6. This could be problematic when there is lack of knowledge (for instance regarding the behavior of a new organic pollutant) or when other hydrogeochemical facies factors dominate over redox level and alkalinity (like ionic strength, temperature or enhanced transport by colloidal particles). Another inaccuracy may arise with VIP_X when there is a very reactive layer in between the depth of the shallow groundwater monitoring network and the greater depth of abstraction by the PSWF; a layer capable of completely removing pollutant X for a very long time, independent of the redox level or alkalinity. In that case VIP_X yields an overestimation.

An erroneously high vulnerability of limestone PSWFs for Ni and Al was caused by taking for their risk factor, the 90th percentile of the whole national monitoring network, which includes acidified sandy regions without limestone. This error indicates that for any region preferably the shallow local monitoring network should be used, if available.

Although here presented specifically for PSWFs, this methodology can also be directly applied to springs (captured or not). Application to groundwater samples from observation wells requires, however, some adaptations, for instance by (1) substituting *%Y* in Eq. (5.3) by the age of the groundwater (preferably scaled between 0 and 100); and (2) tracking back the land use category at the recharge point.

5.6 Conclusions

A new method is presented for the quantification of the intrinsic vulnerability (VIP) of public supply well fields (PSWFs) and their specific vulnerability (VIP_X) towards pollutant X, either a macro constituent, trace element or organic compound. The method requires easy-to-access data, such as (1) the quality of raw water of PSWFs, shallow groundwater as sampled via observation wells, preferably within the WHPA, and surface water prior to its infiltration in case of PSWFs receiving contributions from artificial recharge or river bank filtration; (2) a land use map of the area; and (3) an (inter)national drinking water standard or otherwise some baseline value. More elaborated data, such as the WHPA, the age distribution of the pumped water and the fraction of surface water delivered by a PSWF are not always readily available, but can be estimated by different methods, as discussed.

Our national survey of the intrinsic vulnerability of 241 PSWFs in the Netherlands in 2008 revealed in general a good quality status of the raw water, with a low VIP (<1) in 50% of all PSWFs, an intermediate VIP (1-4) in 41%, and a high VIP (4-10) in 9%. PSWFs with VIP <1 are mainly observed at greater depth, in (semi)confined aquifers or in the exfiltration zones of large hydrosomes. The very vulnerable PSWFs have shallow well screens and are pumping from either acidified, phreatic sandy aquifers, (sub)oxic, artificially recharged coastal dunes, (sub)oxic river banks or oxic limestone. Overall high values of the specific vulnerability are found for Cl and bentazone, which behave conservatively (redox and alkalinity indifferent). PSWFs with the highest bentazone vulnerability are those pumping shallow groundwater from areas with a high density of intensive agriculture. Al and Ni show high vulnerabilities for low alkalinity PSWFs especially when situated in areas with intensive agriculture and forests.

VIP and VIP_X are not based on site specific ranges of varying sets of hydrogeological or geochemical parameters, but on standard factors exclusively derived from the water composition. This makes it a robust objective method that can be applied elsewhere and could therefore serve as a means to standardize vulnerability assessment of PSWFs.

The method is a straight forward procedure that can be easily programmed, so that the vulnerability of PSWFs on, for example, a national scale, can be automatically quantified, provided all the previously mentioned data are available. Some modifications may be needed when applied in other countries or when used for other purposes than drinking water supply, for instance by using each aquifer's baseline concentration instead of the drinking water norm (for normalization in Eq. (5.8) and Eq. (5.9), and by changing the land use categories.

5.7 Acknowledgements

The research was funded by the Joint Research Program of the Dutch Waterworks (BTO) and Delft Cluster, project number CT05.30. H. Dik is greatly acknowledged for supplying data on the well field protection areas, T. van der Heijden for the land use map, H. van der Meij and G. van der Meer for data on the Dutch national and provincial groundwater quality monitoring networks, T. van der Linden and A. Dries for data on pesticides, and G. van de Haar for data from the Dutch national surface water quality monitoring network. H. Boukes is acknowledged for his comments on earlier versions of VIP. H. Haitjema and two anonymous reviewers are greatly acknowledged for their critical review on a previous version of this manuscript, which greatly improved the quality of this contribution.

Chapter 6

6 Hydrochemical trends for public supply well fields in the Netherlands (1898-2008), natural backgrounds and upscaling to groundwater bodies[7]

Abstract

Statistical trend analysis is applied to a 110 years long groundwater quality time series from the national network of public supply well fields (PSWFs) in the Netherlands. Such a groundwater quality monitoring network should be available in many countries, so that approaches and experiences presented here could be interesting world wide.

Trendless concentration data series measured in the early years, which should bear the least anthropogenic influences, are selected to quantify the regional natural background concentration levels (NBLs) of groundwater resources at the depth of abstraction. Trends in the period 1960-2005, which contained a more homogeneous data set, are normalized to drinking water standards, mapped in planar view and cross sections, and used to identify the responsible hydrochemical processes. Seven representative trend bundles are defined by aggregation of trends for individual chemical parameters. Trend reversals due to either environmental sanitation measures or well field adaptation measures are identified by comparing significant trends obtained for two different periods within the time series.

Natural Background Levels (NBLs) for individual PSWFs are upscaled to the national groundwater body level (as reported to EU), by aggregating them according to a PSWF typology based on a Hydrochemical System Analysis. This aggregation method groups together PSWFs that deliver waters of the same origin and similar hydrogeochemical environment. PSWFs delivering old groundwaters with a very stable quality are clearly differentiated from PSWFs pumping highly vulnerable aquifers characterized by strongly deteriorating water quality trends.

Results are presented on national maps of The Netherlands with NBLs and water quality trends for selected major constituents. A normalized concentration change index (NCC) is defined and mapped to relate the quality difference between a recent survey (in 2008) and calculated NBLs, to the EU drinking water standards.

---

[7] This chapter was submitted for publication as Mendizabal, I., Stuyfzand, P.J., Baggelaar, P.K., Hydrochemical trends for public supply well fields in the Netherlands (1898-2008), natural backgrounds and upscaling to groundwater bodies. Journal of Hydrology

6.1 Introduction

European legislation enforces all EU member states to monitor and assess the quality and quantity of their waters on the basis of common criteria and to identify and reverse groundwater pollution trends before 2015 (EU, 2000; 2006b; 2008). For this purpose, numerous national groundwater quality monitoring networks (NGQMNs) are being developed, not only in Europe like in Denmark (Juhler and Felding, 2003), The Netherlands (van Duijvenbooden et al., 1993) and the UK (Ward et al., 2004)), but also in other countries, a.o. Egypt (Dawoud, 2004), Korea (Kim et al., 1995; Lee et al., 2007), New Zealand (Daughney and Reeves, 2005), South Africa (Parsons and Tredoux, 1995) and the US (Rosen and Lapham, 2008). Such networks are regularly monitored to fulfill three main purposes: (1) establish the actual groundwater quality in relation to soil use, soil type and hydrogeological conditions (Boumans et al., 2005; Frapporti et al., 1993; Fraters et al., 1998; Hendrix and Meinardi, 2004; Meinardi, 2003; Pebesma and de Kwaadsteniet, 1997; Reijnders et al., 1998; van den Brink et al., 2007); (2) identify trends in groundwater quality (Batlle Aguilar et al., 2007; Boumans et al., 2005; Broers and van der Grift, 2004; Burow et al., 2007; 2008; Daughney and Reeves, 2006; Frapporti et al., 1994; Reynolds-Vargas et al., 2006; Stuart et al., 2007; Visser et al., 2009; Xu et al., 2007); and (3) establish the regional natural background level of concentrations in groundwater (Coetsiers et al., 2009; Edmunds et al., 2002; Edmunds and Shand, 2008; Fraters et al., 2001; Lee and Helsel, 2005; Limbrick, 2003; Meinardi, 2004; Meinardi et al., 2003; Wendland et al., 2008).

The actual groundwater quality is successfully established with data gathered via these networks. Groundwater quality trend detection and quantification of natural background levels (NBLs) are, however, hindered by insufficient length of time series, which in most cases do not cover the period of interest (Visser, 2009). Such networks are operational for 20 to 30 years at most, while the main groundwater quality deteriorating processes, due to intensive agriculture, urbanization, industrial activities and atmospheric pollution, threaten groundwater resources for more than 60 years.

Establishing the natural background composition of groundwater is crucial to identify and quantify contamination of groundwater by anthropogenic sources. The natural background level (NBL) is defined as the concentration level in water as controlled by natural geogenic, biological and atmospheric processes. The regional background levels obtained for young groundwaters normally show clear anthropogenic influences including contamination, which makes it hard today to define their NBL. The problem is usually solved through backward trend analysis of young groundwaters or by selecting, if available, a data subset from older monitoring networks that is assumed to reflect the natural composition, as evidenced by hydrological and geochemical tracers (Edmunds, 2008). In such cases, the data set selection is crucial and old analyses are the only direct reference to establish the natural background concentration (Griffioen et al., 2008).

A monitoring network that is available in most countries while being also useful to fulfill the above mentioned three purposes, is the network of public supply well fields (PSWFs), which are monitored on a regular basis as an integral part of the quality surveillance of national drinking water supply. The network has already successfully been used in The Netherlands to (1) establish the actual groundwater quality status at the depth of abstraction and on the groundwater body (GWB) level (Mendizabal et al., 2011, Chapter 4), and (2) quantify the intrinsic vulnerability of PSWFs and their specific vulnerability towards numerous pollutants, either macro constituents, trace elements or organic compounds (Mendizabal and Stuyfzand, 2011, Chapter 5).

The advantages and disadvantages of this monitoring network as compared to dedicated networks that use specific monitoring (observation) wells are discussed in Mendizabal and Stuyfzand (2009, Chapter 2). The main advantage of PSWFs is their longer period of record, which in many cases fully covers the period of interest. In The Netherlands, where the centralized monitoring of the raw water quality of PSWFs started in 1898, the earliest data provide a valuable means to assess the NBL of the aquifers they pump. In addition, they can also be considered representative for a huge volume of groundwater, the quantity of which is registered as well. The mixed character of raw water samples from a PSWF is, however, also one of the main disadvantages, due to a more laborious interpretation as compared to samples from conventional observation wells. In Mendizabal and Stuyfzand (2009, Chapter 2), guidelines are introduced to interpret such data, based on (a) historical changes in the well field, (b) the origin of the groundwater mixture (local precipitation, river bank filtrate (RBF), artificially recharged surface water (AR) or recent/ancient sea water), and (c) the approximate age distribution of the water pumped.

In this contribution, a unique database with 110 years of water quality data from a maximum of 351 PSWFs in the Netherlands is used for the first time, to determine NBLs and hydrochemical trends for selected parameters and for individual groundwater bodies. Trends for Dutch PSWFs were investigated before (Cirkel and Stuyfzand, 2004; Reijnders et al., 1983; van Beek et al., 1990), but were limited to a much shorter time interval covering 25 years at most. New approaches presented here include simple statistics for determining NBLs, trends and trend reversals, a normalization procedure for trend mapping, the definition and mapping of so-called trend bundles and the normalized concentration change index, and a method to upscale NBLs for individual PSWFs to their national groundwater body with distinction of hydrochemical zones.

6.2 Materials and methods

6.2.1 Hydrogeological setting

The major fresh groundwater resources in The Netherlands, pumped by PSWFs, are contained in unconsolidated siliclastic sediments of Tertiary and Quaternary age, composed of alternating layers of marine, eolian, fluvial, paludal and glacial origin. Only one, moderately large fresh groundwater body is observed in hardrock, namely in Cretaceous limestone in the south-east of the country (Fig 6.1). A small fresh groundwater body in sandstone located in the eastern part of the Netherlands was also used for drinking water production in the past and is still partly used by one PSWF. The major fresh groundwater bodies with active recharge are found in the Holocene coastal dunes, the northern, eastern, central and southern Pleistocene uplands, and the Cretaceous limestone hills (inset of Fig 6.1). The southern Pleistocene sands are underlain by a deep confined aquifer recharged either in Flanders (Belgium) or in the Dutch province of Brabant (Fig 6.4; N-S and SW-SE), with an estimated age in the order of 1,000 to 10,000 years (Mendizabal et al., 2011, Chapter 4).

Groundwater resources have been supplemented by AR systems mainly in the coastal dunes and by RBF along the rivers Rhine and Meuse. Direct intake of surface water (19% of a total annual production of 1187 Mm^3 of drinking water in 2004) is not considered in this study. Groundwater resources were elsewhere subdivided into fairly homogeneous groundwater bodies with specific origins (hydrosomes) and characteristic hydrochemical zones (facies) within each hydrosome (Mendizabal et al., 2011, Chapter 4). Such a Hydrochemical System Analysis (HCSA) undertaken upon all active 208 PSWFs in 2008 yielded nine hydrosomes (seven hydrosome complexes and two hydrosome types) and eleven facies parameters, defined on the base of age, redox and alkalinity indices. The main characteristics of these major hydrosomes are summarized in Table 6.1.

Table 6.1: Hydrosome complexes (HC) and types (HT) in The Netherlands and their main characteristics. Modified from Mendizabal et al. (2011, Chapter 4).

Code	Hydrosome	Nr PSWFs	Origin[a]	Source[b]	Aquifer material[c]	Sediment age[d]	Depositional environment[e]	% confined
B	Bentheimer sandstone (HC)	2	P	G/G*	SS	CC	M	100
C	Central sands (HC)	88	P	G	S	P	G / F	25
D	Coastal dunes (HC)	27	P	G	S	H	E / M	70
E	Eastern sands (HC)	44	P	G	S	P	G / F	0
F	Flanders (HC)	16	P	G*	S	T	M / F	100
I	Artificial recharge (HT)	12	R	AR	S	H	E / M	0
L	Limestone (HC)	24	P	G	L	C	L	20
N	Northern sands (HC)	30	P	G	S	P	G / F	90
S	Southern sands (HC)	53	P	G	S	P	F	30
U	River bank filtration (HT)	41	R	RBF	S	P	F	60
W	Western sands (HC)	7	P	G	S	P	M / L	80

[a] Origin: P: precipitation; R: river (or lake); [b] Source: G: autochthonous groundwater <1000 years old, with local recharge; G*: autochthonous groundwater >1000 years old; AR: artificially recharged water; RBF: river bank filtrate; [c] Aquifer material: S: sand and gravel; L: limestone; SS = Sandstone; [d] Sediment age: P: Pleistocene (+Tertiary); H: Holocene (+Pleistocene); T: Tertiary; C: Late Cretaceous; CC = Early Cretaceous; [e] Depositional environment: E: eolian; F: fluvial; G: glacial; L: lagunal; M: marine.

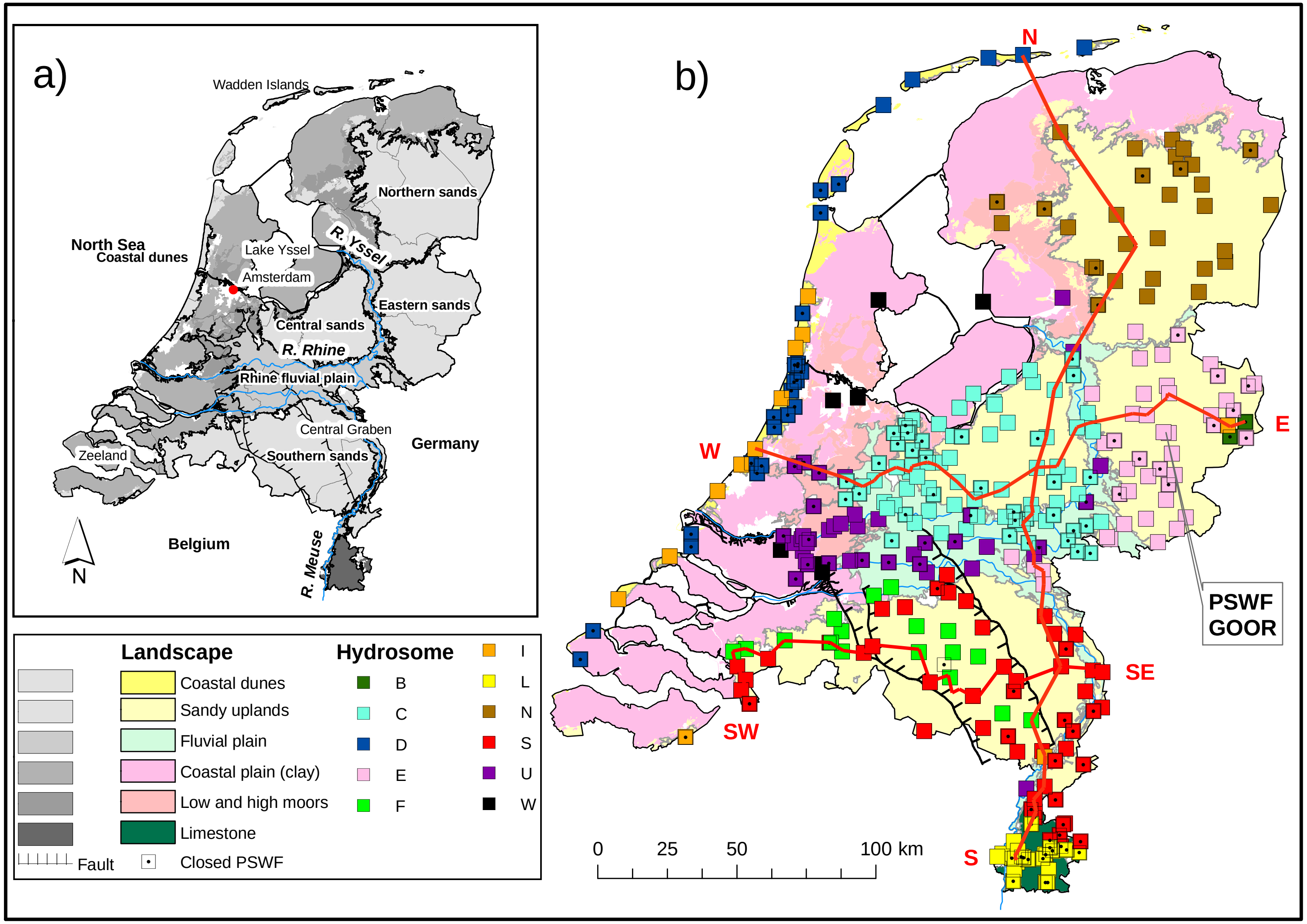


Fig 6.1: Location map of (a) the main recharge areas of groundwater pumped for public drinking water supply in The Netherlands, and (b) the 351 PSWFs used for drinking water production during the 20th century and the hydrosome they belong to (according to Table 6.1). Closed PSWFs are marked and the position of profiles depicted in Fig 6.4 is indicated.

