A new process-based hydro-geochemical classification of groundwater

Application to the Netherlands national monitoring network

Netherlands Institute of Applied Geoscience TNO
- *National Geological Survey*

TNO-report
NITG 00-143-B

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Summary

A groundwater classification based on its geochemical characteristics has been proposed in this report. The 36 water types resulting from this classification contain indications about the salinity, the saturation index of calcite, the pH and the redox level of groundwater. Anthropogenic oxidation capacity and evidence of pyrite oxidation coupled to nitrate reduction in fresh water are illustrated on maps but are not included in the name of the water-type. Salt water intrusion into freshwater and fresh water intrusion into salt water were identified in brackish and salt groundwater and indicated on maps. The classification scheme can be further adapted to meet specific objectives.

The classification was applied to groundwater analysis performed in 1995 in the Netherlands national groundwater quality monitoring network. Eleven water types were distinguished in fresh groundwater and 8 water types in salt and brackish water. The water types were illustrated on simplified geological maps including the three main divisions observed in the Netherlands ((peri)-marine Holocene, fluviatile Holocene and Pleistocene with older sediments) to show their spatial distribution and their relationships with geology.

The relationships between water types, land use and hydrogeology were examined in this study to determine the influence of human activities on groundwater quality in Pleistocene and older sediments. Two case studies are presented to illustrate the use of the classification in a regional Pleistocene setting (Drenthe and Limburg).

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1 Introduction

In the Netherlands, the Stuyfzand classification (Stuyfzand, 1986) is commonly applied to chemical analysis of groundwater to summarise and interpret them. It provides information on the salinity, the hardness, the major cations and anions and the sum of Na, K and Mg corrected for a contribution of sea salt. The classification presented in this report provides additional information helping the interpretation of groundwater analysis in terms of geochemical processes. Some essential parameters such as the pH, the redox level and the saturation index of calcite in groundwater are provided in the new classification. They are not included in the Stuyfzand classification.

The hydrochemical parameters chosen for the classification are the following:
- salinity,
- saturation index of calcite,
- pH
- redox environment,
- anthropogenic oxidation capacity (OXC-ANTRO) for fresh waters,
- cation exchange in brackish and salt groundwater.

The combination of these six parameters defines a specific hydrochemical facies for each groundwater sample. This should enable us to deduce hydrogeochemical processes and conditions directly from the classification. The objective of the classification is to give a first indication of the hydrogeochemical processes that control the major ion water composition. It also can be used to predict probable future changes in this composition. Knowing the pH and the redox environment of a water sample, with indicators of major geochemical processes, it is possible to predict the mobility of specific compounds such as trace metals and organic pollutants. For example, trace metals might be mobile under acid to slightly acid conditions but will be immobilised at neutral pH and sulphur-reducing conditions.

The chemical analyses performed in 1995 in the LMG (national) and PMG (provincial) groundwater quality monitoring networks were used to test the proposed classification scheme. These data were chosen as they presumably give a representative picture of the different water types in the Netherlands. In total, data from 645 wells were used in the classification. Each well contains from 1 to 4 filters that were analysed in 1995. The total number of analysed filters is 1516 including 93 filters with incomplete analysis.

The groundwater classification was performed with Excel 97. The file TNOCLASS_NL1.xls is described in Appendix B. The classification scheme can be easily adapted to meet specific purposes or specific characteristics of data set by changing the class thresholds.

2 Preparation of the data set

A few modifications have been performed in the data set before any calculations and are summarised below:

- the sign "< " indicating the detection limit is replaced by the half of the detection limit.
- the concentrations of DOC, NH_4^+, NO_3^- and PO_4^{3-} are calculated using the concentrations of C in DOC, N in NO_3^- and NH_4^+ and P in PO_4^{3-} provided in the data set.
- the concentrations of elements used for further calculations are all expressed in mg/l or mmol/l.
- a code for geology is added to each groundwater analysis when it is not available in the data set. The code 1 is given for (peri)-marine Holocene sediments, 2 for fluviatile Holocene and 3 for Pleistocene and older sediments.

3 Quality check of analyses

To check the accuracy of chemical analyses, a series of test has been performed, using a pre- and postprocessing subroutine of WATEQ4F (Venema, 2000). The tests are mainly based on the ionic balance and the electrical conductivity. The test results provide a quality label of five digits:

- First digit = ionic balance. Number 1 for the first digit means that the ionic balance is correct, Number 2 means that the difference between the anions and the cations is bigger than 10% and number 3 means that the difference is bigger than 20%.
- Second digit = calculated electrical conductivity (EC). Number 1 for the second digit means that the calculated EC is similar to the measured EC. Number 2 means that the difference between the calculated EC and the measured EC is bigger than 10% and number 3 means that the difference is bigger than 20%.
- Third digit = concentrations higher than maximum values given in the WATEQ4F file maxima.dat. Numbers 1, 2 or 3 mean that 1, 2 or 3 components exceed the maximum values. Number 4 means that 4 or more components exceed the maximum values.
- Fourth digit = suspicious relations between chemical parameters. Numbers 1, 2, 3 indicate the number of suspicious relations. Number 4 means 4 or more suspicious relations.
- Fifth digit = to be filled by the user. Number 0 means that the analysis has not been checked by a specialist, number 1 means that the analysis was checked and is OK, number 2 means that the analysis was checked and is not reliable. The fifth digit should only be checked if the first digit > 2 or the second digit >2 or the third digit > 0 or the fourth digit > 0.

Table 1: Qlabels of chemical analysis with number of data for each code and number of data used for further calculations.

Code	Number of data	Used data
11000	611	611
11010 + 11020 + 11030	36	36
12000	483	483
12010 + 12030 + 12100	32	32
13000 + 13010	156	156
21000+21010	23	23
22000 + 22010	30	30
23000 + 23010	27	27
31000 + 31010	7	-
32000	8	-
33000 + 31010	10	-
Total	**1423**	**1398**

The results of these tests indicate that 98 % of analysis can be used for further calculations considering that Qlabels with the first two index (ionic balance and EC respectively) smaller than 3 are correct. Table 1 summarises the distribution of

Qlabels of the data set. In addition the chemical analysis in 93 filters are not complete (Qlabels with *) and therefore were not used in the classification.

4 Description of hydrochemical parameters used for the new classification scheme

Descriptions of parameters (salinity, saturation index of calcite. pH, redox level, oxidation capacity and cation exchange) are presented in the following chapters. More information concerning threshold limits between classes is provided in Houthuesen and Vink (1996).

4.1 Salinity

Cl concentrations in groundwater define the level of salinity. Three classes of salinity are defined:
1. Fresh: Cl < 200 mg/l
2. Brackish: 200 < Cl < 1000 mg/l
3. Salt: Cl > 1000 mg/l

Table 2 presents the percentage of fresh, brackish and salt groundwater in the three geological divisions. Wells located in the (peri)-marine Holocene contain a significant amount of brackish or salt groundwater (17 and 20 % respectively).

Table 2: Occurrence of fresh, brackish and salt water in the three geological regions of the Netherlands.

Geological region	Fresh	Brackish	Salt
1. (Peri)-marine Holocene	296 (62 %)	76 (16 %)	103 (22 %)
2. Fluviatile Holocene	101 (100 %)	0	0
3. Pleistocene and older sediments	813 (98.9)	8 (1 %)	1 (0.1%)

4.2 Saturation index of calcite

It is particularly important to know the saturation index in Pleistocene and older sediments to determine the zones where calcite was potentially dissolved. Groundwater in Holocene sediments usually appears to be saturated or supersaturated with respect to calcite as it flows in young calcareous sediments (Griffioen et al., 1997).
The saturation index of calcite ($SI_{calcite}$) was calculated in WATEQ4F:

$$SI_{calcite} = \log\left[\frac{[Ca^{2+}][CO_3^{2-}]}{K_{calcite}}\right]$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are activities of Ca^{2+} and CO_3^{2-} and $K_{calcite}$ is the solubility constant.
Samples with $SI_{calcite}$ lower than –0.3 are defined to be subsaturated with respect to calcite and dissolution of calcite is expected. Samples with $SI_{calcite}$ between – 0.3 and 0.3 are in near equilibrium with calcite and samples with $SI_{calcite}$ higher than

0.3 are supersaturated with respect to calcite. In this case, calcite precipitation probably occurs.

Table 3 presents the number of samples that are subsaturated, supersaturated and in equilibrium with respect to calcite. As expected, groundwater in Holocene sediments is mainly in equilibrium with respect to calcite whereas samples in Pleistocene and older sediments are mainly subsaturated although many samples are also in equilibrium.

Table 3: $SI_{calcite}$ classification with number of data in the three geological regions and in the three classes of salinity.

	Subsaturated	Equilibrium	Supersaturated
(Peri)-marine Holocene			
Fresh	49	192	55
Brackish	3	60	13
Salt	11	45	47
Fluviatile Holocene			
Fresh	25	73	3
Pleistocene and older sediments			
Fresh	602	199	12
Brackish	7	1	0
Salt	1	0	0

4.3 pH

Four classes of pH have been proposed:
1. basic: pH > 7.5,
2. neutral: $6 \leq pH \leq 7.5$,
3. slightly-acid: $4.5 < pH < 6$,
4. acid: pH < 4.5.

Remark: the class "neutral" was first defined with a pH ranging from 6.5 to 7.5. However, when pH was combined with $SI_{calcite}$ for the classification, it was noticed that slightly-acid and acid samples were always subsaturated with respect to calcite, except 5 samples that were in equilibrium with calcite with a pH ranging between 6.37 and 6.50. To avoid creating a class "slightly-acid and equilibrium with calcite" for only 5 samples, it was decided that pH ranging from 6 to 7.5 would represent the class "neutral".

The pH classes in the three geological regions are summarised in table 4. Groundwater samples in (peri)-marine and fluviatile Holocene sediments are characterised by neutral pH values whereas the pH tends to be lower in Pleistocene and older sediments (from slightly acid to neutral).

Table 4: pH classification with number of data in the three classes of salinity and in the three geological regions. 23 data are missing.

	Acid	Slightly acid	Neutral	Basic
(Peri)-marine Holocene				
Fresh	0	7	242	47
Brackish	0	0	67	9
Salt	0	2	91	10
Fluviatile Holocene				
Fresh	0	6	90	5
Pleistocene and older sediments				
Fresh	37	287	405	62
Brackish	0	3	4	0
Salt	0	1	0	0

4.4 Redox environment

The redox environments can be empirically deduced from the redox-sensitive dissolved species, i.e. O_2, NO_3^-, SO_4^{2-}, Fe, Mn and CH_4 in groundwater (Stumm, 1984). However, the redox level based on the groundwater composition should be considered as a first indication. Indeed the lack of information about the soil composition, the general absence or the doubtful quality of O_2 and CH_4 measurements in larger data sets, the assumption that iron measured in filtrated groundwater represents the true value of Fe^{2+} may lead to a wrong identification of the redox level. However nitrate and sulphate concentrations are regarded as good indicators of redox conditions prevailing in the groundwater. Some limitations of the redox level identification are outlined at the end of this chapter.

Figure 1 illustrates the classification tree used to identify the redox level of groundwater samples. It was based on the redox classification presented by Houthuesen and Vink (1996) and was modified to take into account fresh, brackish and salt groundwater. The same threshold values were used for the new classification. The threshold values are usually higher than those given in the literature (Stuyfzand, 1993; Christensen et al., 1994) which are often deduced from limited data sets in space (for instance local groundwater characterisation) and in time (monitoring during a limited period of time). The new classification is meant to be applied to larger data sets and must take into account the variability of detection limits over the years and between the laboratories. O_2 and CH_4 measurements are often absent from data sets, which does not allow an accurate determination of the redox level. For instance, O_2 and CH_4 concentrations were not available in the data set of 1995. Therefore oxic waters could not be differentiated from suboxic waters (class "oxic/suboxic") and zones with methane production could not be distinguished from zones with sulphate reduction but without methane production (class "sulphur-reduced/methanogenic").

