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 (¹³H and ¹⁸O) 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 hydrochemical analysis 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\(_2\)S 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<sub>X</sub>), 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<sub>x</sub> is much less static than VIP. VIP<sub>x</sub> 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<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, 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.