A hydrosome complex (HC) is composed of various adjacent hydrosomes with a very similar origin and recharge area and the complex members cannot be easily discerned from each other with environmental tracers. A hydrosome type (HT) is characterized by a similar type of recharge water, like river water in case of RBF or AR hydrosomes. Hydrosomes belonging to the same type may have a totally different chemistry because of different source waters (for instance the Rhine River, Meuse River or Lake Yssel) and they do not need to be adjacent.

Extension of such classification to 143 abandoned PSWFs resulted in the addition of two hydrosome complexes: (1) hydrosome complex B, a small fresh groundwater body in the so-called Bentheimer sandstone, in the eastern part of the Netherlands; and (2) hydrosome complex W, a shallow aquifer system of marine sands in the western polder area. The spatial distribution of the 11 hydrosomes is given in Fig 6.1.

6.2.2 Data collection and preprocessing

In the Netherlands, the raw water quality and volumes pumped from all PSWFs are reported four times a year to the authorities, conform Dutch legislation (Waterleidingbesluit, 1984). These routine data are stored in a national digital database (REWAB) since 1992, but older data, reported since 1898, are only available through annual reports (VWN/VEWIN, 1898-1992). These data have been digitalized for this study, together with the following data: (1) routine data from other national reports; (2) a database from the Dutch National Institute for Public Health and the Environment (RIVM); (3) complementary data available in databases and archives of all Dutch Waterworks; and (4) selected data from incidental national surveys on, for instance, iodine (Gezondheidsraad, 1932), fluoride (Stas et al., 1937) and tritium (Glastra et al., 1989). The combined result is the National Network of Public Supply Well Fields (LMP in its Dutch initials), a digital record of water quantity and quality for all PSWFs over the period 1898-2008.

Time series were preprocessed following the guidelines introduced in Mendizabal and Stuyfzand (2009, Chapter 2). Historical changes in measuring units were identified and converted. Censored data with values far above present detection limits were discarded. For this purpose, a threshold of 2 times the 10th percentile was defined for every parameter in the database and censored values above this threshold rejected.

The following parameters were selected for trend analysis, because their data record showed least gaps and they are considered indicators of specific processes: Cl (general pollution and salinization); NO_3 (agriculture); SO_4, HCO_3 and total hardness (together indicating acidification or hardening). This data set was extended with EC, pH, Na, K, Fe and Mn.

6.2.3 Statistical trend analysis method

Trend analysis was performed with Trendanalist (Baggelaar and Van der Meulen, 2007), a computer program capable of performing a fully automatic trend analysis of a data series in a database. The expert system of the program ensures that for each data series the trend test is used that best fits its relevant statistical characteristics, being the kind of probability distribution (normal or non-normal) and the occurrence or absence of autocorrelation and/or seasonality. Six trend tests are available, based on the parametric linear regression test and the distribution free Mann-Kendall test (Kendall, 1938; 1975; Mann, 1945). For both tests extensions are available to cope with autocorrelation and/or seasonality. The extensions of the linear regression test are dummy variables for the seasons and a first order autoregressive model for the noise (Box and Jenkins, 1976). Extensions of the Mann-Kendall test are given by Hirsch et al. (1982) and Hirsch and Slack (1984).

The statistical trend analysis was applied to the indicated 11 chemical parameters measured in the raw water from each PSWF. The resulting time series were tested for a monotonic trend, according to the following procedure. First, the extended linear regression model is estimated, without extensions for seasonality as our data series contain only yearly values. If necessary, a statistically non-significant model parameter for autocorrelation is removed and the new model is estimated. Then the model residuals are tested for normality with the Kolmogorow-Smirnov test with Lilliefors correction (Lilliefors, 1967; 1969) and for autocorrelation with the Portmanteau test (Ljung and Box, 1978). If the model residuals come from a normal probability distribution and show no autocorrelation, the trend can be tested and quantified with the estimated slope parameter. Otherwise the procedure chooses one of the distribution free Mann-Kendall tests on trend, based upon the occurrence or absence of autocorrelation in the time series (corrected for trend). Autocorrelation is tested with the runs test (Bradley, 1968), a distribution free test. This procedure is somewhat similar to that proposed by Grath et al. (2001), which uses the Shapiro-Wilks test (Shapiro and Wilk, 1965) and Shapiro-Francia test (Shapiro and Francia, 1972) on normality instead of the Kolmogorow-Smirnov test with Lilliefors correction.

A trend is statistically significant if the p-value of the corresponding trend test statistics is less than 0.1. Statistically significant trends were normalized to Dutch drinking water standards (Government, 2001) for mapping purposes, according to

$$\bar{b}_X = \frac{b_X}{MPC_X} \times 100 \quad [\text{year}^{-1}] \qquad (6.1)$$

where $\bar{b}_X$ = is the normalized trend per year for parameter X (year^{-1}) b_X = trend per year for parameter X (concentration units/year) and MPC_X = maximum permissible concentration of parameter X in drinking water (concentration or other quality unit).

Significant trends were classified into three trend classes, also on the basis of drinking water standards: large ($|\bar{b}_X| \geq 2$ MPC$_X$/1000), intermediate (MPC$_X$/1000< $|\bar{b}_X|$ < 2 MPC$_X$/1000) and small ($|\bar{b}_X| \leq$ MPC$_X$/1000).

6.2.4 Identification of trend reversals

Trend reversals were identified in a pragmatic way, by comparing the trends obtained for two contrasting periods: (1) water quality deterioration from the beginning of abstraction until 1970, due to increasing anthropogenic influences, and (2) water quality improvement from 1985 to 2005, due to many sanitation measures in most river catchment areas to restore their quality (with clear effects since the early 70s) and better agricultural practices introduced during the 90s. Combination of the three possible results of trend analysis (U = upward trend; D = downward trend; and N = No trend) over both periods yields nine combinations that can be grouped into four classes: Same judgment, trend reversal, No trend/trend and trend/no trend (Table 6.2).

Trend reversals are either convex (upward trend in first period, downward in second; often indicating quality improvement by sanitation measures or reflecting well field adaptation) or concave (downward trend in first period and upward in second; often indicating quality deterioration).

6.2.5 Defining changes

Changes in water quality at any time can be conveniently quantified for mapping purposes by taking the normalized concentration change index for parameter X in year t (NCC$_{X,t}$), which is defined as follows:

$$NCC_{X,t} = \frac{C_{X,t} - NBL_X}{MPC_X} \times 100 \quad [\%] \qquad (6.2)$$

where: $C_{X,t}$ = Concentration of parameter *X* measured in year t; NBL$_X$ = Natural background level concentrations of parameter *X;* MPC_X = maximum permissible concentration of parameter *X* in drinking water, all of them expressed in the same unit.

How to establish the NBL is shown in section 6.3.1.

6.3 Results

Statistical trend analysis was applied to two datasets corresponding to a specific interval within the time series. The first six years of operation were tested for monotonic trends to select trendless series and determine natural background level concentrations. Time series covering the period 1960-2005 were also tested for monotonic trends. Results were normalized to drinking water standards and used to identify significant trend bundles associated to different hydrochemical processes and classify PSWFs according to such bundles. Trend reversals were identified by comparing the trend obtained from the beginning of abstraction until 1970 with the trend for the period 1985-2005.

Table 6.2: Possible combinations of results of trend analysis applied to two different periods of a single time series grouped into four classes: Same judgment, trend reversal, No trend/trend and trend/no trend.

		Period 2		
		Upward	No trend	Downward
Period 1	Upward	Same judgment	Trend → No trend	Trend reversal
	No trend	No trend → Trend	Same judgment	No trend → Trend
	Downward	Trend reversal	Trend → No trend	Same judgment

6.3.1 Natural background levels of individual PSWFs

Concentrations measured in PSWFs during the early years of the 20th century (roughly prior to 1940; see below) yield a good estimate of the NBL at the depth of abstraction, provided the PSWF itself did not significantly disturb groundwater quality. In order to discard such effects, the time series were tested on the presence of a monotonic trend during the first six years of abstraction. The number of years chosen relies on the number of samples that we consider minimal for trend analysis. The NBL of PSWFs without significant trend was quantified by the average concentration of the earliest six years. In PSWFs with a significant trend, the lowest value was taken as an upper limit to the NBL. NBLs were then upscaled to the GWB level by computing the median of the NBLs obtained for individual PSWFs belonging to a specific GWB. Upper limits of NBL were only used (and marked as such) in GWBs where no NBL could be derived from a trendless data series (Table 6.3).

NBLs should always refer to a relevant hydrochemical facies, which is often related to a specific depth interval within the aquifer system. As a compromise between a useful separation of different facies and a compact presentation of results, hydrosome complexes or PSWFs were subdivided into two parts only, on the basis of their alkalinity and redox index: ‘deep’ if alkalinity index 3 or 4 and redox index anoxic or deeply anoxic, as defined in Mendizabal et al. (2011, Chapter 4), and ‘shallow’ otherwise. This subdivision was based on the most recent water sample available for the PSWF, either a sample obtained in 2008 for active PSWFs or the last sample obtained for PSWFs that were closed down before 2008. PSWFs with a mixed redox were discarded, because NBLs cannot be determined for PSWFs abstracting waters of different sources. PSWFs with NO_3 concentrations above 10 mg/L within the first six years of monitoring were considered anthropogenically influenced and therefore also discarded. PSWFs pumping more than 95 % water infiltrated before 1953 (characterized by an ‘Old’ age index according to Mendizabal et al. (2011, Chapter 4)) were considered regardless of the first year of operation, because they are assumed to be nearly free of any anthropogenic influences. From the remaining population, only PSWFs with at least six yearly measurements before 1940 were considered. The year 1940 was chosen because it marks the start of accelerated anthropogenic pollution.

The method is illustrated by presenting the NBLs for PSWF Goor, which is located in hydrosome E (Fig 6.1) and active since 1915. A detailed description of the PSWF is given in Mendizabal and Stuyfzand (2009, Chapter 2). Time series of 6 main constituents of its raw water are shown in Fig 6.2, together with the water quality obtained in LMG226, the closest piezometer nest of the national groundwater quality monitoring network (NGQMN). LMG226 is situated 2 km to the west of PSWF Goor and regularly monitored at 8 and 24 m BLS. The NBL of the second aquifer (12-32 m BLS) can be better inferred from the historical data record of the PSWF, starting in 1915, than from the 20 years of measurement available in NGQMN. Although time series for PSWF Goor also present significant trends for most parameters, these trends are not significant during the first six years of abstraction and the series can therefore be used to establish the NBL at the depth of abstraction (black line, Fig 6.2).

As the method relies on the first six years of operation, the NBLs are not affected by well field adaptation measures, such as drilling new wells or abandoning polluted ones, which will rarely happen during the first six years of operation.

6.3.2 Natural background levels of groundwater bodies

The NBL of a GWB is estimated by the median of the NBLs obtained for all individual PSWFs belonging to that GWB. Hydrosome complexes have been, when possible, subdivided in deep and shallow PSWFs, as based on alkalinity and redox facies. Note that all PSWFs within Hydrosomes E and D are shallow and all within F and B deep. NBLs for hydrosome type I were not determined, because type I is per definition artificial, by recharge with relatively young, polluted surface water. Most PSWFs pumping from hydrosome type I today, previously extracted groundwater from a natural hydrosome like coastal dune hydrosome D. NBLs for such PSWFs therefore refer to the natural hydrosome prior to the introduction of artificial recharge.

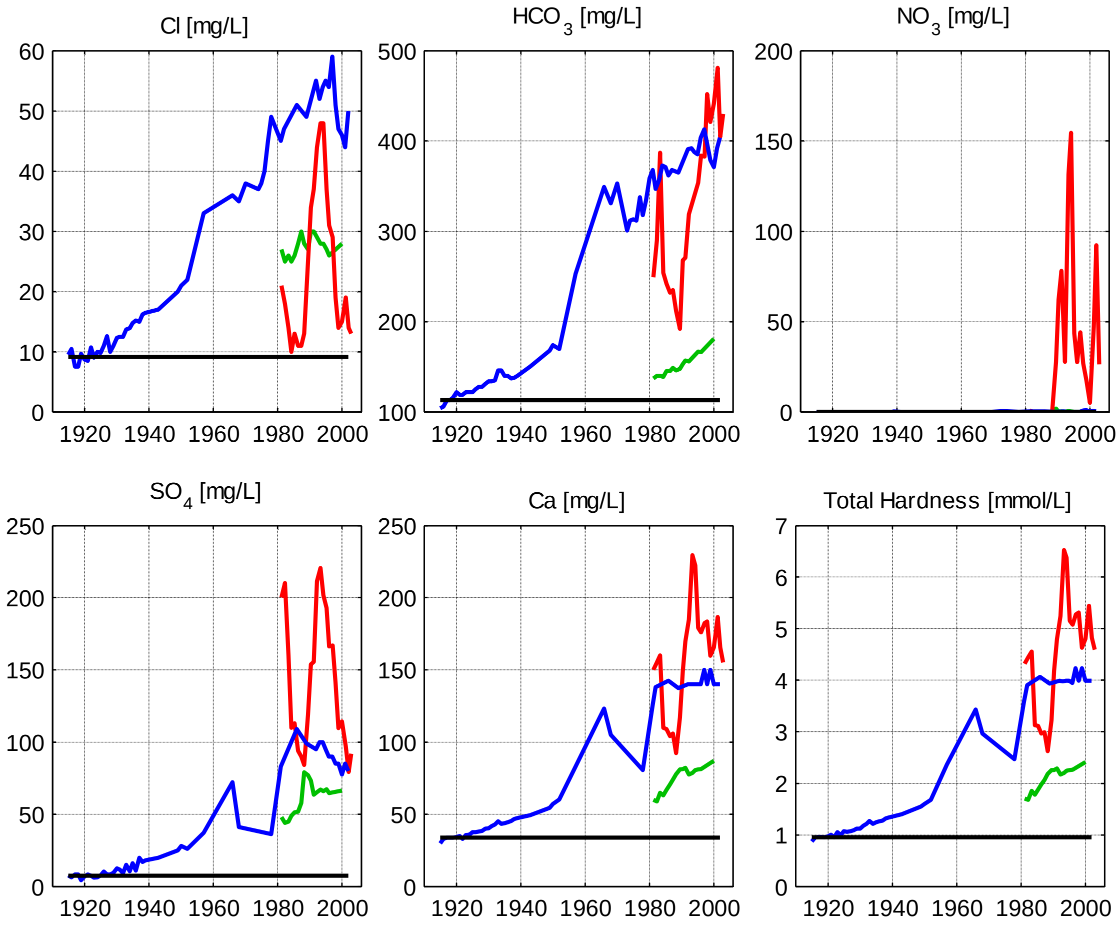


Fig 6.2: Time series of main constituents of the raw groundwater pumped by PSWF Goor (blue) and of groundwater sampled from two piezometers of LMG226, the closest piezometer nest of the National Groundwater Quality Monitoring Network, at resp. 8 (red) and 24 (green) m BLS. Natural background levels for the aquifer at 12-32 m BLS from which PSWF Goor is pumping, indicated by black line.