Redox classification

Figure 1: Identification of redox level in groundwater samples
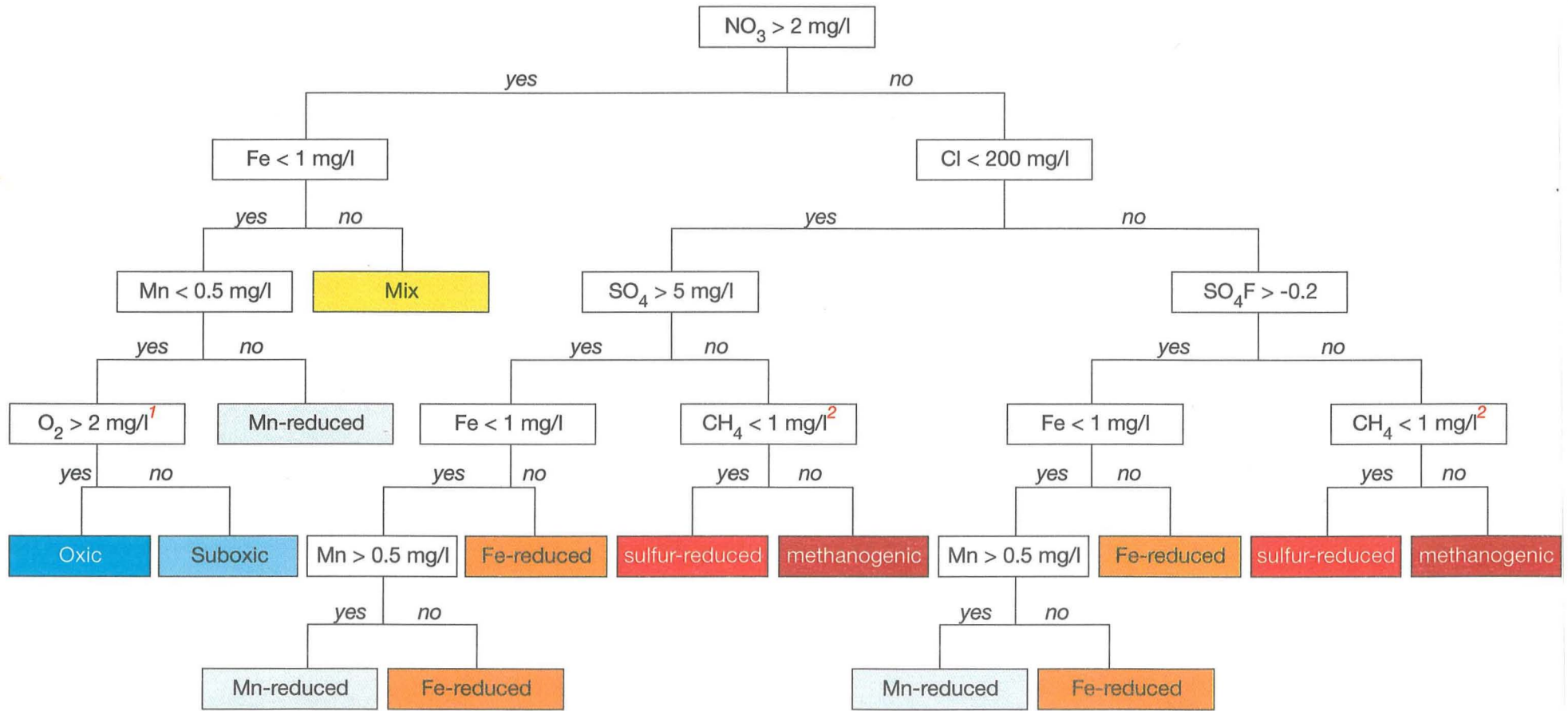
^{1} If O_2 is not measured, the class name is oxic/suboxic
^{2} If CH_4 is not measured, the class name is sulfur-reduced/methanogenic

Figure 1:   Redox classification

Nitrate concentration is the first criterion used to assess the redox level in groundwater. Groundwater analyses are separated in two large groups with nitrate concentration higher and smaller than 2 mg/l (figure 1). Groundwater with nitrate concentration higher than 2 mg/l have a rather high redox potential (usually > + 300 mV) compared to groundwater with lower nitrate concentration (< +160 mV, Stuyfzand, 1993). The redox potential sharply decreases in the so-called "transition zone" where reduction of Mn oxides occurs, causing an increase of Mn concentrations in groundwater (>0.5 mg/l). Scatter plots illustrating nitrate concentrations as a function of Fe or Mn concentrations show that high concentrations of Fe and Mn are mainly found in groundwater containing nitrate concentrations lower than 2 mg/l (appendix A).

The class "mix" indicated in yellow in figure 1 represents groundwater where equilibrium is not reached. These samples are characterised by the co-existence of nitrate and dissolved iron and are differentiated from samples which contain dissolved iron but no nitrate (iron-reduced environment).

Iron and sulphate concentrations are the following parameters used to identify the redox level in groundwater when nitrate and manganese have been already reduced. As sulphate concentrations are naturally higher in brackish and salt groundwater in coastal areas, groundwater samples are separated in two groups defined by chloride concentrations smaller and higher than 200 mg/l (threshold Cl concentration between fresh and brackish water). Fresh groundwater with sulphate concentrations lower than 5 mg/l has been classified as "sulphur-reduced /methanogenic" as sulphate has been probably reduced. The detection limit of sulphate could have been chosen as threshold limit but as detection limits are not similar every year, depending on the quality of analysis, the empirical value of 5 mg/l has been chosen. In brackish and salt water, sulphate concentrations are corrected to subtract the contribution of SO_4 from seawater. The calculated ratio SO_4F is the relative deviation of the sulphate/chloride ratio in groundwater and the sulphate/chloride ratio in seawater:

$$SO_4F = \frac{SO_{4\,groundwater} \times Cl_{\,sea}}{Cl_{\,groundwater} \times SO_{4\,sea}} - 1$$

A ratio SO_4F higher than – 0.2 points out groundwater samples with a high sulphate concentration suggesting an anthropogenic contribution whereas values lower than –0.2 represent samples where sulphate has been reduced. The value – 0.2 has been chosen rather than 0 to avoid that variations due to analytical uncertainties in samples of the same water type induce a different classification. It should be noted that the classes have been called "iron-reduced" or "sulphur-reduced" rather than "iron-reducing" or "sulphate-reducing" as we have no indication if reduction in groundwater is still going on.

As mentioned above, the redox classification is only based on groundwater composition and therefore some limitations of the method should be highlighted (Stuyfzand, 1993; Christensen et al., 1994):

1. precipitation of FeS, FeS_2 or $FeCO_3$ may deplete the water of sulphide or iron,

2. precipitation of $MnCO_3$ may deplete the water of manganese,
3. methane may spread to non-methanogenic parts of the aquifer by the groundwater flow, diffusion or soil gas movement,
4. Fe^{2+} and Mn^{2+} may be transported down-gradient through sections of the aquifer with no iron or manganese reduction if not rapidly precipitated, oxidised or ion-exchanged,
5. in iron-poor sediments, small amounts of Fe^{2+} produced may be undetectable due to ion-exchange with the aquifer material,
6. high total Fe concentrations due to Fe^{3+} dissolution at low pH and high DOC concentrations (pH < 4 and DOC > 10mg/l),
7. nitrate reduction coupled with pyrite oxidation, produces high concentrations of sulfate and Fe^{2+} (Fe(III) oxides if pyrite oxidation is complete). A star (*) is added to the class name when nitrate reduction coupled with pyrite oxidation probably is assumed. The following empirical criteria are used: Cl < 200 mg/l, Fe > 15 mg/l, SO_4 > 150 mgl/l and NO_3 < 1 mg/l. High concentrations of As, Zn or Ni are also usually observed but were not taken as a criterion.

The results of the redox classification are summarised in table 5 where the number of data in the three geological regions and in the three classes of salinity is provided.

Table 5: Redox classification with number of data in the three geological regions and in the three classes of salinity.

	oxic/suboxic	Mn-red.	Mix	Fe-red.	Sulph.-red. /methanogenic
1. (Peri)-marine Holocene					
Fresh	6	6	8	133	144
Brackish	0	4	2	8	62
Salt	0	2	3	13	85
2. Fluviatile Holocene					
Fresh	13	6	1	69	12
3. Pleistocene and older sediments					
Fresh	190	54	35	422	111
Brackish	0	0	2	3	3
Salt	0	0	0	0	1

The most frequent redox environments in the (peri)-marine Holocene are the iron-reduced and sulphur-reduced/methanogenic environments. Groundwater that was sampled in Pleistocene and older sediments is characterised by iron-reduced and oxic/suboxic environments, although Mn-reduced and sulphur-reduced waters count for 7% and 14% respectively of the samples. These observations are consistent with those found in Houthuesen and Vink (1996).
It should be noted that 11 out of 66 samples classified as Mn-reduced in fresh groundwater have low concentrations of nitrate (between detection limit and 1.4 mg/l). They are also characterised by high concentrations of sulfate (between 20 and 165 mg/l) and low concentrations of Fe (bewteen detection limit and 0.9 mg/l). As these samples contain rather high concentrations of Mn (between 0.6 and 2

mg/l), they are classified as "Mn-reduced". Nitrate has been probably reduced whereas reduction of iron oxides has not occurred yet. The same observation can be done for 5 samples in brackish and salt water (6 samples in total).

4.5 Anthropogenic oxidation capacity (OXC-ANTRO)

The oxidation capacity of groundwater (OXC) gives an indication of the anthropogenic contribution of nitrate and sulphate in groundwater. More precisely, it represents the amount of electrons that can be consumed by dissolved electron acceptors such as NO_3^-, SO_4^{2-} or O_2 by redox processes. It is expressed in milli-electrons per liter of groundwater:

$$OXC_{groundwater} = 4(O_2) + 5(NO_3^-) + 8(SO_4^{2-}) + 4(TOC_{water})$$

where brasses indicate molar concentrations that are multiplied by the amount of electrons transferred for the reduction of O_2, nitrate, sulphate and total organic carbon (TOC_{water}). The OXC is then calculated assuming that reduction reactions proceed as given below:

1) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
2) $NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N2 + 3H_2O$
3) $SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$
or $SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S^{0-} + 4H_2O$
4) $CH_2O + 4H^+ + 4e^- \rightarrow CH_4 + H_2O$

Sulphate-reducing environments (reaction 3) are commonly found to be near equilibrium with FeS which at near neutral pH converts slowly to pyrite (Postma and Jakobsen, 1996).
Assuming both O_2 and TOC concentrations near to zero, we will focus on nitrate and sulphate concentrations. Sulphate concentrations must be corrected in order to subtract the seawater contribution, especially in coastal areas.
The anthropogenic oxidation capacity (OXC-ANTRO) is described by the following equation:

$$OXC\text{-}ANTRO = 5(NO_3) + 8(SO_4) - 0.0524\ Cl$$

where the factor 0.0524 is the molar ratio between SO_4 and Cl in seawater.
In this equation, Cl is supposed to come from seawater, which is not necessarily the case. Contribution of Cl in manure can also be important in recent water (up to 100 mg/l), but on basis of many groundwater samples, it can be assumed that the anthropogenic contribution of sulphate is more important than the contribution of chloride. The ratio SO_4/Cl of groundwater, before any SO_4 reduction, is usually larger in groundwater than in seawater. Moreover the dissolution of gypsum in fresh groundwater does not play a major role in the Netherlands (Griffioen et al., 1997).
OXC-ANTRO values higher than 0 indicate that groundwater samples are influenced by anthropogenic inputs of nitrate and sulphate. Values lower than 0 are typical of groundwater samples where sulphate has been reduced.