NBLs for hydrosome type U could be determined, however, because these hydrosomes can be much older with inputs from rivers that were close to their natural backgrounds, like the river Rhine in the 1880s (Molt, 1961). Only three PSWFs of hydrosome U were fed by a river other than the Rhine before 1964. Results are summarized in Table 6.1.

The spatial distribution of NBLs for individual PSWFs regarding Cl, HCO_3, NO_3, SO_4, and total hardness is shown in Fig 6.3, together with the 11 hydrosomes defined. PSWFs without sufficient data for direct determination were assigned the NBL of the groundwater body they pump from. Fig 6.4 shows the extension of hydrosomes with depth and the NBL_{SO4} for individual PSWFs in three cross sections over the country (for location see Fig 6.1).

NBL_{CL} ranges in general from 10 to 20 mg/L. Deep PSWFs of hydrosomes C, S and F yield very old waters with Cl concentrations below 10 mg/L. Hydrosome N presents slightly higher levels, mainly due to PSWFs located closer to the North Sea. Hydrosomes U and D present relatively high levels due to surface water inputs in the former and seaspray effects in the latter. The highest Cl levels are observed in hydrosome W. This is related to contributions of relict Holocene marine transgression water, either directly from the aquifer or indirectly via infiltrating drainage water in shallow polder areas. W type PSWFs have been abandoned either due to salinization or problems with too high concentrations of methane, NH_4, Fe and color.

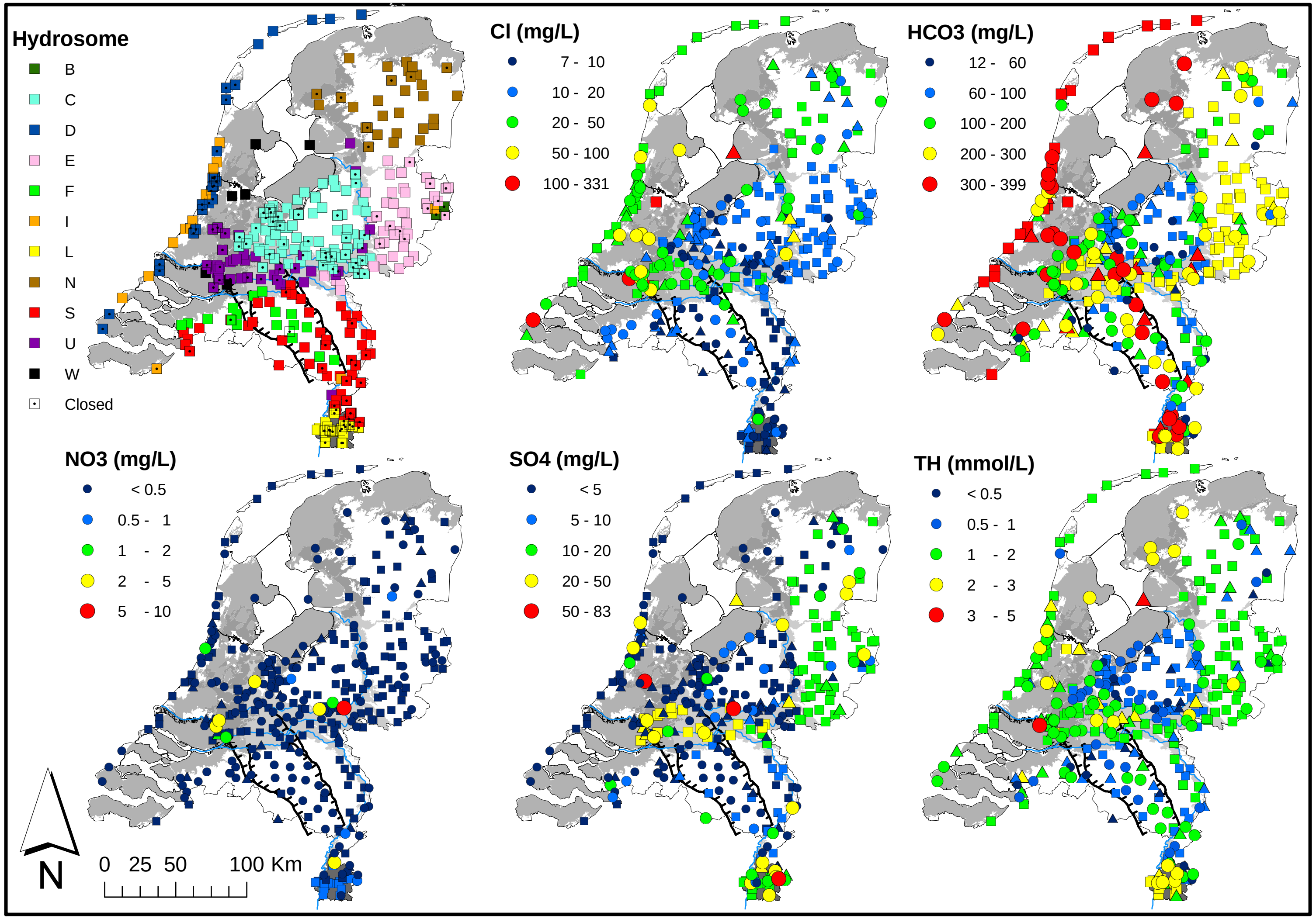


Fig 6.3: Natural background levels (NBL) of selected parameters obtained at the depth of abstraction for the 351 PSWFs that have delivered water for drinking water preparation in the Netherlands, together with the 11 hydrosomes defined in Table 6.1. Calculated NBL (circle), maximum NBL (triangle) and NBL derived from GWB (square) are differentiated.

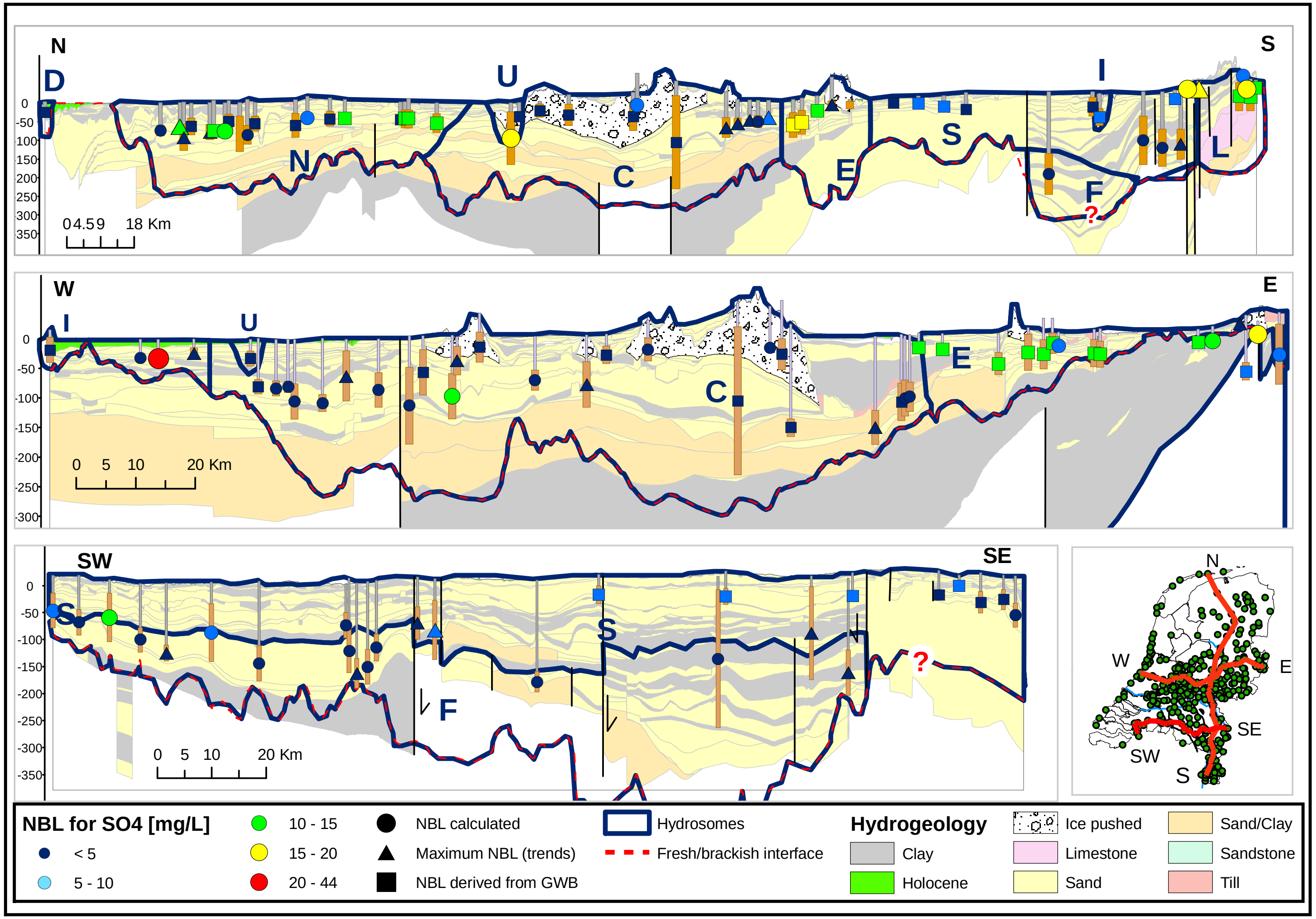


Fig 6.4: NBLs for sulfate along hydrogeological cross sections N-S, W-E and SW-SE over the Netherlands, with the spatial distribution of hydrosomes (groundwater bodies) and well screen position of public supply well fields (PSWFs). The inset location map shows the location of the cross sections and PSWFs. Hydrogeological data obtained from REGIS II.1 (Vernes and van Doorn, 2005). The fresh/brackish water interface (1000 mg/L Cl) is given by the red line (estimated by expert judgment around the question marks, due to lack of data).

Table 6.3: Natural background level (NBL) for the 11 groundwater bodies (hydrosomes) pumped for drinking water supply in the Netherlands, with further subdivision according to hydrochemical facies (d = deep; s = shallow) or surface water type (r = Rhine; o = other). Spatial distribution of hydrosomes shown in Fig 6.3.

Hydrosome	PSWFs	Surface level (m ASL)	Abstraction depth (m BLS)	NBL						
				Cl	HCO_3	NO_3	SO_4	Ca	Mg	TH [a]
B_d	2	43	50 - 116	13	231	<0.5	6	71	5	2.0
C_d	28	7	66 - 110	9	189	0	0	54	6	1.4
C_s	60	14	43 - 87	12	72	<0.5	5	25	2	0.8
D_s	37	5	15 - 32	40	309	<0.5	0	87	7	2.3
E_s	45	22	24 - 49	17	219	<0.5	15	62	5	1.8
F_d	16	10	121 - 189	14	224	0	0	46	6	1.4
L_d	5	76	33 - 85	12 [b]	354 [b]	0	13	98 [b]	13	3.0 [b]
L_s	19	84	16 - 50	9	293	0.7	20	102	7	3.0
N_d	17	5	56 - 105	24	260	0	0	86	6	2.3
N_s	13	9	39 - 68	23	111	<0.5	13	33	6	1.8
S_d	28	28	58 - 135	8	168	0	0	54	7	1.5
S_s	25	30	38 - 89	10	98	<0.5	8	20	3	1.0
U_o	3	2	23 - 53	11 [b]	177	<0.5	0	59 [b]	11	2.0
U_r	37	2	26 - 58	45	226	<0.5	25	62	9	1.9
W	7	0	46 - 68	113	321	0	0	60	22	2.6

[a] TH: Total hardness; [b] Upper limit of NBL obtained based on PSWFs with a significant trend; ASL: Above sea level; BLS: Below land surface.

NBL_{SO4} is below 0.5 mg/L for the deep PSWFs Fd, Cd, Nd and Sd and shallow PSWF Ds (Fig 6.4). For the shallow PSWFs Es, Ls, Ns and Ss, NBL_{SO4} varies in between 5 and 20 mg/L (Fig 6.4; N-S and W-E). This range can be easily explained by atmospheric inputs multiplied with the effects of evapotranspiration losses. Hydrosome U_r presents somewhat higher levels which relate to concentrations in the Rhine.

NBL_{TH} and NBL_{HCO3} are both low in shallow PSWFs Cs and Ss, where they even reach values below the drinking water standard of respectively 1 mmol/L and 60 mg/L (Water Supply Act, 2001). High levels for PSWFs L and W are explained by strong calcite dissolution in connection with high CO_2 levels in löss deposits overlying the limestone aquifer in Limburg and in clay and peat deposits overlying Pleistocene sands in the coastal polder areas.

6.3.3 Trend analysis results

Historical data were tested on significant monotonic trends. From the 351 PSWFs, only the ones fully covering the period 1960-2005 were chosen, because otherwise a comparison of results would be difficult. The heterogeneity is mainly caused by the different periods covered by PSWFs, which are opened or closed down in different years. The start year 1960 resulted in the highest number of PSWFs (118) covering the whole period. Statistically significant trends for these PSWFs were normalized to drinking water standards (Government, 2001) according to Eq. (6.1). The spatial distribution of normalized trends regarding Cl, HCO_3, NO_3, SO_4, and total hardness is shown in Fig 6.5, and normalized trends for SO_4 are shown in three cross sections over the country (Fig 6.6).

Normalized trends for individual PSWFs were upscaled to the GWB level, by taking the median of the normalized trends for individual PSWFs belonging to the GWB. Results are summarized in Table 6.4. Hydrosomes are also subdivided in deep and shallow and hydrosomes I and U on the basis of a different origin of the infiltrating surface water, in respectively Rhine (r) and other (o).

6.3.4 Trend bundles associated to hydrochemical processes

While systematic variations in chemical parameters can easily be recognized, interpretation of time series in terms of hydrochemical trend should be based on the understanding of chemical processes affecting groundwater quality and not just on the results of descriptive statistical procedures (van Camp and Walraevens, 2008). Agricultural activities, for example, are characterized by high input loads in a.o. NO_3, SO_4, K and Cl. Effects of agriculture on groundwater, however, may consist of trends in different chemical parameters (trend bundles) depending on the presence (or absence) of reactive phases in the aquifer system, such as calcite, pyrite and organic matter. Therefore, normalized significant trends for individual chemical parameters were aggregated into seven trend bundles associated to specific hydrochemical processes, defined according to the criteria listed in Table 6.5. Characteristic groundwater quality time series for each bundle are shown in Fig 6.7 and their spatial distribution is presented in Fig 6.5.

Table 6.4: Groundwater quality trends normalized to drinking water standards according to Eq. (6.1), for the 10 relevant groundwater bodies (hydrosomes) in the period 1960-2005, with further subdivision according to depth (d = deep; s = shallow) or surface water type (r = Rhine; o = other).

GWB	nr	Cl	HCO_3	NO_3	SO_4	TH [a]	Na	K	SiO_2	pH	EC
Norm		150	300 [b]	50	150	2.5	150	10 [b]	40 [b]	9.5	1250
B	1	-0.07	-0.55	0.50	2.19	1.08	-0.04	0.01	-0.39	-0.06	0.21
Cd	10	0.00	0.03	0.02	0.00	0.13	0.07	0.02	-0.07	-0.01	0.14
Cs	20	0.05	0.08	0.07	0.09	0.17	0.03	0.00	0.01	-0.03	0.10
D	2	0.69	0.23	0.03	0.12	0.51	0.32	0.54	1.16	-0.02	0.46
E	14	0.12	0.43	0.00	0.57	0.69	0.04	0.26	-0.03	-0.05	0.32
F	4	-0.01	0.00	0.02	0.00	-0.04	0.05	0.14	-0.19	-0.03	0.02
Im	3	-2.55	-0.20	0.17	0.04	-0.87	-0.88	1.23	-1.13	-0.01	-0.92
Io	6	0.45	-0.19	-0.13	0.09	0.17	0.12	0.24	-1.14	0.00	0.18
Ir	1	-1.55	-0.29	0.25	-0.17	-0.57	-0.34	-0.14	-0.29	-0.09	-0.30
Ld	2	0.12	0.12	-0.07	0.36	0.24	0.05	-0.15	-0.02	-0.08	-0.01
Ls	3	0.16	0.10	1.11	0.78	0.58	0.02	-0.03	0.24	-0.07	0.17
Nd	11	0.03	0.07	0.02	0.05	0.12	0.03	0.00	0.00	-0.07	0.10
Ns	5	0.09	0.07	0.02	0.23	0.18	0.08	-0.01	0.09	-0.07	0.16
Sd	12	-0.02	0.46	0.01	0.14	0.41	0.04	0.08	-0.06	-0.04	0.12
Ss	8	0.13	0.03	-0.01	0.72	0.20	0.06	0.05	-0.05	-0.08	0.18
Uo	2	0.11	0.47	-0.25	0.09	0.18	-0.21	0.24	-0.02	-0.06	0.11
Ur	14	0.28	0.09	-0.06	0.15	0.09	0.19	0.30	0.00	-0.08	0.07

[a] TH: Total hardness; [b] Arbitrarily chosen value, due to lack of maximum permissible concentration defined in The Netherlands.