Two classes of OXC-ANTRO were determined. The first one, "high OXC-ANTRO", includes values bigger than 5 me/l and the second one, "low OXC-ANTRO", contains values lower than 5 me/l. This classification aims to point out groundwater samples with high OXC-ANTRO, especially in the Pleistocene and older sediments where a relationship between water quality and soil use is expected. OXC-ANTRO was only calculated in fresh waters.

Table 6: Number of OXC-ANTRO in the different redox environments values and in the three geological regions.

	Oxic/suboxi	Mn-reduced	Mix	Fe-reduced	S-reduced / methanogenic
(Peri)/marine Holocene					
Low OXC	2	1	6	80	144
High OXC	4	5	2	52	0
Fluviatile Holocene					
Low OXC	1	0	0	37	12
High OXC	12	6	1	32	0
Pleistocene and older sediments					
Low OXC	57	8	20	273	112
High OXC	133	46	15	149	0
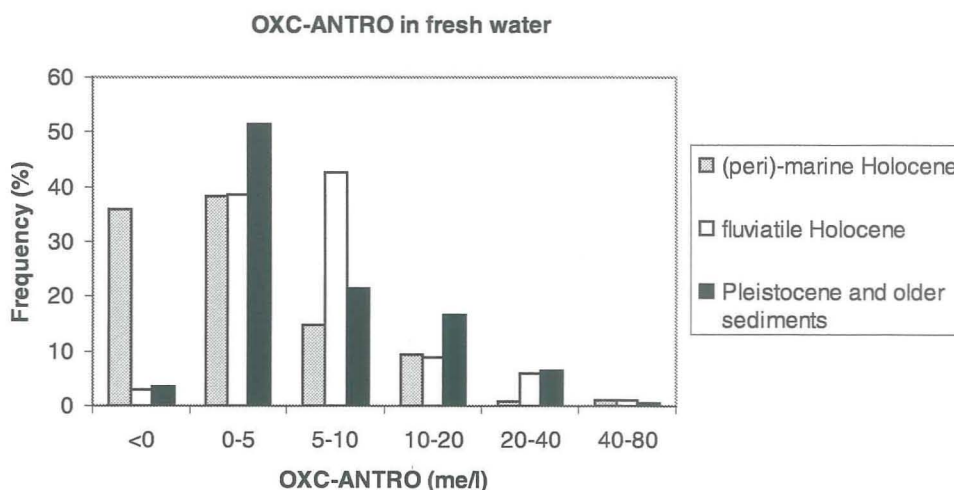
Figure 2: Histogram of anthropogenic oxidation capacity in Holocene, Pleistocene and older sediments.

The proportion of high OXC-ANTRO values is higher in environments with high redox potential such as the oxic/suboxic and Mn-reduced environments as sulphate is not reduced. At the opposite, OXC-ANTRO is always smaller than 0 in sulphur–reduced/methanogenic environments (table 6). In Pleistocene and older sediments the proportion of high OXC-ANTRO values is higher (42 %) than in (peri)-marine Holocene sediments (21%) (figure 2). It should be also noted that 50 % of values

are higher than 5 me/l in fluviatile Holocene sediments. The maps presented in chapter 5.3 indicate the zones with high OXC-ANTRO.

4.6 Cation exchange in brackish and salt groundwater

Processes such as sea water intrusion into freshwater or freshwater intrusion into seawater ("freshening") can be identified by looking at the Na and Mg concentrations. In sea water Na^+ and Cl^- are the dominant ions and sediment in contact with sea water has adsorbed Na^+ for a large part. Fresh water in coastal areas is dominated by Ca^{2+} and HCO_3^- ions as a result of calcite dissolution and cation exchangers in aquifer sediments have mostly Ca^{2+} adsorbed on the surfaces. When seawater intrudes a freshwater aquifer, Na^+ is taken up by the exchanger and Ca^{2+} is then released. The reverse reaction occurs when fresh water flushes a salt water aquifer. Ca^{2+} is adsorbed to the sediment and Na^+ is released, resulting in a $NaHCO_3$ water type. Significant amount of Mg^{2+} can also be released in the water. Freshening or salt water intrusion into freshwater can be identified using Na^+ and Mg^{2+} concentrations in brackish and salt water samples (Cl > 200 mg/l). The amount of cation exchangers (NaZ or MgZ) is calculated and then compared with the amount of the same cations in seawater to determine if the sample is enriched with respect to Na^+ or Mg^{2+}:

$$NaZ = (Na)_{groundwater} - (Na)_{seawater} \frac{(Cl)_{groundwater}}{(Cl)_{seawater}}$$

If NaZ or MgZ is equal to zero, Na^+ or Mg^{2+} has disappeared from the groundwater, probably indicating salt water intrusion into freshwater. At the opposite if NaZ or MgZ are bigger than zero, groundwater is enriched with respect to Na^+ or Mg^{2+}, suggesting fresh water intrusion.

To avoid wrong identification of processes because of analytical uncertainties, the absolute value of NaZ or MgZ must be:

- bigger than the difference between the sum of cations and de sum of anions,
- at least 5% bigger than the total concentrations of Na^+ or Mg^{2+} in groundwater.

Identification of potential freshening or salt water intrusion into freshwater aquifer using Na concentrations is illustrated in figure 3. In the Stuyfzand classification, the sum of Na, K and Mg (corrected for sea salt contribution) are used to infer the predominant cation exchange reactions. As the exchangeable cations Na and Mg do not always ad- or desorb simultaneously during salt or freshwater intrusion respectively, we prefer to consider Na and Mg separately. The same sketch illustrated in figure 3 can be done using Mg concentrations. As the exchangeable Na and Mg cations are considered separately, 9 combinations are possible (combinations between freshening, salt water intrusion and no process occurring).

For the final classification, potential freshening or salt water intrusion are inferred from groundwater samples when Na <u>and</u> Mg concentrations indicate freshening or salt water intrusion (according to figure 3). Potential freshening is also expected

when Na and Mg concentrations indicate freshening for one cation and no process for the second cation. The same is valid for groundwater samples indicating salt water intrusion and no process occurring. If freshening and salt water intrusion have been identified in the same sample, the dominant process occurring in groundwater cannot be identified and no indication is provided in the classification (see "no idea" in table 7). If no process can be deduced from Na <u>and</u> Mg concentrations, the water type name does not include any sign indicating freshening or salt water intrusion (see "no process" in table 7).

Figure 3: Determination of freshening or seawater intrusion in freshwater aquifer with respect to Na. Brackets [ ] followed by subscripts $_{gw}$ and $_{sw}$ represent molar concentrations in groundwater and seawater respectively.
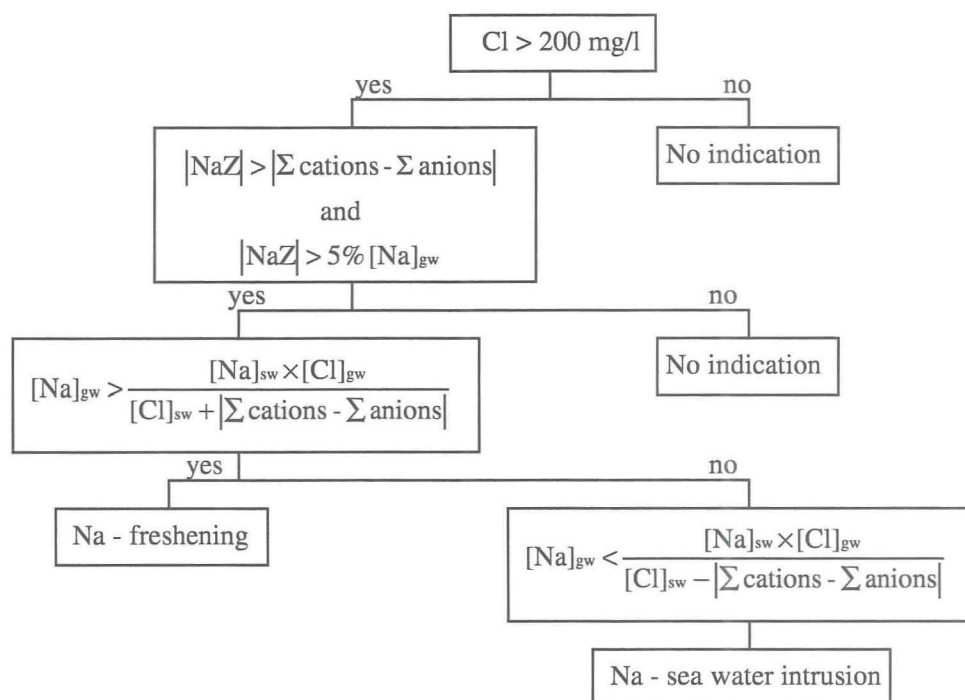

Table 7: Identification of freshening and salt water intrusion in brackish and salt groundwater samples in the (peri)-marine Holocene region (188 data in total).

Processes	Number of data
Freshening	33
Salt water intrusion	51
No process	95
No idea	9

5 The classification scheme

Identification and definition of parameters used for the groundwater classification have been now determined. Considering all parameters together (table 8), the number of different water types can be very large. In fresh water for instance, 120 water type classes could be theoretically possible (5 x 3 x 4 x 2) and 180 in brackish or salt water (5 x 3 x 4 x 3). The classification can be further simplified and adapted to meet specific purposes. In this report a simplified classification is developed for the purpose of the identification of the spatial distribution of hydrogeochemical processes based on water types from the national monitoring network. The resulting classification is called TNOCLASS_NL1 and is described in chapter 5.1 and applied to the monitoring network in chapter 5.2 and 5.3.

To meet other objectives, the classification can be altered, except for the order of the parameters 1 to 6 in table 8. Consequently the proposed classification will always meet the order Salinity - Calcite Saturation – pH – Redox – Oxidation Capacity – Cation Exchange. However class thresholds can vary to meet specific purposes or specific characteristics of a data set. For instance, if detection limits of nitrate exceed 2 mg/L in a specific data set, the threshold value of nitrate is not suitable and the redox classification should be adapted accordingly. It is proposed that adaptations to the classification thresholds and version numbers are emphasised in the second part of the classification name; for instance TNOCLASS_<region/project><version number>.

Table 8: List of parameters for groundwater classification and number of classes per parameter.

Parameters	Number of classes	Classes
1. Salinity	3	fresh, brackish and salt
2. SI$_{calcite}$	3	Subsaturated, equilibrium, supersaturated
3. pH	4	basic, neutral, slightly-acid, acid
4. Redox environment	5	oxic/suboxic, Mn-reduced, Mix, Fe-reduced, Sulphur-reduced/methanogenic
5. OXC-ANTRO (in fresh water only)	2	Low OXC, high OXC
6. Cation exchange (in brackish and salt water only)	3	Freshening, salt water intrusion, no process

5.1 Simplified classification (TNOCLASS_NL1)

The reduction of classes for each parameter is described below and summarised in table 9 and figure 5:

- Salinity: brackish and salt groundwater samples are combined in the same group (Cl > 200 mg/l) as both have been mixed with seawater. Fresh water (Cl <200 mg/l) is considered apart.

- SI$_{calcite}$: groundwater samples supersaturated or in equilibrium with respect to calcite are combined together whereas subsaturated samples constitute a second group. The division of saturation indexes into two classes allows a rapid identification of groundwater where calcite might be dissolved ("aggressive" groundwaters).
- pH: basic and neutral groundwater samples are grouped together (class "pH > 6") whereas slightly-acid and acid samples constitute two other distinct groups. Most basic-classified samples have a pH between 7.5 and 8 (figure 4) and therefore the pH is not drastically different from neutral samples. This classification of pH allows a quick identification of acid groundwater samples.
- Redox environment: redox environments with NO3 > 2 mg/l (oxic/suboxic, Mn-reduced and Mix) are combined together in one group called "NO3 > 2 mg/l". The classes "Fe-reduced" and "Sulphur-reduced/ methanogenic" do not change. The number of classes is now reduced to three classes. Indication of pyrite oxidation coupled to nitrate reduction is illustrated by a star (*) after the class name (see chapter 4.2 and 5.3). The presence or the lack of star does not constitute an additional class.
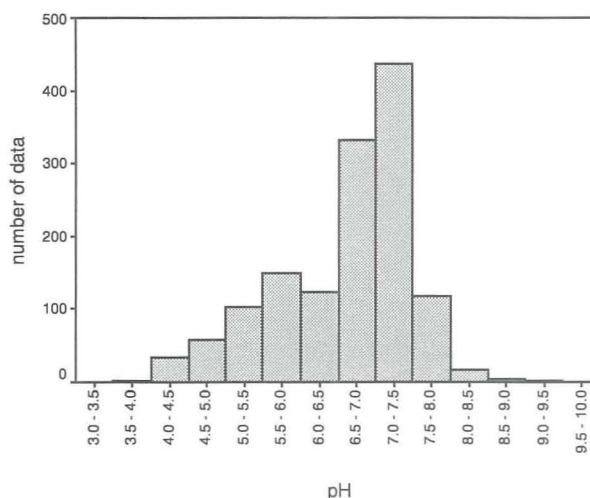
Figure 4: pH distribution in groundwater samples (1995)

Table 9: Simplified classification of groundwater samples with class labels and their description (TNOCLASS_NL1)

Parameters	Class labels	Class description
Salinity	1. F	Fresh
	2. S	Salt + brackish water
SI$_{calcite}$	1. eq	Equilibrium + supersaturated
	2. s	Subsaturated
pH	1. 6	Neutral + basic (pH > 6)
	2. 5	Slightly-acid (4.5 < pH < 6)
	3. 4	Acid (pH < 4.5)
Redox environment	1. N	Oxic/suboxic, Mn-reduced, Mix
	2. Fe	Fe-reduced
	3. S	Sulphur-reduced/methanogenic
OXC-ANTRO (in fresh water only)	1. low OXC	Low OXC-ANTRO
	2. high OXC	High OXC-ANTRO
Cation exchange (in brackish and salt water only)	1. +	Freshening
	2. -	Salt water intrusion

The water type name contains the class labels of salinity, $SI_{calcite}$, pH and redox level, such as F-eq6Fe (see table 9 for class labels and figure 5). Then the level of OXC-ANTRO (high or low) in fresh water and the occurrence of freshening processes or salt water intrusion (+ or -) in brackish and salt water can be added as additional information on maps illustrating the different water types (see chapter 5.3). However they are not included in the water type name to avoid multiplying the number of names.
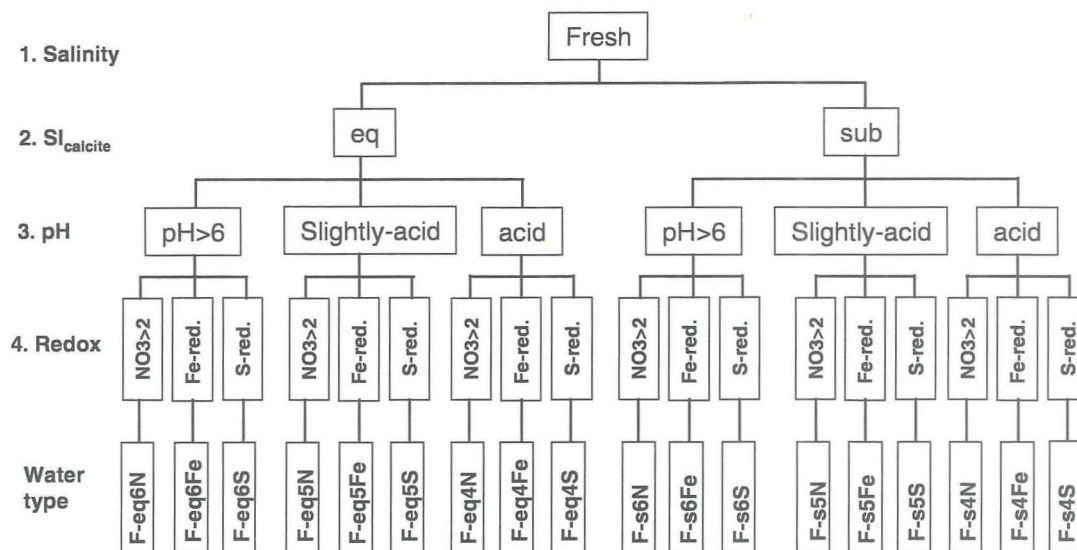
Figure 5: Simplified classification of fresh groundwater TNOCLASS_NL1 (the same tree can be done for brackish and salt groundwater)

5.2 Application of the simplified classification to the national groundwater monitoring network

The simplified classification has been applied to the data set of 1995. The results are presented separately for fresh and salt groundwater (figures 6 and 7). The theoretical number of water types is 18 (2 x 3 x 3) in fresh or salt groundwater.
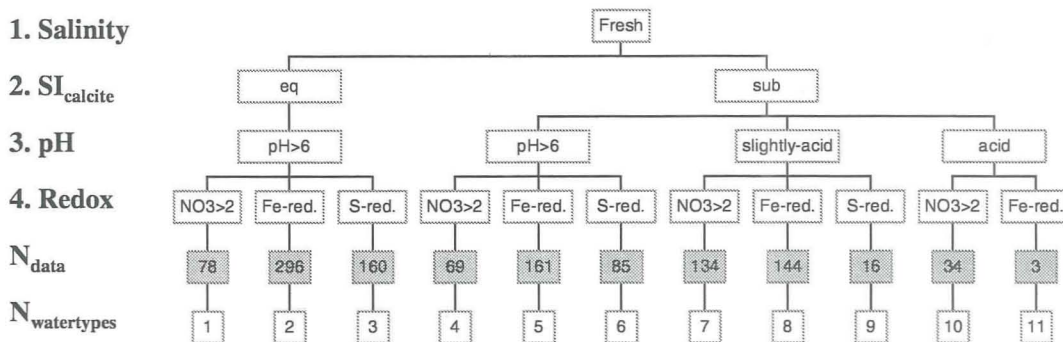
Figure 6: Classification of fresh water samples (TNOCLASS_NL1) and number of data (N_{data}) for each water type ($N_{watertype}$).

In fresh groundwater 11 water types have been found (figure 6). Each water type contains a large number of data except the water type F-s4Fe (subsaturated with respect to calcite, acid and Fe-reduced) that includes only 3 data. This water type is probably irrelevant and will not be illustrated on the maps. Indication of pyrite oxidation and levels of OXC-ANTRO are illustrated on maps in chapter 5.3.
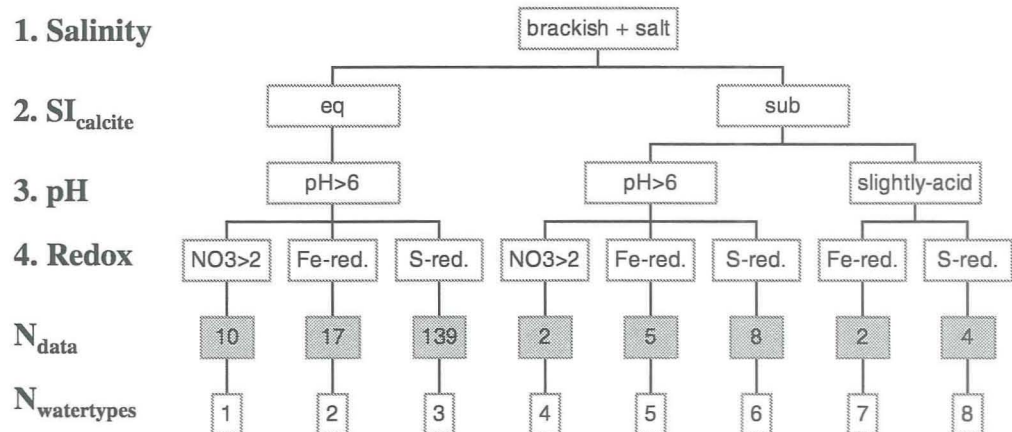
Figure 7: Classification of brackish and salt water samples and number of data (N_{data}) for each water type ($N_{watertype}$).

In brackish and salt groundwater, 8 water types have been determined but only one S-eq6S (equilibrium with respect to calcite, pH>6 and S-reduced) contains a large number of data (figure 7). Occurrence of freshening or salt water intrusion is indicated on maps in chapter 5.3.

5.3 Maps illustrating the various water types

Several maps have been performed to determine the distribution of the various water types in the Netherlands and also to show the relationships between water types and geology (appendix C):
- 2 maps representing the distribution of water types in fresh groundwater between 5 and 15 meters below surface level and between 15 and 30 meters.
- 1 map representing the distribution of water types in brackish and salt groundwater between 5 and 15 meters below surface level and between 15 and 30 meters,
- 4 maps representing the distribution of the 10 major water types in shallow and deep fresh groundwater with indication of pyrite oxidation and levels of OXC-ANTRO,

Simplified geology containing three divisions (marine Holocene, river deposits or called also fluviatile Holocene and Pleistocene with older sediments) has been illustrated on the maps to determine the relationships between water types and geology.
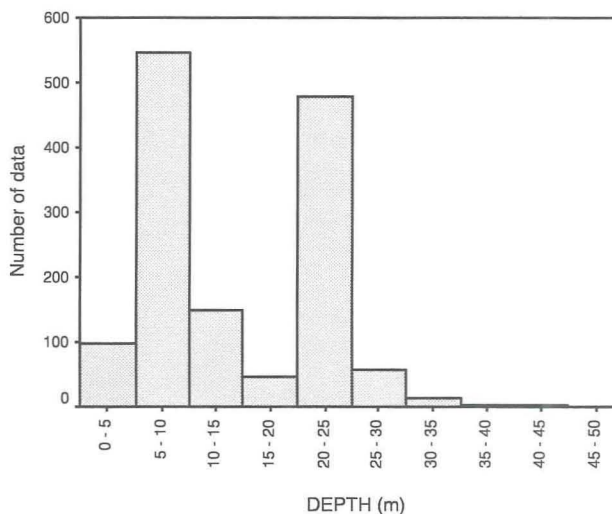
Figure 8: Depth of groundwater samples (1393 samples) in the 1995 data set. Fours samples were collected between 55 and 104 m below surface.

Chemical analyses of groundwater sampled between 5 and 15 meters below the surface level (shallow groundwater) and between 15 and 30 meters (deep groundwater) have been selected (figure 8), as groundwater is yearly sampled at these depths. It should be noticed that two analyses in the same well might be available in the same class of depth but usually the water type in both samples is similar. In the data set of 1995, less than 7 wells have two analyses in the same class of depth with similar water type. In some cases (less than 8 wells in the 1995 data set), the water type in the two samples is different, resulting in a superposition of two different water types on the map. It must be checked that the number of these cases is limited.

Symbols of different colours are used to represent the various water types on the maps. Light colours indicate high redox potential such as oxic/suboxic, Mn-reduced or Mix environments ($NO_3 > 2$ mg/l) whereas dark colours point out highly reduced environment (Sulphur-reduced/methanogenic). The blue colour scale represents groundwater samples with pH higher than 6 and saturated or supersaturated with respect to calcite. The green colour scale characterises groundwater samples with pH higher than 6 and subsaturated with respect to calcite. The orange colour scale represents slightly-acid samples and subsaturated with respect to calcite. And finally yellow indicates acid and subsaturated groundwater samples.