PSWFs are first tested on the fraction of surface water they deliver, either by AR or RBF, quantified by multitracing techniques according to the method introduced in Mendizabal and Stuyfzand (2009, Chapter 2) and further developed in Mendizabal et al. (2011, Chapter 4).

PSWFs delivering more than 20 % of infiltrate correspond to trend bundle 1. They are mainly located along the coast and in the Rhine fluvial plain and they are further subdivided in Rhine (R), Meuse (M) and other (O), because their water quality trends are mainly dictated by the quality of the infiltrating surface water.

Non fluvial PSWFs are further tested on conditions 2 to 6. The tests can be applied in any order, because they are all exclusive (there can be no PSWFs testing positive for two of them). PSWFs tested positive for the second condition are assigned bundle 2. Such PSWFs present a significant upward trend in NO_3 derived from atmospheric deposition, but relatively low median concentrations in NO_3 remain, due to the lack of agriculture. They also present downward trends in pH and low HCO_3, pointing at acidification of a non calcareous aquifer (Fig 6.7.2). Total dissolved solids are extremely low and the effect of atmospheric deposition is significant, with increasing trends in NO_3 and SO_4. Although HCO_3 is rather low and constant, PSWFs present a significant positive trend in Ca, due to (1) cation exchange where Ca is displaced by H and Al in the advancing acidified groundwater, or (2) dissolution of calcium containing aluminium silicates in acidic environment. This bundle is typical for the ice pushed ridges in the central part of hydrosome C, known as the Veluwe.

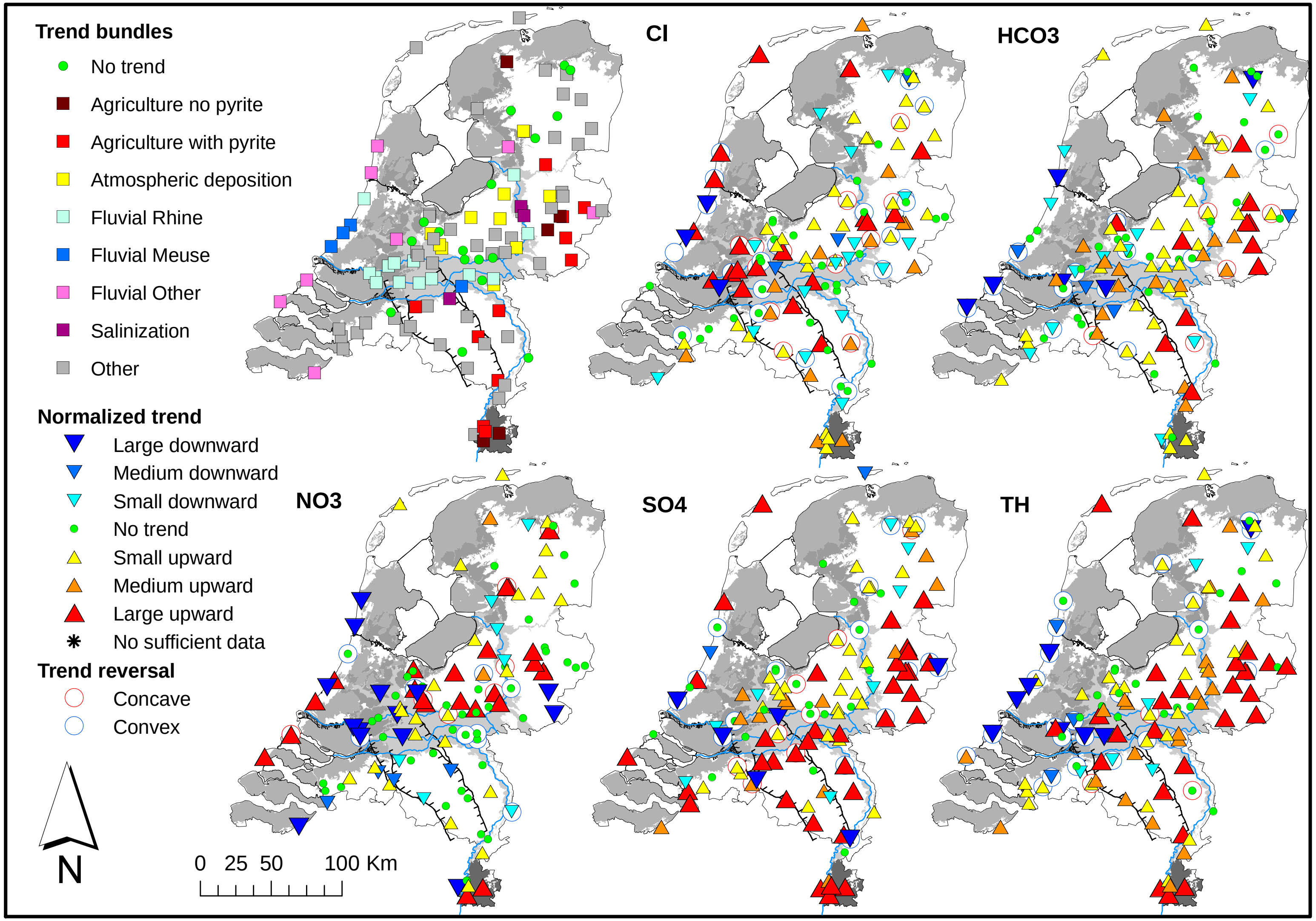


Fig 6.5: Spatial distribution of hydrochemical trend bundles and individual water quality trends for PSWFs in the period 1960-2005. Quality trends are normalized to drinking water standards according to Eq. (6.1). See text for trend magnitude criteria.

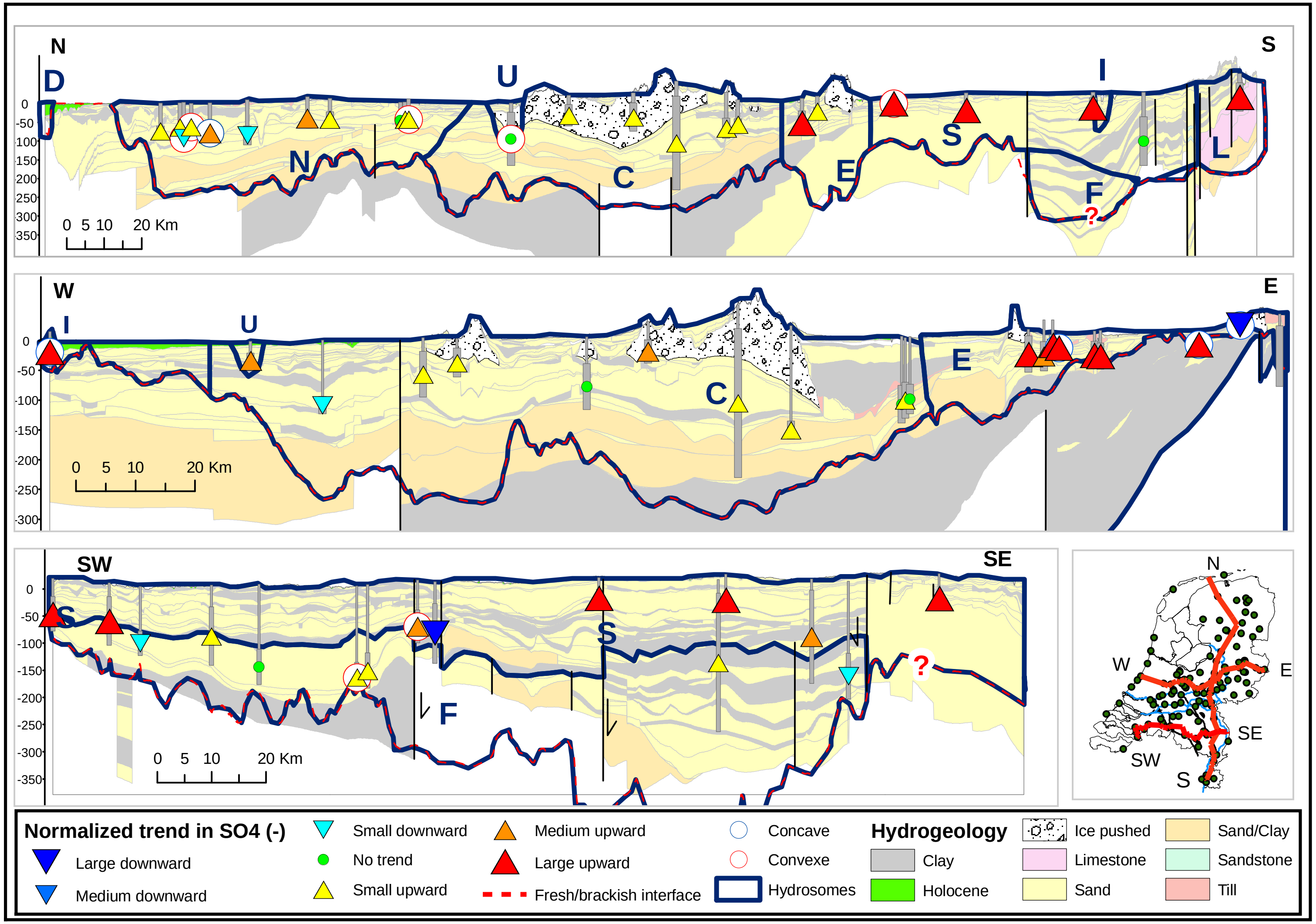


Fig 6.6: Normalized SO_4 trends for 108 PSWFs in the period 1960-2005, along three hydrogeological cross sections over the Netherlands. Trend reversals are marked. See text for trend magnitude criteria. Geological data obtained from REGIS II.1 (Vernes and van Doorn, 2005). The inset location map shows the position of cross sections and selected PSWFs. Hydrosomes (groundwater bodies) delimited by dark blue. The fresh/brackish water interface (1000 mg/L Cl) is delimited by the red line.

Table 6.5: Trend bundles with their criteria. Bundle 1 to be tested first. Bundles 2 to 6 are exclusive and can be applied in any order.

no	Trend bundle	Trend bundle criteria
1	Fluvial	either % AR or % RBF >20 [a]
2	Acidification by atmospheric deposition	upward trend in NO_3, downward trend in pH and %agric[b]<20
3	Agriculture in calcareous pyritiferous aquifer	upward trend in SO_4, HCO_3 [#] and TH [c], median NO3<5 and %agric[b]>20
4	Agriculture in calcareous nonpyritiferous aquifer	upward trend in NO_3, HCO_3 [#] and TH [c] and %agric[b]>20
5	Salinization	upward trend in Cl and Na and median Cl>80
6	No trend	no significant trend in Cl, HCO_3, NO_3, SO_4 and TH [c]
7	Other	None of the above criteria fulfilled

[a] % AR and RBF determined by multitracing techniques as presented in Mendizabal and Stuyfzand (2009, Chapter 2) and Mendizabal et al. (2011, Chapter 4); [b] % agriculture within WHPA; [c] TH: Total hardness; [#] Either upward trend in HCO_3 or median HCO_3>300.

PSWFs are also tested for the influence of agricultural activities. In the presence of pyrite and/or organic matter, the high NO_3 loads trigger the oxidation of pyrite and/or organic matter, thereby reducing the NO_3 load either completely or partially, depending on the reduction capacity of the aquifer and the input flux at the surface. When NO_3 is fully reduced, the effect of agriculture is not observed in upward trends in NO_3, but in upward trends for SO_4 or HCO_3. The acidifying reaction of pyrite oxidation is neutralized in a calcareous aquifer by calcite dissolution, resulting in increasing trends for HCO_3 and Ca or total hardness. PSWFs showing such trends are grouped under trend bundle 3. In the absence of pyrite, acidification processes are not so strong, but calcite dissolution is still triggered by agriculture, yielding increasing trends in HCO_3 and total hardness. There can be a slow trend in SO_4 derived from atmospheric deposition, but not necessarily. Such PSWFs are grouped under bundle 4. In PSWFs with median concentrations in HCO_3 > 300 mg/L, such as the ones belonging to the limestone hydrosome, the trend in HCO_3 might not be significant anymore. In such cases, the trend in HCO_3 is replaced by the median concentration in HCO_3 in the trend bundle criteria Table 6.5. Note that although trend bundles 3 and 4 are defined for the effects of agriculture, the same water quality trends can be obtained where water tables decline by excessive pumping.

Trend bundle 5 covers PSWFs affected by salinization, a relatively common water quality problem in PSWFs. The most direct indicator of salinization is the increase in chloride concentration. Sodium will initially increase, but it will also partly be involved in cation exchange processes with Ca, in extreme cases leading to the $CaCl_2$ water type.

Trend bundle 6 holds for PSWFs that deliver old water of good and stable quality from deep confined aquifers, without any of the previously mentioned trends. PSWFs showing trend bundle 6 display characteristic low Cl concentrations and complete absence of NO_3 and SO_4. PSWFs fulfilling none of the six conditions are gathered in the group ‘Other’.

Median groundwater quality trends for the seven trend bundles, normalized to drinking water standards according to Eq. (6.1), are presented in Table 6.6.

6.3.5 Situation in 2008 compared to NBLs

The most recent year with water quality data for PSWFs in our database was 2008. Comparing these results with the NBLs for 5 indicator parameters via the normalized concentration change index (NCC) according to Eq. (6.2) yields the ‘change’ maps presented in Fig 6.8. The changes quantified by NCC are mainly due to anthropogenic influences, including influences of the PSWF itself. The latter include oxidizing and salinizing effects of a drawdown of groundwater tables, and well head adaptation measures like abandoning polluted wells and drilling new wells in unpolluted parts of the aquifer system (Mendizabal and Stuyfzand, 2009, Chapter 2).

The overall largest NCC_X with highest frequency is displayed by SO_4 and total hardness, due to a multitude of processes triggering their increase. For SO_4 these are mainly composed of: increased inputs via atmospheric and fluvial pollution, and pyrite oxidation by agricultural NO_3 inputs and declining groundwater tables. Most buffering of the resulting acid load is accomplished by dissolution of $CaCO_3$ as evidenced by the increases for total hardness. NO_3 is presenting a relatively low NCCx, testifying of a high redox buffer capacity of the aquifer system. Negative NCC_X values for Cl, SO_4 and NO_3 (blue dots in Fig 6.8) are often connected with well field adaptation by extending the PSWF with new wells in deeper aquifers, in order to counteract rising concentration levels. In that case frequently a positive NCC_{SIO2} is observed due to higher concentrations of SIO_2 in deeper aquifers. Changes from dune water to AR systems along the coast are reflected in strongly positive NCCs for Cl, SO_4 and NO_3, and a negative NCC for HCO_3. Hydrogen carbonate displays both strongly positive and negative NCC_X values, positive where $CaCO_3$ is dissolving and soil organic matter is an important redox buffer, negative where $CaCO_3$ has been leached and HCO_3 constitutes the acid buffer.