Some comments on water type distribution and their relationships with geology are presented below.

5.3.1 (Peri)-marine Holocene

The most frequent fresh water types in (peri)-marine Holocene are F-eq6S and F-eq6Fe. The most common water type in aquifers of the dune area, in Zeeland and in the area of Utrecht (river sediments) is the iron-reduced type. In the polder areas,

the sulphur-reduced/methanogenic water type is more frequent. The soil composition probably explains this difference in redox potential as more anoxic aquifers contain mainly marine clays and peat whereas Fe-reduced or even nitrate-reducing environments are found predominantly in the dune sand areas and in river deposits close to Utrecht (table 10).

Groundwater in Holocene sediments is mainly in equilibrium or supersaturated with respect to calcite as it flows in young calcareous sediments.

Table 10: Soil type in Fe-reduced and S-reduced environments in (peri)-marine Holocene

Soil type	% samples in Fe-red.	% samples in S.-red.	% samples in S.-red.
	In fresh groundwater		Brackish/Salt
Sand	33.3	14	11.6
Marine clays	9.8	20.8	37.4
Peat	3.1	23.6	13.6
River clays	30.3	6.9	0.7
Others	3.8	8.3	12.2
Unknown	19.7	26.4	24.5

Brackish and salt groundwater are mostly found in (peri)-marine Holocene.

5.3.2 Fuviatile Holocene (river deposits)

The most frequent fresh water types in fluviatile Holocene are F-eq6Fe, followed by F-eq6N in shallow groundwater (5-15m). Deep groundwater is characterised by the water types F-eq6Fe and F-eq6S as in (peri)-marine Holocene. The apparent calcite equilibrium probably points out the presence of calcite in the shallow river sediments (until a depth of 25m).

5.3.3 Pleistocene and older sediments

Water types in Pleistocene and older sediments vary much more than water types in the Holocene. Roughly groundwater is characterised by higher redox potential, lower pH and lower saturation index of calcite than groundwater in Holocene sediments. The most frequent water types are F-s5N (15.9 %), F-s5Fe (18.8 %), F-s6Fe (17.7 %), and F-eq6Fe (15 %). The spatial distribution of water types in the Pleistocene area is described using the maps showing the distribution of single water types (appendix C, 4 maps "Redox level in fresh water types"). On the left side, the maps show the shallow samples (5-15 m), on the right side the deeper samples (15-30 m). Samples with high oxidation capacity (larger than 5 electron equivalents) are marked in red; samples with low oxidation capacity are marked in blue.

A first look at the maps shows that the water types occur in clearly limited areas of the Netherlands; they are certainly not randomly distributed. This paragraph contains a short description of the spatial distribution of the selected water types which are listed below:

- acid to slightly acid, high redox potential groundwater (Fs-4N, Fs-5N)
- acid to slightly acid, low redox potential groundwater (F-s5Fe, F-s5S)
- neutral, high redox potential groundwater (F-eq6N)

- neutral, low redox potential groundwater (F-eq6S).

Geological map of the Netherlands

Holocene
- brook valley deposits
- dunes + coastal barriers
- young marine deposits
- old marine deposits
- clay on peat
- peat + clay on peat
- fluvial deposits

Pleistocene
- Brabantse loam or brook valley deposits
- Fluvio (peri) glacial, deposits
- ice pushed ridges
- glacial deposits (till)
- young fluvial deposits
- old fluvial deposits
- fine sands "Potklei"
- cover sands

Olderdeposits
- Tertiary
- Cretaceous
- Carboniferous
- Fault

0   50 km

Figuur 9: Geological map of the Netherlands with deposits lying below the cover sands (hatched area) (after Griffioen & Broers, 1999).

The illustration serves to investigate possible relationships with the subsurface geology of the Netherlands, which is shown in figure 9. Special attention is paid to the vulnerability of the groundwater to acidification and the leaching of nitrate. The presence of acid water generally points to the absence of a carbonate buffer that neutralises the pH. The presence of a high redox potential points to the absence of a redox buffer (reactive organic matter or sulphides) that transforms oxidising

components such as oxygen and nitrate. Apparently, areas with acid and high redox potential groundwater (water types F-s4N and F-s5N) are vulnerable to acidification and to the input of oxidising components by excessive use of manure.

5.3.3.1 Acid to slightly acid, high redox potential groundwater (F-s4N, F-s5N)

Main occurrences of water types F-s4N and F-s5N (appendix C, 2 maps "Redox level in fresh water types") are:
- the ice pushed ridges (Veluwe, Utrecht Hill Ridge, Nijmegen, Texel, Wieringen, Gaasterland, Montferland)
- the Drenthe Glacial Plateau
- the Peel Horst and Venlo Graben (eastern Brabant)
- western Brabant.

In the two first mentioned areas the water types can also be found at larger depth (15-30 m). In most cases the ice pushed ridges are made of medium to coarse-grained fluvial sands from Pleistocene age. The Drenthe Glacial Plateau is characterised by glacial till underlying Pleistocene fluvial formations. The occurrences in western and eastern Brabant are known to have very vulnerable coarse sands and gravels from fluvial origin (Veghel and Kedichem Formations). The presence of water types F-s4N and F-s5N points to the absence of a carbonate and redox buffer in those areas. Especially the Veluwe ice pushed ridge and the Drenthe Glacial Plateau are vulnerable to acidification and nitrate leaching at greater depths. The occurrence of water types F-s4N and F-s5N is further investigated in the Drenthe area in paragraph 6.3. It appears that those water types are most common in the recharge areas of the Drenthe plateau.

5.3.3.2 Acid to slightly acid, low redox potential groundwater (F-s5Fe, F-s5S)

Water types F-s5Fe and F-s5S represent slightly acid groundwater (pH 4,5-6) which is Fe- or S-reduced. Groundwater pH in the water types points to the absence of a carbonate buffer. The absence of nitrate might be caused by either redox buffering by organic matter or sulphides or a very limited input of nitrogen during infiltration. Water type F-s5Fe shows 4 main occurrences (appendix C, map "Redox level in fresh water type F-s5"):
- western and central Brabant
- the western part of the Drenthe Glacial Plateau
- the Hunze Valley
- the Peel Horst and Venlo Graben.

At shallow depth, water types in the north show low oxidation capacity (OXC), whereas in the south it shows high OXC, especially in western Brabant. The difference in OXC is accounted for by sulphate concentrations, since nitrate is absent in the water type. Indications of pyrite oxidation occur both in Brabant and Drenthe, especially between 15 and 30 m depth. The high OXC in Brabant is probably caused by the input of agricultural nutrients. There, the Fe reduced status of groundwater is attributed to redox buffering of the oxidising components. The indications of pyrite oxidation point to pyrite as a major redox buffer in those areas. This is confirmed by earlier local studies in the area. The situation is more

obvious in the Peel Horst and Venlo Graben areas. At shallow depth, water type F-s5N is common and at larger depth water type F-s5Fe is found frequently, together with indication of pyrite oxidation. Coarse fluvial formations are underlain by peri-marine formations that often contain pyrite as a secondary mineral.

Groundwater F-s5Fe in the northern occurrences is poor in both nitrate and sulphate (low OXC). This is probably caused by a lower nutrient input in the Drenthe plateau. It might also been caused by the process of denitrification by organic matter. This would indicate that the organic matter is the main redox buffer in the northern areas.

The distribution of S reduced groundwater, F-s5S, (appendix C, map "Redox level in fresh water type F-s5") is restricted to the areas of major peat bogs. Recharge in the peat bogs apparently causes the reduction of nitrate and sulphate. However, the pH is not buffered in those areas, probably because of the absence of carbonates in the subsoil.

5.3.3.3 Neutral, high redox potential groundwater (F-eq6N)

Water type F-eq6N is characterised by calcite saturation, a pH higher than 6 and the presence of nitrate. This water type shows a very pronounced spatial distribution (appendix C, map "Redox level in fresh water type F-eq6"). Its occurrences are limited to:

- the area in the west of the IJssel River, including Montferland, the Achterhoek en Salland
- the Gelderse Vallei
- South Limburg
- the West Coast dunes
- the South Limburg limestone plateau (not shown on the maps, depth > 30 m)

The total absence of F-eq6N in the Drenthe Glacial Plateau and the province of Brabant is striking. The spatial patterns of the nitrate containing water types F-s4N + F-s5N and F-eq6N are completely complementary. Although the presence of nitrate suggests the absence of a redox buffer in both complementary areas, the overall groundwater quality is very different. The calcite equilibrium in water type F-eq6N is probably caused by the presence of carbonates in the subsurface sediments. Clearly, calcite equilibrium is found in the limestone aquifers of South Limburg. This area is known to be very vulnerable to nitrate leaching. In the dune areas, calcite is present in the form of shell fragments. Problems with nitrate leaching to drinking water pumping stations are known in the Achterhoek and Montferland areas. These problems coincide with increasing hardness of groundwater due to increased dissolution of carbonates.

Input of nitrate has completely different effects in the province of Brabant (water types F-s4N, F-s5N, F-s5Fe) than in the Achterhoek (water type F-eq6N). In Brabant, the redox buffering of nitrate by pyrite oxidation might decrease pH and raise sulphate and trace metals concentrations. Trace metals stay mobile under the current redox and pH conditions. In the Achterhoek however, the carbonate buffer fixes the pH at neutral values. Possible acidification by pyrite oxidation is buffered

by dissolution of carbonates, which yields raising concentrations of calcium and magnesium. The resulting effect is an increase of total hardness and a limited mobility of trace metals. In Brabant however, the resulting effect is an increase of sulphate and trace metals concentrations.

5.3.3.4 Neutral, low redox potential groundwater (F-eq6S)

Water type F-eq6S represents fresh groundwater in equilibrium with respect to calcite with the lowest redox potential. Both oxidation and acidification are buffered in this water type. Main occurrences of F-eq6S are located in the lower part of the Netherlands (appendix C, map "Redox level in fresh water type F-eq6"):

- the Holocene polder areas in South and North Holland (peri-marine clay on peat + land reclamation polders with marine deposits)
- the IJssel Valley (Holocene River deposits)
- the northern fringe of the Drenthe Glacial Plateau
- small occurrences in the Pleistocene areas (Drenthe, Brabant etc.).

The presence of this water type in Holocene areas is the result of the ample presence of shell fragments plus fresh organic matter (peat) in the rather young deposits. The Pleistocene occurrences are very few and often represent wells in discharge areas. In these areas, upward seepage of older groundwater that contacted carbonates and organic matter in deeper aquifer layers occurs.

Much more can be learned from the maps showing the individual water types. The previous examples show that the water type classification is suitable to reveal regional differences in groundwater quality in the Netherlands. The classification yields opportunities for an educated guess on the future groundwater quality evolution.

6 Relationship between water types, land use and hydrogeology in the Pleistocene area of the Netherlands

Pleistocene and older sediments are mainly composed of sands and therefore groundwater in shallow aquifers may be significantly influenced by anthropogenic activities. Land use and hydrogeology are probably two important parameters affecting the groundwater quality and therefore the water type The relationships between water-types, land use and hydrogeology will be examined in this chapter.

6.1 Relationships between groundwater quality and land use

The relationship between water types and land use in shallow aquifers is not obvious. 10 water types have been found below forest, grassland and arable land and their distribution is rather similar in the three land groups (table 11):

- water types below forest are mainly F-s5N (subsaturated, slightly-acid, NO3>2 mg/l) or F-s5Fe (subsaturated, slightly-acid, Fe-red.). Water type F-eq6Fe (equilibrium, pH>6, Fe-red.) is also present,
- water types below grassland are mainly neutral, Fe-reduced and in equilibrium with respect to calcite (F-eq6Fe) or subsaturated (F-s6Fe). It also can be subsaturated, slightly-acid and Fe-reduced (F-s5Fe).
- water types below arable land are dominated by F-s5N (subsaturated, slighty-acid and NO3>2mg/l), followed by F-s5Fe (subsaturated, slightly-acid, Fe-red.) and F-s6N (subsaturated, pH>6 and NO3>2 mg/l).

Table 11: Percentage of water types in forest, grassland and arable land in shallow groundwater (5-15m) in the Pleistocene areas.

Water type	% in forest	% in grassland	% in arable land
F-eq6Fe	12.3	23.4	7.2
F-eq6N	9.6	5.6	10.8
F-eq6S	1.4	3.7	1.2
F-s6Fe	11.0	18.7	10.8
F-s6N	9.6	0.9	12
F-s6S	4.1	8.4	7.2
F-s5Fe	20.5	20.6	13.3
F-s5N	23.3	13.1	24.1
F-s5S	0	0	4.8
F-s4Fe	1.4	0	0
F-s4N	6.8	2.8	8.4

In other words, shallow groundwater below forest is often subsaturated with respect to calcite, iron-reduced or nitrate-reducing and neutral or slightly-acid. Groundwater below grassland is mainly neutral, more anoxic (iron- or sulphur-reduced) and subsaturated with respect to calcite. Groundwater below arable land is frequently nitrate-reducing, neutral or slightly-acid and subsaturated with respect to calcite.

The large variation of water types in Pleistocene areas can be explained in the following way: water types characterise hydrogeochemical processes which are mainly influenced by reactive properties of subsoil and not solely by input of solutes from land use origin.

The anthropogenic oxidation capacity is higher in groundwater below grassland and arable land than in groundwater below forest. It decreases in deep groundwater (15-30 m) (figure 10).
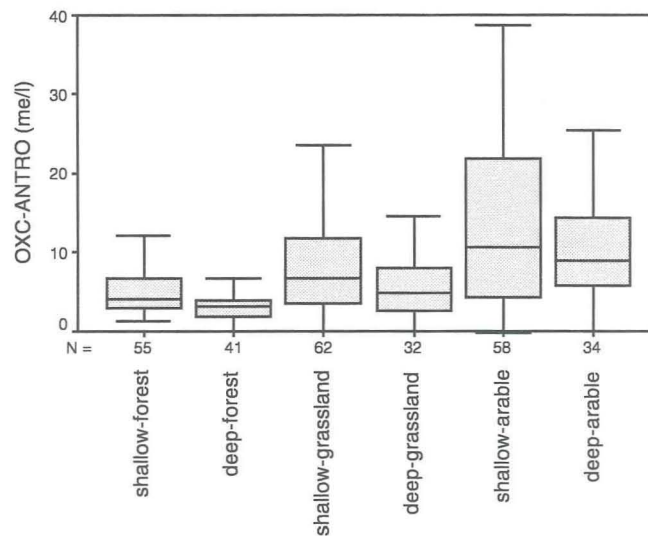

Figure 10: Boxplot of OXC-ANTRO in forest, grassland and arable land in shallow (5-15 m) and deep (15-30 m) groundwater in Pleistocene areas.

6.2 Relationships between groundwater quality and hydrogeology

Indications about potential flow direction such as recharge or discharge areas are included in the data set of 1995. However these data are not used to determine the relationships between groundwater quality and hydrogeology because they are based on groundwater head differences and not on a hydrogeological survey. The data set also gives an indication on the period of infiltration of groundwater. Recent and non-recent groundwater has been distinguished based on tritium concentrations. Groundwater with tritium unit higher than 5 has been mixed with water infiltrated after 1950 and is called "recent" groundwater. Groundwater with tritium unit lower than 5 has been mixed with water infiltrated before 1950 and is qualified " non-recent".

Table 12 presents the different water types found in recent and non-recent groundwater in Pleistocene areas. Dominant water types in recent shallow groundwater are F-s5N (subsaturated, slightly-acid, NO3>2, F-s5Fe (subsaturated, slightly-acid, Fe-red.) and F-eq6Fe (equilibrium, pH>6, Fe-red.). Non-recent shallow groundwater is frequently F-s6S (subsaturated, pH>6, S-red.) and F-s6Fe (subsaturated, pH>6, Fe-red.). In other words, shallow recent groundwater is often characterised by a high redox potential (nitrate-reducing) and a pH between 4.5 and

6. It should also be noted that water type F-s4N (subsaturated, acid, NO3>2 is only encountered in large proportion (8.3 %) in shallow recent groundwater. At the opposite, non-recent groundwater has often a lower redox potential (often sulphur-reduced) and a pH higher than 6. Deep recent groundwater (15-30 m) is usually characterised by iron-reducing conditions. Dominant water types are F-s5Fe (subsaturated, slightly-acid, Fe-red.), F-s6Fe (subsaturated, pH>6, Fe-red.) and F-eq6Fe (equilibriumq, pH>6, Fe-red.) Nitrate-reducing conditions still occur but less often than in shallow recent groundwater. The pH also tends to be higher in deep groundwater than in shallow groundwater. Deep and non-recent groundwater is characterised by a higher percentage of samples with low redox potential (sulphur-reduced) and with pH higher than 6. Table 12 also shows that groundwater in Pleistocene areas is mostly subsaturated with respect to calcite (on average 70 % of groundwater samples), without distinction between recent, non-recent, shallow or deep groundwater.

Table 12: Percentage of water types in shallow (5-15 m) and deep (15-30 m) recent and non-recent groundwater in Pleistocene areas.

	% in recent groundwater		% in non-recent groundwater	
	5-15 m	15-30 m	5-15 m	15-30 m
F-eq6Fe	15.9	16.7	13.9	16.4
F-eq6N	9.9	8.7	4.7	1.7
F-eq6S	0.8	1.6	4.7	11.2
F-s6Fe	11.1	21.4	16.3	22.4
F-s6N	7.9	8.7	0	0.9
F-s6S	1.6	3.2	27.9	15.5
F-s5Fe	17.0	21.4	14	24.1
F-s5N	25.4	15.9	6.9	1.7
F-s5S	0.8	0	11.6	5.1
F-s4Fe	1.2	0	0	0
F-s4N	8.3	2.4	0	0.9

6.3 Relationships between groundwater quality, landuse and hydrogeology: application to the province of Drenthe

TNO developed in 1991 a monitoring network in the province of Drenthe to characterise the groundwater quality. To get a comprehensive overview of the chemical composition of groundwater in the province, land use, hydrogeolgy and soil type were examined as they might influence the groundwater quality. Using a geographical information system, regions with different combinations of land use, soil type and hydrology were determined. The different regions represent homogenous areas (with a specific combination of land use, soil type) and geohydrology, and wells representative of each area were selected. In total 79 wells were selected (51 from the provincial monitoring network and 28 from the national network) and groundwater was yearly sampled and analysed at two different depths (at about 9 and 24 meters of depth).

Eight homogenous areas were identified:

1. arable land (sand) – recharge,

2. grassland (sand) – recharge,
3. forest/natural (sand) – recharge,
4. arable land (sand) – intermediate,
5. grassland (sand) – intermediate,
6. grassland/arable land (peat) - intermediate,
7. discharge areas,
8. built-up areas.

The results from the 1995 data set were described in Broers (1996). This data set is used as an illustration of the newly developed water type classification in a Pleistocene environment. Tables 13 and 14 summarise the water types encountered in the eight homogenous areas defined above in shallow and deep groundwater.

Table 13: Water types over 8 homogeneous areas in the province of Drenthe in shallow groundwater (5-15 m)

	F-eq6Fe	F-eq6S	F-s6N	F-s5Fe	F-s6S	F-s5N	F-s5Fe	F-s5S	F-s4N	S-eq6S	S-s6S
Arable land– recharge						7	1	1			
Grassland-recharge						3	2		1		1
Forest-recharge			1			1	4		1		
Arable land-intermediate			1	1	3	2	5	1			
Grassland-intermediate	1	1		4		2	5	1			
Grass/arable land (peat)-intermediate				1	2			2	1		
Discharge areas		2		3	4		1			1	
Built-up areas	2		1	1		1	1				

Table 14: Water types over 8 homogeneous areas in the province of Drenthe in deep groundwater (15-30 m)

	F-eq6Fe	F-eq6S	F-s6Fe	F-s6S	F-s5N	F-s5Fe	F-s5S	S-eq6Fe	S-s6N	S-s6S	S-s5Fe
Arable land– recharge					7	2					1
Grassland-recharge			1		2	3					
Forest-recharge					2	5					
Arable land-intermediate		3	4	1		2	3				
Grassland-intermediate	2		3	3	1	4	1		1	1	
Grass/arable land (peat)-intermediate			1	1		3					
Discharge areas	1	1	2	4		1	1	1			
Built-up areas	2	1	2			1					

The data are presented in figures 11 and 12, showing the proportion of a certain water type in the 8 homogeneous areas. Water types that occasionally occur in the eight areas, such as F-s5S, F-eq6Fe, Feq6S, F-s6N and F-s4N, are not illustrated in

the figures but their occurrence is given in tables 13and 14. A 95% confidence interval around the estimated proportion was calculated using the method of Blyth & Still (1983) described in Gilbert (1987, table A4). For example, a proportion of 78 % of water type F-s5N was estimated (7 of the 9 wells in this area yield water type F-s5N, table 13). The probability is < 2,5 % that this proportion is lower than 45 % or higher than 95%. The presentation used is comparable to the presentation of box-plots and "proportions of groundwater exceeding environmental standards" that is used for the regular reports over groundwater quality in the Netherlands (van Drecht et al., 1996, Venema et al., 2000).

The following patterns can be deduced from figures 11 and 12:

- F-s5N, F-s5Fe, F-s6Fe and F-s6S are the most common water types in the province of Drenthe, both in shallow and deeper groundwater (between 5-15 m and 15-30 m respectively). Calcite equilibrated water is seldom found in Drenthe.

- Water type F-s5N (subsaturated, pH 4,5-6, N-oxic water) is commonly found in the arable and recharge areas of Drenthe, both in the shallow and deep screens. Proportions of this water type are low in intermediate areas, and zero in discharge areas or peat areas. This pattern reflects the dominance of manure loads in recharge areas, resulting in nitrate leaching into groundwater. In the recharge areas reduction capacity and acid neutralising capacity are not sufficient to buffer the leaching of nitrate or the pH of the groundwater. Denitrification apparently occurs more frequently in the intermediate areas.

- Water type F-s5Fe (subsaturated, pH 4,5-6, Fe-reduced water) occurs in all homogeneous areas and shows proportions > 25% in grass-rech, forest-rech, arable-int, grass-int and grass-int-peat. Thus subsaturated groundwater with pH<6 is commonly found in large parts of Drenthe pointing to the absence of pH buffering due to calcite. Contrary to the F-s5N water type, in most of those areas denitrification of nitrate has occurred, probably using organic matter or pyrite as a source of electron donors.

- Water type F-s6Fe (subsaturated, pH>6, Fe-reduced water) is almost absent in the recharge areas, but shows amounts of 15-35% in the intermediate areas, discharge areas and built-up areas. Apparently pH is buffered in those areas, although calcite saturation is not reached. It was found earlier that many of those water samples show siderite saturation instead of calcite saturation (Broers, 1996). Siderite possibly controls the pH in those cases. The higher pH and lower redox potential in the intermediate areas could be due to the groundwater age, the proportion of pre-1950 water being higher in the intermediate and discharge areas.