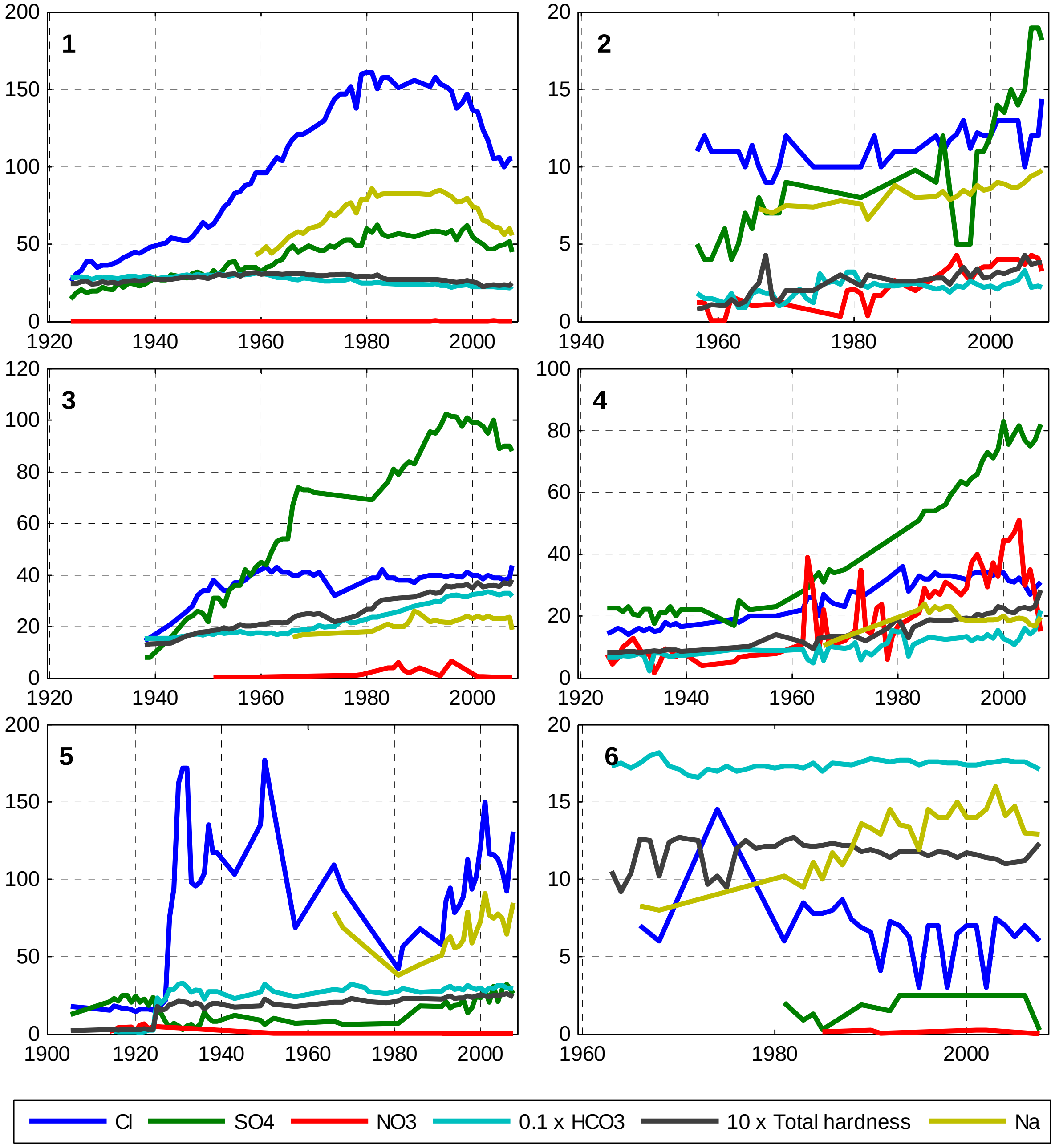


Fig 6.7: Characteristic groundwater quality trends associated to the specific trend bundles. All concentrations in mg/L, except for total hardness (mmol/L). Note that HCO_3 concentrations are multiplied by a factor f=0.1 and Total hardness by f=10.

Table 6.6: Median groundwater quality trends for the seven relevant trend bundles. Results normalized to drinking water standards according to Eq. (6.1). Trend bundle Fluvial subdivided according to the source water into Rhine, Meuse and other.

Trend bundle	Nr	Cl	HCO_3	NO_3	SO_4	TH [a]	K	SiO_2
Norm	PSWFs	150	300 [b]	50	150	2.5	10 [b]	40 [b]
Fluvial Meuse	4	-1.33	-0.10	0.10	0.22	-0.42	0.63	-1.13
Fluvial Rhine	14	0.28	0.09	-0.06	0.10	0.01	0.30	-0.04
Fluvial other	8	0.21	-0.06	-0.13	0.09	0.18	0.24	-0.66
Atm. Deposition	9	0.09	0.08	0.32	0.15	0.19	0.08	0.06
Agric. + Pyrite	11	0.13	0.52	-0.01	0.64	0.73	0.11	0.00
Agric. – Pyrite	6	0.19	0.26	1.04	0.60	0.92	0.13	0.09
No trend	17	0.02	0.04	0.01	0.05	0.09	0.00	0.00
Salinization	3	0.85	0.06	-0.01	0.15	0.27	-0.02	-0.07
Other	46	0.01	0.12	0.01	0.08	0.21	0.04	0.00

[a] TH: Total hardness.

6.4 Discussion

6.4.1 Influences of well field adaptation measures

Well field adaptation measures will rarely have an effect on the calculated NBLs, because they rarely take place within the first six years of operation. However, they may have a large impact on trends in water quality from PSWFs. An example is offered by trend bundle 5 in Fig 6.7, showing incidental Cl peaks in the period 1930-2008 and a Cl minimum around 1980. These variations closely correspond with the pumping rate, which was high during Cl peaks and low in 1980.

A good indicator of well field adaptation measures is a strong trend in SiO_2 concentration, because this constituent is little affected by environmental changes and very much by changes in the depth of abstraction or shifts to deeper or shallower aquifer layers. Clear examples of this are found in the coastal dune area regarding hydrosomes D and I. PWSFs pumping dune groundwater started in the upper phreatic aquifer with low SiO_2 concentrations, and steadily increased the abstraction from the semiconfined deeper aquifer with much higher SiO_2 concentrations. This led to the strong positive SiO_2 trend, and also explains the other increasing trends noted in Table 6.4. The contrary holds for hydrosome types I with AR, because of a steady decline in the admixing of deep dune groundwater high in SiO_2.

6.4.2 Trend reversal

The Water Framework Directive (EU, 2000; 2008) and its daughter Groundwater Directive (EU, 2006b), enforce all EU member states to identify and report water quality trends and, when present, trend reversals. Clear trend reversals are identified in PSWFs delivering a significant fraction of surface water from the river Rhine, either by AR or RBF systems. The extreme water quality deterioration due to increasing industrial activities and increasing discharges of sewage treatment plants in the period 1945-1970 has been significantly reversed, since many sanitation measures were implemented in the whole catchment area under auspices of IAWR (http://www.iawr.org/). Relatively short travel times to type I and U PSWFs (with AR and RBF respectively) explain that the trend reversal in the infiltrating surface water can already be noted in the raw water from these PSWFs.

A second trend reversal to be expected is a declining SO_4 concentration for shallow PSWFs in nature reserves, thanks to declining atmospheric SO_4 inputs since the early 70s. This trend reversal has been clearly observed in shallow monitoring networks (Visser, 2009), but not yet in PSWFs pumping from shallow aquifers. Obviously there is a significant delay due to longer travel times and more mixing with older groundwater.

A third trend reversal to be expected in PSWFs is the reduction of NO_3 concentrations in groundwater as result of improved agricultural practices resulting in less excessive manure and fertilizer applications. At the end of the 80’s, the whole country of the Netherlands was categorized as vulnerable to nitrate and several measures based on the European Nitrate Directive (EU, 1991) were taken to improve the situation: (1) reduction of the number of livestock by limiting the manure production rights; (2) limitation of the milk quotation, which together with the rise in milk production per cow, reduces the number of cows required; (3) limitation of animal manure application in PO_4 saturated soils; (4) reduction of the manure spreading period to February-August in sandy soils; (5) implementation of emission-free manure spreading, with the consequent reduction of atmospheric deposition and direct eutrophication of surface waters; and (6) obligation to cover manure storages in order to avoid atmospheric emissions. The trend reversal resulting from these measures has been successfully identified in shallow observation wells of the national groundwater quality monitoring network (Visser et al., 2007). However, such trend reversals are only present in a very limited number of shallow PSWFs of hydrosomes C and E. Also in this case the delay is due to longer travel times and buffering mechanisms like the mixing of waters of different origin, composition and ages. Even the shallow PSWFs of hydrosome L, which are strongly affected by agricultural activities and yield relatively young waters in many cases, present no trend reversal yet.

6.4.3 Trends and future outlook

The trend analysis reveals a number of characteristic regional patterns in the study area. All PSWFs tapping hydrosome W have been abandoned, because of water quality problems due to salinization, too high concentrations of NH_4, Fe, CH_4 and DOC, or a too strong color. From the ones still active those in hydrosomes E and L present the most severe water quality problems, mainly due to their relatively short travel times and the high NO_3 and SO_4 loads from agricultural activities, atmospheric deposition of acidifying compounds and pyrite oxidation. Their quality evolution needs to be carefully monitored, and agriculture within the WHPAs should be either abandoned or altered into ecological farming. Mitigation measures will have no immediate impact on water quality, however, while the most polluted water is expected to be still underway to the PSWFs. High NO_3 and/or SO_4 concentrations can be corrected to some extent by WFA measures, but several PSWFs will probably have to be abandoned. Water quality problems in hydrosome L have already been partly solved by starting a large AR project in 1994. The new PSWF, which is fed by surface water from the river Meuse, has a capacity of 20 Mm^3/year, which is sufficient to gradually replace the most affected PSWFs in the limestone aquifer.

Hydrosome C is extremely vulnerable towards pollution because of the lack of reactive phases within the aquifer (Mendizabal et al., 2011, Chapter 4). Nevertheless the water most PSWFs deliver is of great quality and will be so in future, because of predominance of nature within their WHPA. Only a few PSWFs show significant effects of acidification, which calls for monitoring with a focus on specific trace elements like Al, Be, Ni and rare earth elements. This also applies to some strongly acidified shallow PSWFs of hydrosome S.

PSWFs abstracting from hydrosome D in the coastal dunes of the mainland and in the delta, have been abandoned or replaced by AR systems because of declining groundwater tables, salinization and ecological problems. On the Wadden Islands PSWFs tapping hydrosome D survived, however, because their supply from the mainland is difficult and expensive, while the pumping rate is still acceptable. The number of AR and RBF systems is still slightly increasing in order to reverse declining groundwater tables, which pose problems due to land subsidence and desiccation of wetlands. Although AR and RBF systems already show beneficial trend reversals for inorganic compounds like Cl, SO4 and Na, and for some conservative organic pollutants like bentazone, other compounds like various pharmaceuticals are displaying increasing trends that are quite worrying.

PSWFs pumping from hydrosome F and deep PSWFs extracting water from hydrosomes C and S present an excellent and very stable water quality that is guaranteed for the coming hundreds of years. Therefore they constitute valuable strategic groundwater resources. Their only concern is the upconing of brackish water from deeper layers due to excessive pumping, as already noted in some cases.

6.5 Conclusions

The usually long water quality records from public supply well fields (PSWFs) provide an easy way to determine natural background levels (NBLs) and hydrochemical trends for selected parameters and for individual groundwater bodies. Our study demonstrates this for the Netherlands, but also shows that there are various drawbacks that need serious attention.

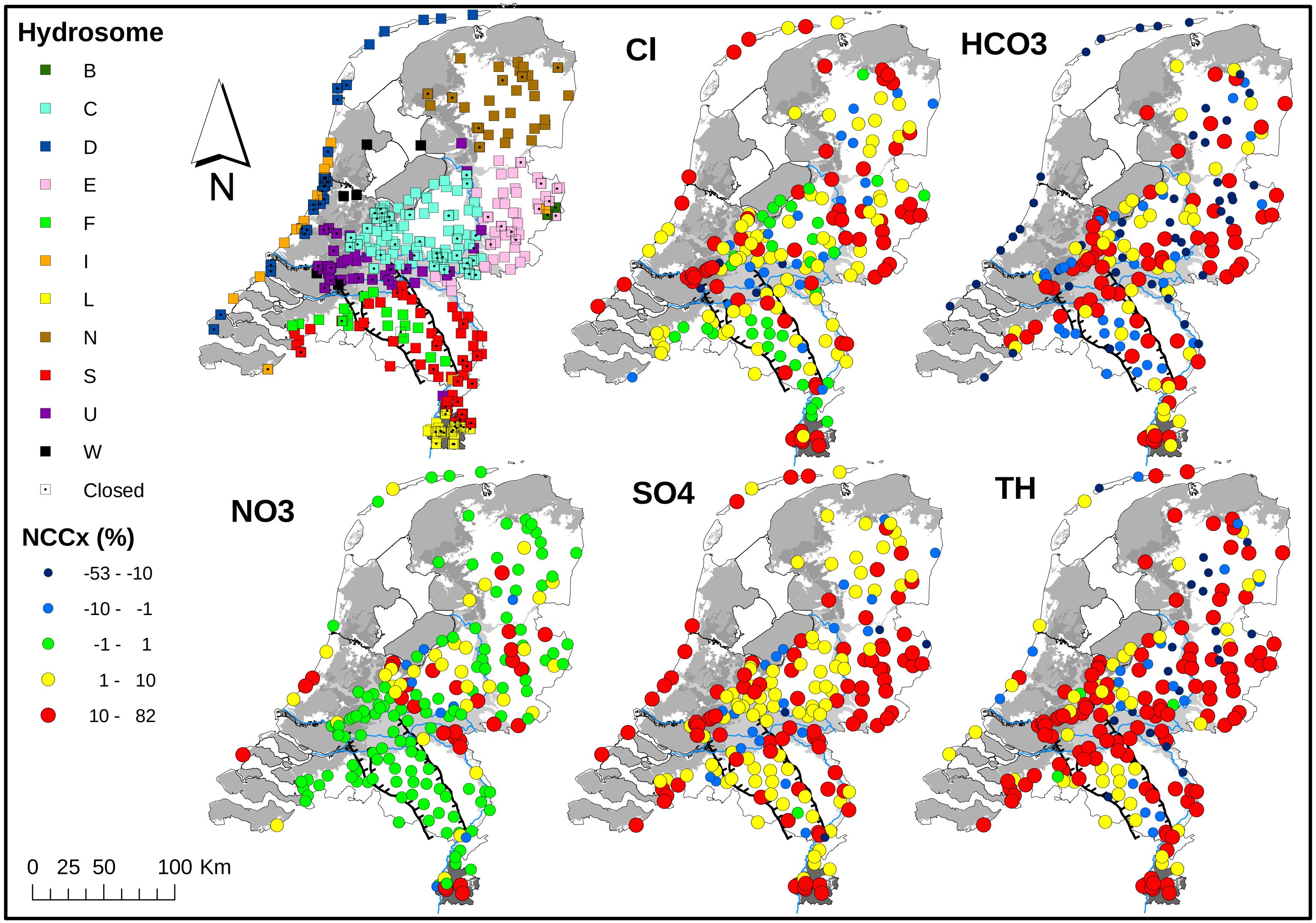


Fig 6.8: The normalized concentration change index (NCC_X; see Eq. (6.2) for 5 quality indicators of groundwater resources at the depth of abstraction by 206 active PSWFs in the Netherlands in 2008, together with the 11 hydrosomes.

NBLs are preferably derived from the first six years of operation of a PSWF that started before 1940, or from PSWFs that may have started later but are abstracting from sufficiently deep or confined aquifers with relatively old groundwater. Thus obtained NBLs refer to the depth interval of groundwater abstraction within the whole field, and as such they represent a large volume which, however, may be composed of a mixture of several water qualities. A check on the mixing of different water qualities should be performed, because NBLs should refer to homogeneous water masses. In addition, it should be checked which aquifer at which depth was tapped at that time, because changes in PSWFs may have occurred under the pressure of environmental pollution or salinization.

Trends could be easily determined in an automatized way by using Trendanalyst (www.amo-nl.com/english/index.htm). A very simple way of identifying trend reversals was followed by comparing trends from the beginning of abstraction until 1970 with trends over the period 1985-2005. The interpretation of trends requires a thorough analysis of well field adaptation measures during the whole abstraction period, because these may dominate trends in the water quality record. Trend bundles were defined in order to identify different hydrochemical processes affecting specific areas and to classify PSWFs according to such bundles.

In this contribution some new ways are proposed to present and map trends. A normalization procedure prior to trend mapping is introduced in order to produce identically scaled trend maps that facilitate the interpretation and integration of trends for different hydrochemical parameters. A normalized concentration change index is also presented as a means to quantify changes in water quality at any time. Finally, a simple method is given to upscale NBLs for individual PSWFs to their national groundwater body with distinction of hydrochemical zones.

Evaluating the total picture for the Netherlands, a diverse situation is encountered. Very stable PSWFs such as the ones pumping very high quality groundwater from deep parts of the Flanders or the Northern hydrosomes, are discerned from more vulnerable PSWFs, characterized by ongoing water quality deterioration, such as in hydrosomes E and L, which are substantially affected especially by agricultural activities.

The very shallow, vulnerable PSWFs without artificial recharge (AR) or river bank filtration (RBF) do not show yet the effects of sanitation measures adopted in compliance with European legislation, such as the Water Framework Directive (EU, 2000), the Groundwater Directive (EU, 2006b) or the European Nitrate Directive (EU, 1991). PSWFs with AR and RBF are, however, already showing trend reversals, thanks to short travel times and strong quality improvements of the rivers through intensive international sanitation measures.

6.6 Acknowledgements

The research was funded by the Joint Research Programme of the Dutch Waterworks (BTO) and Delft Cluster, project number CT05.30.