- Water type F-s6S (subsaturated, pH>6, S-reduced water) is never found in recharge areas and shows the highest proportions in discharge areas and peat areas. Long residence times of groundwater and the presence of oxidizable organic matter in the deeper surface and peat layers are thought to be responsible for the sulphur-reduced state of the groundwater. It is also concluded that pH buffering plays a role in those areas.
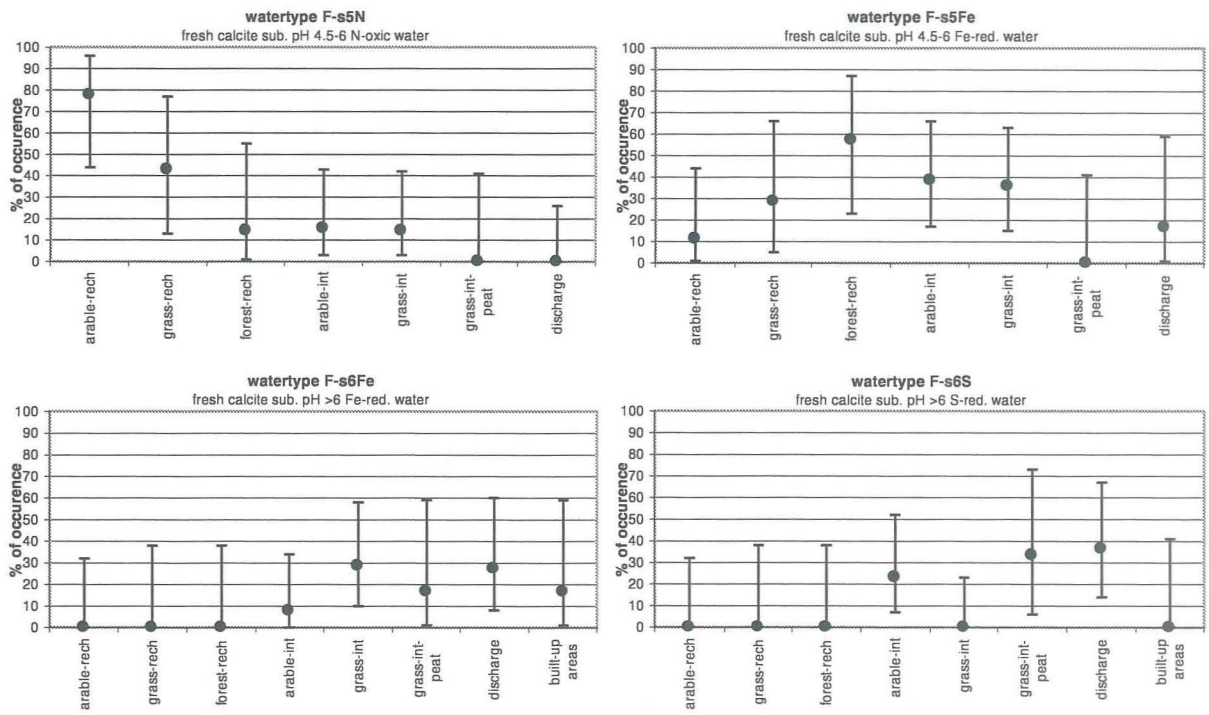
Figure 11: Distribution of water types in shallow groundwater (5-15 m) over 8
homogeneous areas in the province of Drenthe. Error bars indicate the 95%
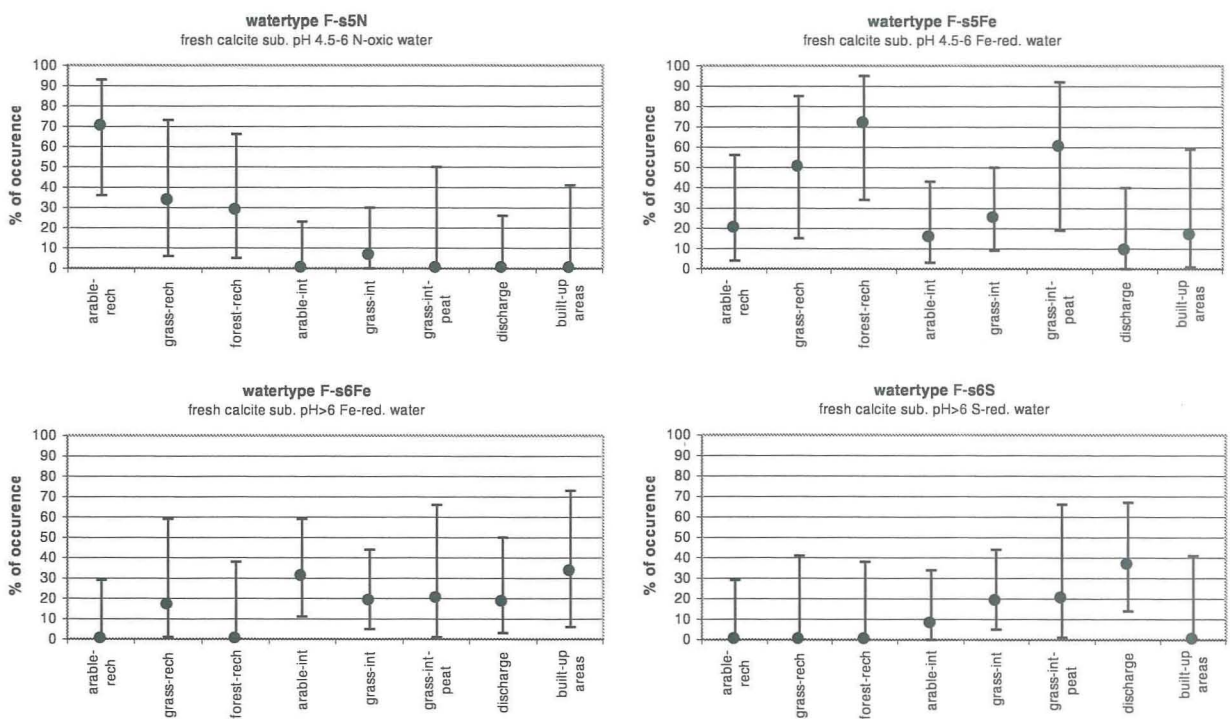confidence interval around the population estimate.

Figure 12: Distribution of water types in deep groundwater (15-30 m) over 8 homogeneous
areas in the province of Drenthe. Error bars indicate the 95% confidence interval
around the population estimate.

In short, a trend was found from low pH and high redox potential in agricultural recharge areas (F-s5N) towards intermediate pH and redox potential in forested recharge areas and agricultural intermediate areas (F-s5Fe and F-s6Fe) and near neutral pH, low redox potential in discharge and peat areas (F-s6S). However, no complete separation of water types is achieved using the homogeneous area approach.

6.4 Use of water type classification in cross sections: an illustration from the Oostrum well field (province of Limburg)

The water type classification can easily be used to identify hydrogeochemical patterns in a local groundwater quality study. This is illustrated by the Oostrum case study that was reported earlier in Broers & Buijs (1997). The sample data from nine mini-screen wells were classified using the unaltered classification scheme TNOCLASS_NL1. The water type distribution is shown in two cross sections (figure 13). The cross sections are located under a forest (wells 36-38) and under arable lands (wells 35, 39-42) in the contributing area of the Oostrum well field (pumping wells PPI ad PPIII). The well field suffers from contamination by trace elements, especially Ni and As.

Four main water types were identified: F-s4N, F-s5N and F-s5Fe and F-s6Fe. F-s4N and F-s5N represent the nitrate-rich, acid to slightly-acid groundwater that is found in the upper coarse aquifer. Nitrate concentrations up to 500 mg/L were occasionally found under arable land. Except in well 36, the main water types are the same under forested and arable land, but the concentrations of manure-related ions as nitrate and potassium differ. Still, the hydrogeochemical environment is comparable; both under arable land and forests it is anticipated that trace metals are mobile because of the low pH. Indeed high Ni, Co and Zn concentrations were found in these areas. Arsenic, however, was not found in water types F-s4N and F-s5N.

At larger depth a transition is found to water type F-s5Fe. At the boundary of F-s5N and F-s5Fe the process of nitrate reduction by pyrite oxidation is active, which can be deduced from increasing Fe and SO_4 concentrations. The water types indicate that the pH does not drop significantly and remains between 4,5 and 6. However, at one specific depth in well 41, pH values below 4.5 were observed, yielding water type F-s4Fe. In water type F-s5Fe, high concentrations of Ni, Co and As were found, especially under the F-s5N/F-s5Fe transition (Broers & Buijs, 1997). It was concluded that Ni, Co and As were mobilised from the pyrite-rich sediments. However, the highest concentration of Ni and Co was found in water type F-s4Fe, probably due to the enhanced mobility of the species at low pH. The transition from F-s5Fe to F-s6Fe at greater depth was probably caused by the dissolution of iron carbonates. Calcite equilibrium was not reached and the water remains subsaturated.

At larger depth in the aquifer, two N-oxic water types were observed (F-s4N, F-s6N). Both samples contained Fe (7.5 and 15 mg/L) and NO_3 (2.3 and 3.6 mg/L)

and can be characterised as MIX (see paragraph 4.4). The simplified classification groups those samples under N (table 9).

High oxidation capacity (OXC) of groundwater is illustrated as large dots in figure 13. High OXC values are due to anthropogenic pollution and are generally found in arable land and extend deeper. In the case of Oostrum, all F-s4N and F-s5N water has a high OXC, but even F-s5Fe and F-s6Fe water shows high OXC in the whole aquifer under arable land.

For this particular case study, it was concluded that the water type classification yielded a fast and complete picture of the main hydrogeochemical patterns that were earlier observed at the Oostrum well field. The patterns of trace element distribution were found consistent with the hydrogeochemical environments that were distinguished. Application of the classification can be used as a first step for further exploration of the data.

Forest-section
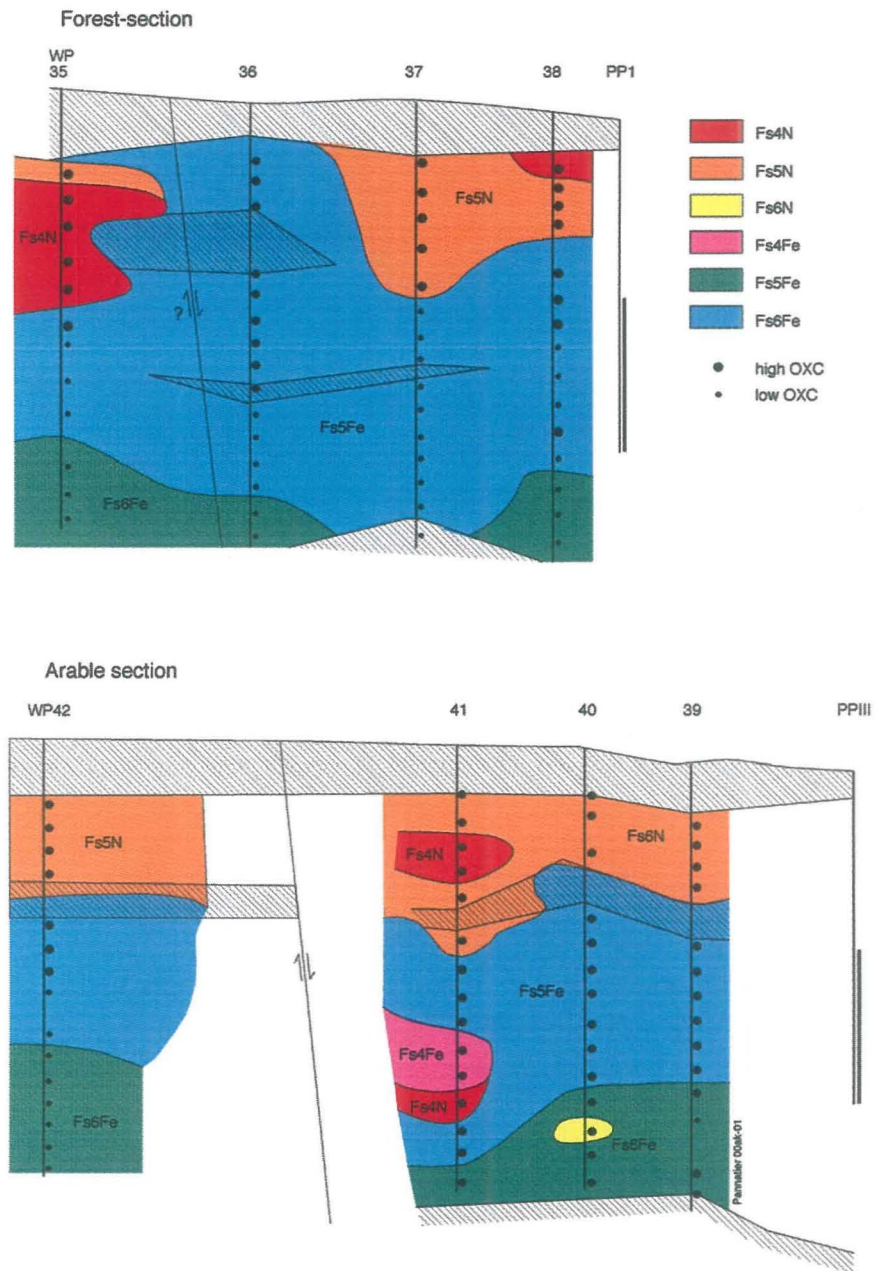
Arable section

*Figure 13: Cross sections of water types under forested land (wells 36-38) and under
arable land (wells 35, 39-42) in the Oostrum well field (province of Limburg)*