Chapter 7

7 Conclusions and recommendations

7.1 Main conclusions

Public supply well fields (PSWFs) constitute a precious (inter)national monitoring system for evaluating the chemical state of groundwater, due to their spatial distribution throughout the country and the long time series available. They are monitored on a regular basis and they have been so for a long time. Therefore, such a network has a great potential to establish (a) the hydrochemical status of groundwater bodies (GWBs) at the depth of abstraction as shown in Mendizabal et al. (2011, Chapter 4); (b) the vulnerability of groundwater resources as shown in Mendizabal and Stuyfzand (2011, Chapter 5); and (c) pollution trends and natural background levels (NBLs) as illustrated in Mendizabal et al. (2012, Chapter 6) . However, the mixed character of water samples obtained from PSWFs requires a more laborious interpretation than samples from conventional observation wells, due to misleading effects resulting from variable pumping schemes during sampling and/or well field adaptation measures. In Mendizabal and Stuyfzand (2009, Chapter 2), guidelines are presented to avoid this problem and to better interpret the data.

Recent intensive monitoring practices require sophisticated tools, capable of dealing in an efficient way with numerous activities, such as data acquisition, control, analysis and reporting. In Mendizabal and Stuyfzand (in prep., Chapter 3), such a tool is presented.

The new international PSWF typology presented in Mendizabal et al. (2011, Chapter 4), which combines age, redox and alkalinity indices, is taking account of the origin of water, the hydrogeochemical environment and the potential proximity of anthropogenic (modern) pollutants. The age index is a good indicator of vulnerability towards all hazardous compounds released at the surface; the alkalinity index gives an indication of the vulnerability towards acidifying processes; and the redox index is a measure of the capacity of the aquifer to reduce undesired oxidants like NO_3 and SO_4 and to eliminate specific pollutants through specific oxidation or reduction processes, such as organic micropollutants, including pesticides and pharmaceuticals. This information, together with the vulnerability maps presented in Mendizabal and Stuyfzand (2011, Chapter 5), helps to fine-tune the monitoring program to those parameters that are likely to be found in a specific water source and in a specific environment, so that costs are minimized and benefits maximized.

This PSWF typology yields more homogeneous GWBs than the guidelines established within the European Water Framework Directive (2000; 2008). They are more logically delimited for water quality protection purposes and for answering international questions on transboundary aquifers, and also better extrapolated in depth following the groundwater flow system. The underlying hydrochemical system analysis (HCSA), applied to PSWFs (Mendizabal et al., 2011, Chapter 4), observation wells or both, also covers the need to delineate GWBs with artificial recharge (AR) and river bank filtration (RBF), which are rapidly increasing in number and volume in many countries. A three-dimensional map of such groundwater bodies and hydrochemical facies on a European scale could serve as a means to summarize the quality status of European groundwater resources, to visualize the extent of GWBs, and to follow up their dynamics (growth and shrinking). This is not possible with single value maps of specific parameters.

The usually long water quality records from PSWFs provide an easy way to determine NBLs for selected parameters and for individual groundwater bodies, as shown in Mendizabal et al. (2011, Chapter 4). The aggregation of NBLs according to the PSWF typology defined in Mendizabal et al. (2011, Chapter 4) yields homogeneous groups of PSWFs that deliver waters of the same origin and similar hydrogeochemical environments. As the method relies on the first six years of operation, the NBLs are not affected by well field adaptation measures (Mendizabal and Stuyfzand, 2009, Chapter 2), such as drilling new wells or abandoning polluted ones, which will rarely happen during the first six years of operation.

7.2 Practical implications

This research offers several tools for better management of drinking water resources in general and PSWFs in particular. New methods have been developed or previous ones optimized for the determination of: (1) the origin of the water; (2) the hydrological response curve; (3) the hydrochemical water type; (4) the intrinsic and specific vulnerability; (5) the redox level of mixed waters in a well; (6) the natural background level; and (7) trend bundles, at both the PSWF level and GWB level. Additionally, a software package is presented for the efficient management, control, analysis and presentation of water quality data in four dimensions (X, Y, Z, t).

The results of amongst others PSWF typology, trend analysis and natural background definition are presented in various maps and cross sections. They translate complex hydrochemical patterns into easily interpretable maps by showing for example in one picture the PSWFs, groundwater bodies and hydrochemical facies (Mendizabal et al., 2011, Chapter 4). Such maps aim at facilitating communication between researchers, water resources managers and policy makers, by showing what is otherwise more difficult to achieve with single value maps of specific parameters. Their combination in the maps presented, like those for VIP and VIP_X (Mendizabal and Stuyfzand, 2011, Chapter 5) and NBLs (Mendizabal et al., 2012, Chapter 6), yields a better means to understand and solve complex groundwater resources management problems at different scales, ranging from a single well(field) or region to the national or European scale.

On a smaller scale than presented here, similar maps can be used to assess the vulnerability of a single well for specific pollution sources. The HCSA also reveals hydrochemical patterns within the well field that can be used to design a proper management strategy for the individual wells and optimize their pumping regime to guarantee the best quality. In addition, the HCSA can be used to decide the best location and screening depth of new wells when more capacity is required, or to choose the wells to close down in order to reduce capacity or improve the quality of the well field.

The methods here presented can easily be upscaled to develop strategic plans on the availability of groundwater resources and their protection, on a regional or national scale. A water-supply company can use them to optimize the management of its groundwater resources by regulating production rates of individual PSWFs according to their vulnerability or quality, and also to decide which PSWFs to expand or close down, in order to satisfy water demands at the lowest purification costs or with reduced complexity of purification technology, in compliance with the EU Water Framework Directive.

The vulnerability indices developed in Mendizabal and Stuyfzand (2011, Chapter 5) are not based on site specific ranges of varying sets of hydro- or geochemical parameters, but on standard factors exclusively derived from the water composition. This makes it a robust, objective method that can be applied elsewhere and could therefore serve as a means to standardize the vulnerability assessment of PSWFs.

7.3 Remaining challenges

The research presented in this thesis can be further extended in various directions. On the one hand, zooming in from the national scale to a regional scale or to the catchment area of a specific well field of a water utility will provide new insights in the main hydrochemical processes affecting the quality of the water they deliver. On the other hand, many data gathered during this study, like on various trace elements, numerous organic micropollutants and the stable isotopes of ^{15}N and ^{34}S, were not analyzed in this thesis and deserve to be analyzed elsewhere. The first step in this direction has already been set by Stuyfzand et al. (2008) regarding arsenic and by Stuyfzand and Mendizabal (2010) regarding most trace elements, with focus on the distinction between natural and anthropogenic sources.

^{15}N has been used extensively to provide information on the origin and transformation of nitrate, which may be derived from soil organic nitrogen, synthetic fertilizers, livestock wastes, sewage effluents, and atmospheric deposition. These sources produce in many cases nitrate with distinguishable $^{15}N/^{14}N$ ratios. Analogously, ^{34}S can be used to determine the origin of sulfate, which may be derived from pyrite oxidation, synthetic fertilizers, livestock wastes, sewage effluents and atmospheric deposition. Quantification of the fraction of NO_3 and SO_4 deriving from these natural or anthropogenic inputs is needed to determine the vulnerability of the water resources towards different polluting processes, and to predict their quality evolution.

The data of some organic micropollutants, such as Bentazone, Carbendazim and Mecoprop, were used in Mendizabal and Stuyfzand (2011, Chapter 5), but not in detail, because this thesis was mainly focused on inorganic chemistry. The data of organic micropollutants can further be used to present specific maps and to refine the vulnerability indices here presented and to further develop protection strategies.

References

Akulov, Y.A. and Mamyrin, B.A., 2004. Difference between the triton beta decay constants in atomic and molecular tritium measured by the helium isotope method. Physics Letters B, 600(1-2): 41-47.

Albinet, M. and Margat, J., 1970. Cartographie de la vulnérabilité à la pollution des nappes d'eau souterraine Bull BRGM 2(4): 13-22.

Alcalá, F.J. and Custodio, E., 2005. Use of the Cl/Br ratio as a tracer to identify the origin of salinity in some coastal aquifers of Spain. In: L. Araguas, E. Custodio and M. Manzano (Editors), Groundwater and saline intrusion, selected papers from the 18th SWIM, Cartajena 2004. Serie Hydrogeologica y aguas subterraneas. Inst. Geol. y Minero de Espana, pp. 481-495.

Aller, L., Bennett, T., Lehr, J.H., Petty, R.H. and Hackett, G., 1987. DRASTIC: a standardised system for evaluating groundwater pollution potential using hydrogeologic settings. EPA 600/2-85/018, U.S. Environmental Protection Agency, Oklahoma City.

Appelo, C.A.J., Drijver, B., Hekkenberg, r. and de Jonge, M., 1999. Modeling in situ iron removal from ground water. Ground Water, 37(6): 181-187.

Appelo, C.A.J. and Postma, D., 1983. Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536 pp.

Appelo, C.A.J. and Postma, D., 2005. Geochemistry, groundwater and pollution. Balkema, Rotterdam, 536 pp.

Back, W., 1960. Origin of hydrochemical facies of ground water in the Atlantic coastal plain, 21st Internat. Geol. Cong. Rept.pt.1, Copenhagen, pp. 87-95.

Backman, B., Bodiš, D., Lahermo, P., Rapant, S. and Tarvainen, T., 1998. Application of a groundwater contamination index in Finland and Slovakia. Environmental Geology, 36(1): 55-64.

Baggelaar, P.K. and Van der Meulen, C.J., 2007. Trendanalist. User Guide.

Batlle Aguilar, J., Orban, P., Dassargues, A. and Brouyère, S., 2007. Identification of groundwater quality trends in a chalk aquifer threatened by intensive agriculture in Belgium. Hydrogeology Journal, 15(8): 1615-1627.

Berkhoff, K., 2008. Spatially explicit groundwater vulnerability assessment to support the implementation of the Water Framework Directive - a practical approach with stakeholders. Hydrology and Earth System Sciences, 12(1): 111-122.

Berner, R.A., 1981. A new geochemical classification of sedimentary environments. JOURNAL OF SEDIMENTARY RESEARCH, 51(2): 359-365.

Beusen, A.H.W. et al., 2008. Considerations of Groundwater Quality Characterisation for the Water Framework Directive. 500003006 (in Dutch), Planbureau voor de Leefomgeving (PBL), Bilthoven.

Blanquet, P., 1946. Détermination de parameters permettant le calcul de la conductivité de certaines solutions salines complexes : application à la vérification de l'analyse chimique d'une eau minerale. Annales Instit. Hydrol, 62: 131-143.

Boumans, L.J.M., Fraters, D. and van Drecht, G., 2005. Nitrate leaching in agriculture to upper groundwater in the sandy regions of The Netherlands during the 1992-1995 period. Environmental Monitoring and Assessment, Volume 74: 2225-241.

Boumans, L.J.M., Fraters, D. and van Drecht, G., 2008. Mapping nitrate leaching to upper groundwater in the sandy regions of The Netherlands, using conceptual knowledge. Environmental Monitoring and Assessment, Volume 137(1-3): 243-249.

Box, G.E.P. and Jenkins, J.M., 1976. Time series analysis, forecasting and control. Holden-Day, San Francisco.

Bradley, J., 1968. Distribution-free statistical tests. Prentice-Hall.

Broers, H.P. and van der Grift, B., 2004. Regional monitoring of temporal changes in groundwater quality. Journal of Hydrology, 296(1-4): 192-220.

Broers, H.P. and van Geer, F.C., 2005. Monitoring Strategies at Phreatic Wellfields: A 3D Travel Time Approach. Ground water, 43(6): 850-862.

Brooks, D. and Cech, I., 1979. Nitrates and bacterial distribution in rural domestic water supplies. Water Research, 13(1): 33-41.

Burkart, M.R. and Feher, J., 1996. Regional estimation of ground water vulnerability to nonpoint sources of agricultural chemicals. Water Science and Technology, 33(4-5): 241-247.

Burkart, M.R., Kolpin, D.W. and James, D.E., 1999. Assessing groundwater vulnerability to agrichemical contamination in the Midwest US. Water Science and Technology, 39(3): 103-112.

Burow, K., Dubrovsky, N. and Shelton, J., 2007. Temporal trends in concentrations of DBCP and nitrate in groundwater in the eastern San Joaquin Valley, California, USA. Hydrogeology Journal, 15(5): 991-1007.

Burow, K.R., Shelton, J.L. and Dubrovsky, N.M., 2008. Regional Nitrate and Pesticide Trends in Ground Water in the Eastern San Joaquin Valley, California. J Environ Qual, 37(5_Supplement): S-249-263.

CBW, 1980. Richtlijnen en aanbevelingen voor de bescherming van waterwingebieden. (in Dutch), VEWIN-RID Commissie Bescherming Waterwingebieden.

Cech, I., Lemma, M., Kreitler, C.W. and Prichard, H.M., 1988. Radium and Radon in water supplies from the Texas Gulf Coastal aquifer. Water Research, 22(1): 109-121.

Ceric, A. and Haitjema, H.M., 2005. On using simple time-of-travel capture zone delineation methods. Ground water, 43(3): 408-412.

Chapelle, F.H., 2001. Ground-Water Microbiology and Geochemistry. John Wiley & Sons, New York.

Cirkel, D.G. and Stuyfzand, P.J., 2004. kwaliteit van de KRW-grondwaterlichamen op de diepte van de Nederlandse drinkwaterwinningen. KWR.04.014 (in Dutch), Kiwa Water Research, Nieuwegein.

Civita, M., 1994. Le Carte della vulnerabilità degli acquiferi all'inquinamento. In: Pitagora (Editor), Teoria & practica, Bologna, pp. 325.

Clark, I.D. and Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, New York, 328 pp.

Coetsiers, M., Blaser, P., Martens, K. and Walraevens, K., 2009. Natural background levels and threshold values for groundwater in fluvial Pleistocene and Tertiary marine aquifers in Flanders, Belgium. Environmental Geology, 57(5): 1155-1168.

Daly, D. et al., 2002. Main concepts of the "European approach" to karst-groundwater-vulnerability assessment and mapping. Hydrogeology Journal, 10(2): 340-345.

Daughney, C.J. and Reeves, R.R., 2005. Definition of hydrochemical facies in the New Zealand National Groundwater Monitoring Programme. Journal of Hydrology New Zealand, 44(2): 105-130.

Daughney, C.J. and Reeves, R.R., 2006. Analysis of temporal trends in New Zealand's groundwater quality based on data from the National Groundwater Monitoring Programme. Journal of Hydrology New Zealand, 45(1): 41-62.

Davis, S.N., Fabryka-Martin, J. and Wolfsberg, L., 2004. Variations of Bromide in potable ground water in the United States. Ground water, 42(6): 902-909.

Dawoud, M.A., 2004. Design of national groundwater quality monitoring network in Egypt. Environmental Monitoring and Assessment, 96(1): 99-118.

de Boer, J.L.M., Verweij, W., van der Velde-Koerts, T. and Mennes, W., 1996. Levels of rare earth elements in Dutch drinking water and its sources. Determination by inductively coupled plasma mass spectrometry and toxicological implications. A pilot study. Water Research, 30(1): 190-198.

Driscoll, F.G., 1986. Groundwater and Wells. Johnson Division, St. Paul, Minnesota, 1089 pp.

Dunlap, H.F. and Hawthorne, R.R., 1951. The calculation of water resistivities from chemical analyses. J. Petr. Techn, 3(1): 17.

Dutch Government, 1979. Wet milieubeheer 1979 (in Dutch) (Environment Protection Act, 1979), The Hague: The Netherlands.

Dutch Government, 1986. Wet bodembescherming 1986 (in Dutch) (Soil Protection Act,1986), The Hague: The Netherlands.

Dutch Ministry of Environment, 2001. Waterleidingbesluit 2001 (in Dutch) (Water Supply Act, 2001). In: D. Government (Editor). Staatsblad, pp. 1-28.

Edmunds, W.M., 2008. The baseline inorganic chemistry of European groundwaters. In: W.M. Edmunds and P. Shand (Editors), Natural groundwater quality. John Wiley & Sons, pp. 22-58.

Edmunds, W.M., Carrillo-Rivera, J.J. and Cardona, A., 2002. Geochemical evolution of groundwater beneath Mexico City. Journal of Hydrology, 258(1-4): 1-24.

Edmunds, W.M. and Shand, P., 2008. Natural groundwater quality. John Wiley & Sons, 469 pp.

Engelen, G.B., 1981. A systems approach to ground water quality-methodological aspects. The Science of the Total Environment, 21: 1-15.

Engelen, G.B. and Jones, G.P., 1986. Developments in the analysis of ground water flow systems. IAHS Publications, 163: 356.

EU, 1991. Directive 91/676/EC of the European parlament and the Council of 12 December 1991. Concerning the protection of waters against pollution caused by nitrates from agricultural sources. In: E. Commission (Editor).

EU, 2000. Water Framework Directive, 2000, Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000. Establishing a framework for Community action in the field of water policy. In: E. Commission (Editor), Official Journal of the European Communities, pp. L 327/1.

EU, 2003. Horizontal guidance on the application of the term "water body" in the context of the Water Framework Directive, European Commission.

EU, 2006a. Directive 2006/118/EC of the European parlament and the Council of 12 December 2006. On the protection of groundwater against pollution and deterioration., European Commission.

EU, 2006b. Groundwater Directive, 2006, Directive 2006/118/EC of the European Parliament and the Council of 12 December 2006. On the protection of groundwater against pollution and deterioration. In: E. Commission (Editor), Official Journal of the European Union, pp. L 372/19.

EU, 2008. Water Framework Directive Amendment, 2008, Directive 2008/32/EC of the European Parliament and the Council of 11 March 2008. Amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, as regards the implementing powers conferred on the Commission. In: E. Commission (Editor), Official Journal of the European Union, pp. L 81/60.

Foster, S.S.D., Hirata, R.A., Gomes, D., D'elia, M. and Paris, M., 2002. Groundwater quality protection - a guide for water utilities, municipal authorities, and environment agencies. World Bank Publication, Washington DC, USA, 101 pp.

Franke, O.L., Reilly, T.E., Pollock, D.W. and LaBaugh, J.W., 1998. Estimating areas contributing recharge to wells. Lessons from previous studies. Circular 1174, U.S. Geological Survey, Denver.

Frapporti, G., 1994. Geochemical and statistical interpretation of the Dutch national groundwater quality monitoring network, Utrecht University, Utrecht.

Frapporti, G., Vriend, S.P. and van Gaans, P.F.M., 1993. Hydrogeochemistry of the shallow Dutch groundwater: Interpretation of the National Groundwater Quality Monitoring Network. Water Resour. Res., 29(9): 2993-3004.

Frapporti, G., Vriend, S.P. and van Gaans, P.F.M., 1994. Qualitative time trend analysis of ground water monitoring networks Environmental Monitoring and Assessment, 30(1): 81-102.

Fraters, B., Boumans, L.J.M. and Prins, H.P., 2001. Background concentrations for 17 trace elements in groundwater in The Netherlands. Report nr. 711701017 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Fraters, D., Boumans, L.J.M., van Drecht, G., de Haan, T. and de Hoop, W.D., 1998. Nitrogen monitoring in groundwater in the sandy regions of The Netherlands. Environmental Pollution, Volume 102(Number 1): 479-485.

Gezondheidsraad, 1932. Het krop-probleem in Nederland (The struma problem in The Netherlands). Staatsuitgeverij, Den Haag (in Dutch).

Glastra, P., van Zanten, R., Drost, R.M.S. and Mattern, F.C.M., 1989. Examination of the radioactivity of drinking water over the period 1981-1984. Report nr. 248201001 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Glynn, P.D. and Plummer, L.N., 2005. Geochemistry and the understanding of ground-water systems. Hydrogeology Journal, 13(1): 263-287.

Gogu, R.C. and Dassargues, A., 2000. Current trends and future challenges in groundwater vulnerability assessment using overlay and index methods. Environmental Geology, 39(6): 549-559.

Goss, M.J., Barry, D.A.J. and Rudolph, D.L., 1998. Contamination in Ontario farmstead domestic wells and its association with agriculture: 1. Results from drinking water wells. Journal of Contaminant Hydrology, 32: 267-293.

Government, D., 2001. Waterleidingbesluit 2001 (in Dutch). Staatsblad, pp. 1-28.

Grath, J. et al., 2001. The EU Water Framework Directive: Statistical aspects of the identification of groundwater pollution trends, and aggregation of monitoring results. Final report. Ref. 41.046/01-IV1/00 and GZ 16 2500/2-I/6/00, Austrian Federal Ministry of Agriculture and Forestry, Environment and Water Management.

Griffioen, J., Passier, H.F. and Klein, J., 2008. Comparison of Selection Methods To Deduce Natural Background Levels for Groundwater Units. Environmental Science & Technology, 42(13): 4863-4869.

Griffioen, J. and van der Aa, N.G.F.M., 2002. Argumentation for the division of The Netherlands in geohydrological management units. TCB R16(2002), Soil Protection Technical Committee (TCB), The Hague.

Groundwater Directive, 2006. Directive 2006/118/EC of the European Parliament and the Council of 12 December 2006. On the protection of groundwater against pollution and deterioration. In: E. Commission (Editor), Official Journal of the European Union, pp. L 372/19.

Haitjema, H.M., 1995. On the residence time distribution in idealized groundwatersheds. Journal of Hydrology, 172(1-4): 127-146.

Hallberg, R.O. and Martinell, R., 1976. Vyredox in situ purification of groundwater. Ground water, 14(2): 88-93.

Hazeu, G.W., 2006. Land use mapping and monitoring in The Netherlands (LGN5), 2nd EARSeL Workshop on Land Use and Land Cover, Bonn, Germany, pp. 323-329.

Helsel, D.R., 1990. Less than obvious - statistical treatment of data below the detection limit. Environ. Sci. Technol., 24(12): 1766-1774.

Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water 3rd edition. 2254, U.S. Geological Survey.

Hendrix, P.A.M. and Meinardi, C.R., 2004. Springs and small streams in Southern-Limburg; Quality of groundwater, spring water and streams. Report nr. 500003003 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Hirsch, R.M. and Slack, J.R., 1984. A nonparametric trend test for seasonal data with serial dependence. Water Resources Research, 20(6): 727-732.

Hirsch, R.M., Slack, J.R. and Smith, R.A., 1982. Techniques of trend analysis for monthly water quality data. Water Resources Research, 18(1): 107-121.

Houben, G. and Treskatis, C., 2007. Water well. Rehabilitation and reconstruction. The McGraw-Hill Companies, Inc., 391 pp.

Juhler, R.K. and Felding, G., 2003. Monitoring Methyl Tertiary Butyl Ether (MTBE) and other Organic Micropollutants in Groundwater: Results from the Danish National Monitoring Program. Water, Air, & Soil Pollution, 149(1): 145-161.

Kass, W., 1998. Tracing Technique in Geohydrology. Balkema, Rotterdam, 581 pp.

Kelly, W.R., 2008. Long-term trends in Chloride concentrations in shallow aquifers near Chicago. Ground Water, 46(5): 772-781.

Kendall, M.G., 1938. A new measure of rank correlation. Biometrika, 30(1938): 81-93.

Kendall, M.G., 1975. Rank correlation methods. Charles Griffin & Company, London.

Kim, N.J., Cho, M.J. and Woo, N.C., 1995. Developing A National Groundwater-Monitoring Network In Korea. Hydrogeology Journal, 3(4): 89-94.

KNMI-RIVM, 1978-1988. Chemical composition of precipitation in The Netherlands, National monitoring network for the composition of precipitation. KNMIpubl. 156-1 t/m 156-11 (in Dutch), Dutch national institute of meteorology De Bilt.

Knorr, M., 1937. Die Schutzzonenfrage in der trinkwasser-hygiene. Das Gas- Wasserfach, 80: 350-355.

Kross, B.C., Hallberg, G.R., Bruner, D.R., Cherryholmes, K. and Johnson, J.K., 1993. The nitrate contamination of private well water in Iowa. American Journal of Public Health, 83(2): 270-272.

Kruskal, W. and Wallis, A., 1952. Use of ranks in one-criterion variance analysis. Journal of the American Statistical Association, 47(260): 583-621.

Lalumandier, J.A. and Jones, J.L., 1999. Fluoride concentrations in drinking water. Journal AWWA, 91(10): 42-51.

Lee, J.-Y. et al., 2007. A review of the National Groundwater Monitoring Network in Korea. Hydrological Processes, 21(7): 907-919.

Lee, L. and Helsel, D., 2005. Baseline models of trace elements in major aquifers of the United States. Applied Geochemistry, 20(8): 1560-1570.

Lilliefors, H.W., 1967. On the Kolmogorov-Smirnov test for normality with mean and variance unknown. Journal of the American Statistical Association(62): 399-402.

Lilliefors, H.W., 1969. Correction to the paper: On the Kolmogorov-Smirnov test for normality with mean and variance unknown. Journal of the American Statistical Association(64): 1702.

Limbrick, K.J., 2003. Baseline nitrate concentration in groundwater of the Chalk in south Dorset, UK. The Science of The Total Environment, 314-316: 89-98.

Lindberg, R.D. and Runnells, D.D., 1984. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. Science, 225(4665): 925-927.

Ljung, G.M. and Box, G.E.P., 1978. On a measure of lack of fit in time series models. Biometrika, 65: 297-303.

Lobo Ferreira, J.P. and Oliveira, M.M., 2004. Groundwater vulnerability assessment in Portugal. Geofsica Internacional, 43(4): 541-550.

Loftis, J.C., 1996. Trends in groundwater quality. Hydrological Processes, 10(2): 335-355.

Logan, J., 1961. Estimation of electrical conductivity from chemi¬cal analyses of natural waters. Journal of Geophysical Research, 66: 2479-2483.

Makkink, H.J., Balemans, M.L.M. and Schrama, E.J., 2000. Knowledge document well(field)s. Design, construction and exploitation of pumping wells. BTO 2000-110(C), Kiwa, Nieuwegein.

Mann, H.B., 1945. Non-parametric tests against trend. Econometrica, 13: 245-259.

Matthess, G., 1982. The properties of groundwater. John Wiley & Sons, Inc, 406 pp.

Matthess, G., 1990. Die Beschaffenheit des Grundwassers, Band 2. Gebrüder Borntraeger, Berlin, 498 pp.

McNeal, B.L., Oster, J.D. and Hatcher, J.T., 1970. Calculation of electrical conductivity from solution composition data as an aid to in-situ estimation of soil salinity. Soil science, 110: 405-414.

Meinardi, C., 2004. Basiswaarden in neerslag en grondwater : basiswaarden voor 50 spoorelementen in grondwater en neerslag. Bodem, 13(1): 17-19.

Meinardi, C.R., 2003. Travel times and groundwater recharge determined from the national and provincial monitoring networks. Report nr. 714801027 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Meinardi, C.R., Groot, M.S.M. and Prins, H.F., 2003. Basis values for trace elements in groundwater sampled in national and provincial monitoring networks (LMG; PMG; LMB; Veluwe springs). Report nr. 714801028 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Melloul, A.J. and Collin, M., 1998. A proposed index for aquifer water-quality assessment: the case of Israel's Sharon region. Journal of Environmental Management, 54(2): 131-142.

Mendizabal, I., Stuyfzand, P. and Wiersma, A., 2011. Hydrochemical system analysis of public supply well fields, to reveal water-quality patterns and define groundwater bodies: The Netherlands. Hydrogeology Journal, 19(1): 83-100.

Mendizabal, I. and Stuyfzand, P.J., 2009. Guidelines for interpreting hydrochemical patterns in data from public supply well fields and their value for natural background groundwater quality determination. Journal of Hydrology, 379(1-2): 151-163.

Mendizabal, I. and Stuyfzand, P.J., 2011. Quantifying the vulnerability of well fields towards anthropogenic pollution: The Netherlands as an example. Journal of Hydrology, 398(3-4): 260-276.

Mendizabal, I. and Stuyfzand, P.J., in prep. HyCA, the all in one approach for the efficient spatial and temporal analysis of large groundwater quality databases.

Mendizabal, I., Stuyfzand, P.J. and Baggelaar, P.K., 2012. Hydrochemical trends for public supply well fields in the Netherlands (1898-2008), natural backgrounds and upscaling to groundwater bodies.

Molt, E.L., 1961. Pollution of Rhine River water, 13e Vakantiecursus Drinkwatervoorziening Rijksinstituut voor Drinkwatervoorziening, Leidschendam, pp. 46-71 (in dutch).

Mook, W.G., 1968. Geochemistry of the stable carbon and oxygen isotopes of natural waters in The Netherlands. PhD Thesis, Groningen, 157 pp.

Oliver, B.G., Thurman, E.M. and Malcom, R.L., 1983. The contribution of humic substances to the acidity of colored natural waters. Geochimica et Cosmochimica Acta, 47: 2031-2035.

Paradis, D. et al., 2007. Comparative study of methods for WHPA delineation. Ground Water, 45(2): 158-167.

Parkhurst, D.L., 2005. PHREEQC Interactive, A graphical user interface to PHREEQC. .

Parkhurst, D.L. and Appelo, C.A.J., 1999. PHREEQC (version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations USGS.

Parsons, R. and Tredoux, G., 1995. Development Of A Strategy To Monitor Groundwater Quality On A National Scale South Africa. Hydrogeology Journal, 3(1): 50-56.

Pebesma, E.J. and de Kwaadsteniet, J.W., 1997. Mapping groundwater quality in The Netherlands. Journal of Hydrology, 200(1-4): 364-386.

Peiffer, S., Klemm, O., Pecher, K. and Hollerung, R., 1992. Redox measurements in aqueous solutions -- A theoretical approach to data interpretation, based on electrode kinetics. Journal of Contaminant Hydrology, 10(1): 1-18.

Post, V.E.A., 1999. PHREEQC for Windows, a graphical user interface to PHREEQC. .

Reed, P.A., 1987. National pesticides in well water survey, Rural groundwater contamination. Lewis publishers Inc., Chelsea Michigan, pp. 253-260.

Reijnders, F.R., van Drecht, G., Prins, H.F. and Boumans, L.J.M., 1998. The quality of the groundwater in The Netherlands. Journal of Hydrology, Volume 207(3-4): 179-188.

Reijnders, H.F.R., van Staden, J.J. and Nagtegaal, N.W., 1983. Prevention and trends in some chemical compounds found in raw water of public supply well fields in the Netherlands. Report nr. 218108001 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Reynolds-Vargas, J., Fraile-Merino, J. and Hirata, R., 2006. Trends in Nitrate Concentrations and Determination of its Origin Using Stable Isotopes (18O and 15N) in Groundwater of the Western Central Valley, Costa Rica. AMBIO: A Journal of the Human Environment, 35(5): 229-236.

RIWA, 2002. Annual Report 1999-2000. Part D. The Rhine and the Scheldt, Association of River Waterworks.

Rosen, M.R. and Lapham, W.W., 2008. Introduction to the U.S. Geological Survey National Water-Quality Assessment (NAWQA) of Ground-Water Quality Trends and Comparison to Other National Programs. J Environ Qual, 37(5_Supplement): S-190-198.

Rossum, J.R., 1975. Checking the accuracy of water analyses through the use of conductivity. Journal of the American Water Works Association, 67: 204-205.

Rudolph, D.L., Barry, D.A.J. and Goss, M.J., 1998. Contamination in Ontario farmstead domestic wells and its association with agriculture: 2. Results from multilevel monitoring well installations. Journal of Contaminant Hydrology, 32: 295-311.

Saeedi, M., Abessi, O., Sharifi, F. and Meraji, H., 2009. Development of groundwater quality index. Environmental Monitoring and Assessment.

Safe Drinking Water Act, 1974. Safe Drinking Water Act. In: r.U.S. Congress (Editor).

Schwientek, M., Maloszewski, P. and Einsiedl, F., 2009. Effect of the unsaturated zone thickness on the distribution of water mean transit times in a porous aquifer. Journal of Hydrology, 373(3-4): 516-526.

Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. Journal of American Statistics Asociation, 63(1): 1379-1389.

SGBP, 2009. Catchment management plans. Summary Eems, Meuse, Rhine delta and Schelde (in Dutch), Ministry of Transport, Public Works and Water Management.

Shapiro, S.S. and Francia, R.S., 1972. An approximate analysis of variance test for normality. Journal of the American Statistical Association, 67(337): 215-216.

Shapiro, S.S. and Wilk, M.B., 1965. An analysis of variance test for normality (complete samples). Biometrika, 52: 591-611.

Squillace, P.J., Scott, J.C., Moran, M.J., Nolan, B.T. and Kolpin, D.W., 2002. VOCs, pesticides, nitrate and their mixtures in groundwater used for drinking water in the United States. Environmental Science & Technology, 36: 1923-1930.

Stas, M.E., Louwe Kooijmans, L.H. and van Ijssel, J.J., 1937. Research on the presence of Fluoride in water in The Netherlands. Water (in Dutch), 21: 1-5 + 9-14.

Stigter, T.Y., Ribeiro, L. and Carvalho Dill, A.M.M., 2006. Application of a groundwater quality index as an assessment and communication tool in agro-environmental policies - Two Portuguese case studies. Journal of Hydrology, 327(3-4): 578-591.

Stuart, M.A., Rich, F.J. and Bishop, G.A., 1995. Survey of nitrate contamination in shallow domestic drinking water wells of the inner coastal plain of Georgia. Ground water, 33(2): 284-290.

Stuart, M.E., Chilton, P.J., Kinniburgh, D.G. and Cooper, D.M., 2007. Screening for long-term trends in groundwater nitrate monitoring data. Quarterly Journal of Engineering Geology and Hydrogeology, 40(4): 361-376.

Stumm, W., 1984. Interpretation and measurement of redox intensity in natural waters. Aquatic Sciences - Research Across Boundaries, 46(2): 291-296.

Stuyfzand, P., van Rossum, P. and Mendizabal, I., 2008. Does arsenic, in groundwaters of the compound Rhine-Meuse-Scheldt-Eems delta, menace drinking water supply in the Netherlands?

In: T. Appelo (Editor), Arsenic in groundwater - A world problem. NNC-IAH Publication. Netherlands National Committee of the IAH, Utrecht, pp. 102-125.

Stuyfzand, P.J., 1983. Een zeer nauwkeurige berekening van het elektrisch geleidingsvermogen ter controle en aanvulling van wateranalyses. H2O, 16(16): 358-361.

Stuyfzand, P.J., 1986a. Behavior of main constituents and sum parameters upon artificial recharge of surface water in the dutch coastal dunes. Kiwa Mededeling 82 (in Dutch), Kiwa Water Research, Nieuwegein.

Stuyfzand, P.J., 1986b. Een nieuwe hydrochemische classificatie van watertypen, met Nederlandse voorbelden van toepassing. H2O (in Dutch), 19(23): 562-568.

Stuyfzand, P.J., 1987a. Een zeer nauwkeurige berekening van het elektrisch geleidingsvermogen ter controle en aanvulling van wateranalyses : 2e versie. SWE 87.006 (in Dutch), Kiwa Water Research, Rijswijk.

Stuyfzand, P.J., 1987b. Influences of Filtration and Storage of Groundwater Samples on Sample Composition. Trends in Analytical Chemistry, 6(2): 50-54.

Stuyfzand, P.J., 1989a. Hydrology and water quality aspects of Rhine bank groundwater in The Netherlands. Journal of Hydrology, 106(3-4): 341-363.

Stuyfzand, P.J., 1989b. A new hydrochemical classification of watertypes. IAHS Publications, 182: 89-98.

Stuyfzand, P.J., 1990. Hydrochemical facies analysis of coastal dunes and adjacent low lands: The Netherlands as an example. In: T.W.M. Bakker, P.D. Jungerius and J.A. Klijn (Editors), "Dunes, European coasts". Catena Supplement 18, pp. 121-132.

Stuyfzand, P.J., 1993. Hydrochemistry and hydrology of the coastal dune area of the Western Netherlands. PhD Thesis, VU University Amsterdam, Amsterdam, 366 pp.

Stuyfzand, P.J., 1998a. Fate of pollutants during artificial recharge and bank filtration in the Netherlands. In: J.H. Peters (Editor), Artificial recharge of groundwater. Proc. 3rd Intern. Symp. on Artificial Recharge. Balkema, Amsterdam the Netherlands, pp. 119-125.

Stuyfzand, P.J., 1998b. Geohydrochemical screening for optimizing groundwater quality monitoring networks. H2O (in Dutch), 31: 85-88.

Stuyfzand, P.J., 1999. Patterns in groundwater chemistry resulting from groundwater flow. Hydrogeology Journal, 7(1): 15-27.

Stuyfzand, P.J., 2005. Mapping groundwater bodies with artificial or induced recharge, by determination of their origin and chemical facies, ISMAR-5, Berlin, Germany, pp. 839-850.

Stuyfzand, P.J., 2006. Mapping groundwater bodies with artificial or induced recharge, by determination of their origin and chemical facies, Proc. 5th Intern. Symp. on Management of Aquifer Recharge, ISMAR-5. Series on Groundwater, Berlin, Germany, pp. 839-850.

Stuyfzand, P.J., 2007. Towards a more effective diagnosis, therapy and prevention of chemical well and drain clogging. H2O, 2007(8): 44-47.

Stuyfzand, P.J., 2008a. Base exchange indices as indicators of salinization or freshening of (coastal) aquifers, 20th Salt Water Intrusion Meeting. IFAS Research, Naples (Fl) USA, Univ Florida, pp. 262-265.

Stuyfzand, P.J., 2008b. Multitracing of Rhine River water amidst coastal dune groundwater in the Amsterdam dune catchment area. KWR report 08.064 (in Dutch), KWR Watercycle Research Institute, Nieuwegein.

Stuyfzand, P.J. and Bannink, A.D., 2003. Are Dutch well fields sufficiently protected against pathogenic micro-organisms? KWR 2003.021 (in Dutch), Kiwa Water Research, Nieuwegein.

Stuyfzand, P.J., Juhàsz-Holterman, M.H.A. and de Lange, W.J., 2006. Riverbank Filtration in the Netherlands: Well Fields, Clogging and Geochemical Reactions. In: S.A. Hubbs (Editor), Riverbank Filtration Hydrology. Springer NATO Science Series IV, Earth and Envir Sciences 60, pp. 119-153.

Stuyfzand, P.J. and Luers, F., 2000. Balans van milieugevaarlijke stoffen in natuurterreinen met en zonder kunstmatige infiltratie. KIWA mededeling 126 (in Dutch), Kiwa Water Research, Nieuwegein.

Stuyfzand, P.J. and Mendizabal, I., 2010. Trace element concentrations of groundwater from public supply well fields, and their relation with marine sedimentary environments of the aquifer and postdepositional salinity changes, Proc. SWIM-21, Acores.

Stuyfzand, P.J., Segers, W. and Rooijen, N., 2007. Behaviour of pharmaceuticals and other emerging pollutants in various artificial recharge systems in the Netherlands. In: P. Fox (Editor), Management aquifer recharge for sustainability. Proc ISMAR-6, Phoenix, Arizona USA, pp. 231-245.

Stuyfzand, P.J. and Stuurman, R.J., 2008. Origin, distribution and chemical mass balances for brackish and saline groundwaters in the Netherlands. In: G. Barrocu (Editor), 1st SWIM-swica Joint Saltwater Intrusion Conference, Cagliari-Baia de Chia, pp. 151-164.

TCB, 1988. Besluit grondwaterbeschermingsplan. (in Dutch), Soil Protection Technical Committee (TCB), The Hague.

TCB, 1989. Rapport grondwaterbescherming. TCB A88/04R (in Dutch), Soil Protection Technical Committee (TCB), The Hague.

Theil, H., 1950. A rank-invariant method of linear and polynomial regression analysis, 1, 2 and 3, Nederlandse Akademisch Wetenschap, pp. 386-392, 521-525, 1397-1412.

Toth, J., 1963. A theoretical analysis of ground water flow in small drainage basins. Journal of Geophysical Research, 68: 4795-4812.

USEPA, 1974. Safe Drinking Water Act. In: r.U.S. Congress (Editor).

USEPA, 1993. A review of methods for assessing aquifer sensitivity and ground water vulnerability to pesticide contamination. EPA-813R93002, U.S. Environmental Protection Agency.

USEPA, 1996. 1996 Amendments to the Safe Drinking Water Act. In: t.U.S. Congress (Editor), Public Law 104-182.

USEPA, 1997. Glossary, abbreviations, and acronyms. EPA175-B-97-001, U.S. Environmental Protection Agency, Washington DC.

USEPA, 1998. Literature review of methods for delineating wellhead protection areas. EPA 816-R-98-021, U.S. Environmental Protection Agency, Office of Water, Washington DC.

van Beek, C.G.E.M., Hettinga, F.A.M. and Baggelaar, P.K., 1990. Onderzoek naar trendmatige veranderingen in de kwaliteit van het grondwater onttrokken door de nederlandse waterleidingbedrijven. SWE 90.013 (in Dutch), Kiwa Water Research, Nieuwegein.

van Beek, C.G.E.M. and Vaessen, F., 1979. Iron removal from groundwater within the aquifer. H2O (in Dutch), 12(1): 15-19.

van Camp, M. and Walraevens, K., 2008. Identifying and interpreting baseline trends. In: W.M. Edmunds and P. Shand (Editors), Natural groundwater quality. John Wiley & Sons, pp. 131-154.

van den Brink, C., Frapporti, G., Griffioen, J. and Zaadnoordijk, W.J., 2007. Statistical analysis of anthropogenic versus geochemical-controlled differences in groundwater composition in The Netherlands. Journal of Hydrology, 336(3-4): 470-480.

Van der Linden, A.M.A., Reijnders, H.F.R., Zijp, M.C. and Durand-Huiting, A.M., 2007. Residuen van gewasbeschermingsmiddelen in het grondwater. Een analyse voor de KRW. Report nr. 607310001/2007 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

van Duijvenbooden, W., 1987. Groundwater quality monitoring networks: design, and results. In: W. van Duijvenbooden and H.G. van Waegeningh (Editors), Vulnerability of soil and groundwater to pollutants. Proceedings and information, The Hague, The Netherlands, pp. 179-191.

van Duijvenbooden, W., Taat, J. and Gast, L.F.L., 1993. Groundwater quality monitoring in The Netherlands. In: W.M. Alley (Editor), Regional Groundwater Quality. van Nostrand Reinhold, New York, pp. 515-535.

van Lanen, H.A.J., 1984. Transit time of water in the unsaturated zone of sandy soils in areas with deep groundwater tables. H2O (in Dutch), 17(1): 9-16.

van Leeuwen, M., te Stroet, C.B.M., Butler, A.P. and Tompkins, J.A., 1998. Stochastic Determination of Well Capture Zones. Water Resour. Res., 34(9): 2215-2223.

van Ommen, H.C., 1986. Influence of diffuse sources of contamination on the quality of outflowing groundwater including non-equilibrium adsorption and decomposition. Journal of Hydrology, 88(1-2): 79-95.

van Wirdum, G., 1980. Eenvoudige beschrijving van de waterkwaliteitsverandering gedurende de hydrologische kringloop ten behoeve van de natuurbescherming. CHO-TNO rapporten en nota's 5: 118-143.

Vernes, R.W. and van Doorn, T.H.M., 2005. From guide layer to hydrogeological unit. Explanation on the synthesis of the dataset REGIS II. NITG 05-038-B (in Dutch), Netherlands Instituut voor Toegepaste Geowetenschappen NITG-TNO, Utrecht.

Visser, A., 2009. Trends in groundwater quality in relation to groundwater age. PhD thesis Thesis, University of Utrecht, Utrecht, 188 pp.

Visser, A., Broers, H.P., Heerdink, R. and Bierkens, M.F.P., 2009. Trends in pollutant concentrations in relation to time of recharge and reactive transport at the groundwater body scale. Journal of Hydrology, 369(3-4): 427-439.

Visser, A., Broers, H.P., van der Grift, B. and Bierkens, M.F.P., 2007. Demonstrating trend reversal of groundwater quality in relation to time of recharge determined by 3H/3He. Environmental Pollution

AquaTerra: Pollutant behavior in the soil, sediment, ground, and surface water system, 148(3): 797-807.

Vogel, J.C., 1967. Investigation of groundater flow with radiocarbon. In: IAEA (Editor), Isotopes in Hydrology, Vienna, pp. 355-369.

Vrba, J. and Zaporozec, A., 1994. Guidebook on mapping groundwater vulnerability, International contributions to hydrogeology, Heise, Hannover, Germany, pp. 160.

VWN/VEWIN, 1898-1992. Statistical overview of the drinking water supply in The Netherlands, with results of physic and chemical research. (in Dutch).

Ward, R.S., Streetly, M.J., Singleton, A.J. and Sears, R., 2004. A framework for monitoring regional groundwater quality. Quarterly Journal of Engineering Geology and Hydrogeology, 37(4): 271-281.

Water Framework Directive, 2000. Directive 2000/60/EC of the European Parliament and the Council of 23 October 2000. Establishing a framework for Community action in the field of water policy. In: E. Commission (Editor), Official Journal of the European Communities, pp. L 327/1.

Water Framework Directive Amendment, 2008. Directive 2008/32/EC of the European Parliament and the Council of 11 March 2008. Amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, as regards the implementing powers conferred on the Commission. In: E. Commission (Editor), Official Journal of the European Union, pp. L 81/60.

Water Supply Act, 2001. Waterleidingbesluit 2001 (in Dutch). In: D. Government (Editor). Staatsblad, pp. 1-28.

Waterleidingbesluit, 1984. Staatsblad 1984, pp. 1-13.

Wendland, F. et al., 2008. Derivation of natural background levels and threshold values for groundwater bodies in the Upper Rhine Valley (France, Switzerland and Germany). Desalination

10th IWA International Specialized Conference on Diffuse Pollution and Sustainable Basin Management, 226(1-3): 160-168.

Wever, D., Bronswijk, J.J.B., 1998. Optimalisatie van het Landelijk Meetnet Grondwaterkwaliteit, Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven.

Wuijts, S., Rijswick, H. and Dik, H.H.J., 2007. Dossiers for the area for drinking water resources, elaboration of risks and measures. Report nr. 734301032 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Wuijts, S., Rutjes, S.A., van der Aa, N.G.F.M., Mendizabal, I. and de Roda Husman, A.M., 2008. The influence of human and animal sources on groundwater abstraction. From field study to protection policy. Report nr. 734301031 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Xu, Y., Baker, L.A. and Johnson, P.C., 2007. Trends in Ground Water Nitrate Contamination in the Phoenix, Arizona Region. Ground Water Monitoring & Remediation, 27(2): 49-56.

List of publications

Mendizabal, I., Stuyfzand, P.J., 2006. HyCA: Nieuwe software realiseert droom van een ieder die waterkwaliteitsgegevens verwerkt. Tijdschrijft Bodem (in Dutch), 5(2006): 169.

Mendizabal, I., Stuyfzand, P.J., 2007. New software for ground- and surface water quality data. H2O (in Dutch), 9(2007): 40.

Stuyfzand, P., van Rossum, P., Mendizabal, I., 2008. Does arsenic, in groundwaters of the compound Rhine-Meuse-Scheldt-Eems delta, menace drinking water supply in the Netherlands? In: Appelo, T. (Ed.), Arsenic in groundwater - A world problem. NNC-IAH Publication. Netherlands National Committee of the IAH, Utrecht, pp. 102-125.

Mendizabal, I., Stuyfzand, P.J., 2009. Guidelines for interpreting hydrochemical patterns in data from public supply well fields and their value for natural background groundwater quality determination. Journal of Hydrology, 379(1-2): 151-163.

Stuyfzand, P.J., Mendizabal, I., 2010. Trace element concentrations of groundwater from public supply well fields, and their relation with marine sedimentary environments of the aquifer and postdepositional salinity changes, Proc. SWIM-21, Acores.

Mendizabal, I., Stuyfzand, P., Wiersma, A., 2011. Hydrochemical system analysis of public supply well fields, to reveal water-quality patterns and define groundwater bodies: The Netherlands. Hydrogeol. J., 19(1): 83-100.

Mendizabal, I., Stuyfzand, P.J., 2011. Quantifying the vulnerability of well fields towards anthropogenic pollution: The Netherlands as an example. Journal of Hydrology, 398(3-4): 260-276.

Mendizabal, I., Stuyfzand, P.J., submitted. HyCA, the all in one approach for the efficient spatial and temporal analysis of large groundwater quality databases.

Mendizabal, I., Stuyfzand, P.J., Baggelaar, P.K., submitted. Hydrochemical trends for public supply well fields in the Netherlands (1898-2008), natural backgrounds and upscaling to groundwater bodies Journal of Hydrology.

Wuijts, S., Rutjes, S.A., van der Aa, N.G.F.M., Mendizabal, I., de Roda Husman, A.M., 2008. The influence of human and animal sources on groundwater abstraction. From field study to protection policy. Report nr. 734301031 (in Dutch), Dutch national institute of public health and environment (RIVM), Bilthoven.

Curriculum vitae

Igor Mendizabal was born in Beasain (Spain) in 1973 and grew up in Pamplona, where he graduated from secondary school. In 1999 Igor obtained his first M.Sc degree in Chemical Sciences, with specialization in Geochemistry, at the Autonomous University of Madrid (Spain). He joined water utility Gemeentewaterleidingen (Amsterdam; nowadays Waternet) in October 2000, where he worked under supervision of Theo Olsthoorn. In 2002, while still working at Gemeentewaterleidingen, he started a second Masters in Hydrogeology at VU University of Amsterdam, where he graduated in 2004. In January 2005 Igor initiated the PhD study, the results of which are presented in this book. This study was conducted within the framework of a collaboration between VU University of Amsterdam and Kiwa (nowadays KWR Watercycle Research Institute). During this PhD research Igor also developed the software package HyCA, which is presented in Mendizabal and Stuyfzand (in prep., Chapter 3). Since November 2011 Igor is working as hydrologist at PWN, the provincial drinking water supply company of Noord-Holland in The Netherlands.