7 Conclusions and validation

7.1 Parameters used for the classification

A groundwater classification based on geochemical processes has been proposed in this report. The parameters included in the classification are the salinity, the saturation index of calcite, the pH and the redox level. The classification can be extended with the anthropogenic oxidation capacity in fresh groundwater and cation exchange in brackish/salt groundwater to identify salt-water intrusion into freshwater or fresh water intrusion into salt water ("freshening"). Each parameter contains a range of values that is divided in several classes. The number of classes becomes large when parameters are combined, resulting in a very large number of different water types. Therefore it was chosen to propose a simplified groundwater classification by reducing the number of classes of each parameter. The parameters used for the simplified classification are the salinity (fresh or brackish+salt groundwater), the saturation index (subsaturated or in equilibrium + supersaturated) and the redox level (NO_3>2 mg/l, iron-reduced or sulphur-reduced). The anthropogenic oxidation capacity and the assumption of pyrite oxidation in fresh water, cation exchange in brackish and salt water are not included in the name of the water-type but can be illustrated on maps as additional information. The resulting number of water-types is 36 (18 for fresh groundwater and 18 for brackish/salt water).

7.2 Application of the classification to the 1995 data set of the national groundwater monitoring network

The simplified classification was applied to the data set of 1995. In fresh groundwater 11 water-types were found. The number of groundwater samples is important in each water type (from 34 to 296 data) except in two water types, F-s5S (16 data with subsaturated, slightly-acid and S-red.) and F-s4Fe (3 data with subsaturated, acid and Fe-red.). The most frequent water-types are F-eq6Fe (296 data with equilibrium, pH>6 and Fe-red.), F-eq6S (160 data with equilibrium, pH>6 and S-red.), F-s6Fe (161 data with subsaturated, pH>6 and Fe-red.) and F-s5Fe (144 data with subsaturated, slightly-acid and Fe-red.). In brackish and salt groundwater, 8 water types have been determined but only one water-type, S-eq6S (equilibrium, pH>6 and S-red.) is dominant (139 data). The number of samples in the seven other water-types varies between 2 and 17 per water-type.
Soil type or geology, land use and hydrogeology are assumed to be major factors to understand the distribution of water types in the Netherlands. In (peri)-marine and fluviatile Holocene, the low permeability of clayey sediments, the occurrence of calcite in marine sediments and the presence of peat probably explains the groundwater quality (neutral pH, supersaturated or in equilibrium with respect to calcite, anoxic). The dominant water types are F-eq6S (equilibrium, pH>6, S-red.) and F-eq6Fe (equilibrium, pH>6, Fe-red.).

More anoxic aquifers (sulphur-reduced) are found in marine clayey sediments and in peat whereas Fe-reduced or even nitrate-reducing environments are found predominantly in sands (dunes) and in river deposits close to Utrecht. Brackish and salt groundwater are found predominantly in marine Holocene sediments. Pleistocene and older sediments are mainly composed of sands and therefore groundwater quality can be significantly influenced by human activities (land use) and hydrogeology. A major difference between groundwater sampled in Holocene and Pleistocene is the large amount of water samples subsaturated with respect to calcite in Pleistocene and older sediments.

The examination of the relationships between land use and water types in Pleistocene and older sediments shows that shallow groundwater below forest is often subsaturated with respect to calcite, iron-reduced or nitrate-reducing and neutral or slightly-acid. Groundwater below grassland is mainly neutral, more anoxic (iron- or sulphur-reduced) and subsaturated with respect to calcite. Groundwater below arable land is frequently nitrate-reducing, neutral or slightly-acid and subsaturated with respect to calcite.

Water types in recent and non-recent groundwater in Pleistocene and older sediments were also characterised. Dominant water types in recent shallow groundwater are F-s5N (subsaturated, slightly-acid, NO3>2mg/l), F-s5Fe (subsaturated, slightly-acid, Fe-red.) and F-eq6Fe (equilibrium, pH>6, Fe-red.). Non-recent shallow groundwater is frequently F-s6S (subsaturated, pH>6, S-red.) and F-s6Fe (subsaturated, pH>6, Fe-red.). In other words, shallow recent groundwater is often characterised by a high redox potential (nitrate-reducing) and a pH between 4.5 and 6 while non-recent groundwater has often a lower redox potential (often sulphur-reduced) and a pH higher than 6. Deep recent groundwater (15-30 m) is usually characterised by iron-reducing conditions. Dominant water types are F-s5Fe (subsaturated, slightly-acid, Fe-red.), F-s6Fe (subsaturated, pH>6, Fe-red.) and F-eq6Fe (equilibrium, pH>6, Fe-red.). Nitrate-reducing conditions still occur but less often than in shallow recent groundwater. The pH also tends to be higher in deep groundwater than in shallow groundwater. Deep and non-recent groundwater is characterised by a higher percentage of samples with low redox potential (sulphur-reduced) and with pH higher than 6.

7.3 Application of the classification to two cases studies in the Netherlands

A 1995 data set from a monitoring network in the province of Drenthe was used as an illustration of the newly developed water type classification in a Pleistocene environment. The data set contains information about land use, soil type, hydrology, and groundwater quality. The simplified classification scheme was applied to this data set to verify if areas with a given combination of land use and hydrogeology were characterised by specific water types. Based on the classification results, the most common water types are F-s5N, F-s5Fe, F-s6Fe and F-s6S, both in shallow and deeper groundwater (between 5-15 m and 15-30 m respectively). A trend was found from low pH and high redox potential in

agricultural recharge areas (F-s5N) towards intermediate pH and redox potential in forested recharge areas and agricultural intermediate areas (F-s5Fe and F-s6Fe) and near neutral pH, low redox potential in discharge and peat areas (F-s6S). However, no complete separation of water types is achieved using the homogeneous area approach (area defined as a specific combination of land use and hydrogeology).

The water type classification was also used to identify hydrogeochemical patterns in a local groundwater quality study. The sample data from nine mini-screen wells in Oostrum (province of Limburg) were classified using the simplified classification scheme and water type distribution over depth was illustrated on cross sections. Four main water types were identified: F-s4N, F-s5N and F-s5Fe and F-s6Fe. The upper part of the aquifer is characterised by water types F-s4N and F-s5N, both under forested and arable land. At larger depth a transition is found to water type F-s5Fe. At the boundary of F-s5N and F-s5Fe the process of nitrate reduction by pyrite oxidation is probably active, which can be deduced from increasing Fe and SO_4 concentrations. In water type F-s5Fe, high concentrations of Ni, Co and As were found, especially under the F-s5N/F-s5Fe transition. It was concluded that the water type classification yielded a fast and complete picture of the main hydrogeochemical patterns that were earlier observed at the Oostrum well field. The patterns of trace element distribution were found consistent with the hydrogeochemical environments that were distinguished.

7.4 Validation of the classification

To validate the classification used in this report, two suggestions are proposed:
1. To apply the same classification to another data set. If the selected year is close to 1995 (1996 or 1997), the water type distribution should be similar to the one determined in this study. If the water type distribution in the Netherlands is very different, it means probably that the classification is not robust enough unless water quality has dramatically changed between 1995 and the date of the new data set.
2. To compare water types found in this study with information from other sources. For instance detailed monitoring of aquifer sediments and groundwater have been performed in specific regions of the Netherlands. These data could be compared to the water types obtained in this study. Information on the geochemical composition of sediments would enable to check the validity of the redox level determination. Indeed one of the major problem is the lack of information concerning precipitation of secondary minerals (such as $FeCO_3$ or FeS) or pyrite oxidation, inducing for instance decreases or increases of Fe^{2+} in groundwater. This could result in a wrong determination of redox level.

## 7.5 Implementation of the classification

If the groundwater classification is validated, it can be implemented in the pre- and postprocessing software WATEQ that is available at TNO. Several subroutines (quality check of chemical analysis, Stuyfzand classification) were already implemented (Venema, 2000).

8 References

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Appendix A   Threshold limits

Scatterplots showing Fe, NO$_3$ and Mn concentrations. Most samples with high Fe or Mn concentrations have nitrate concentrations lower than 2 mg/l.
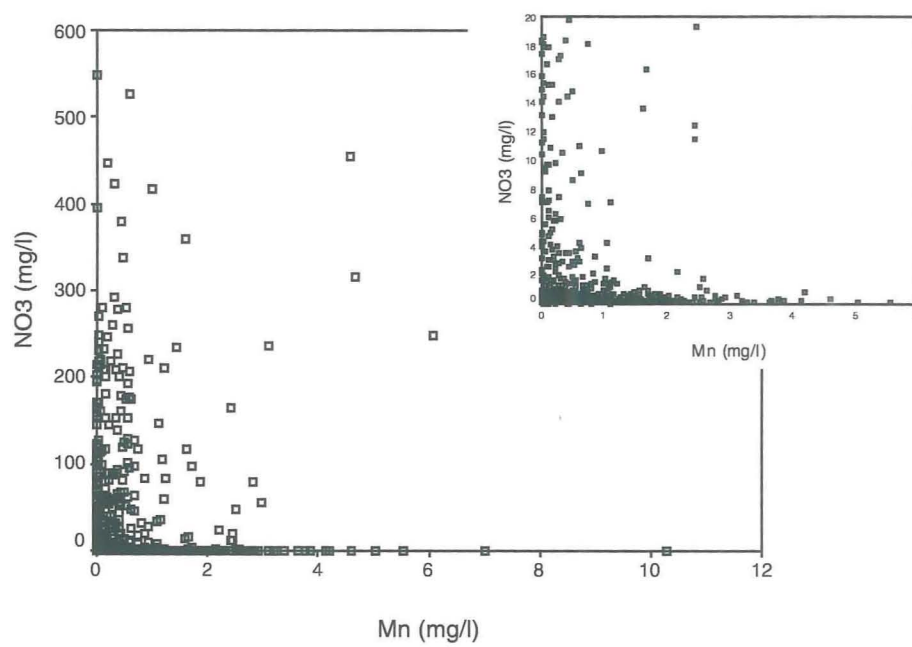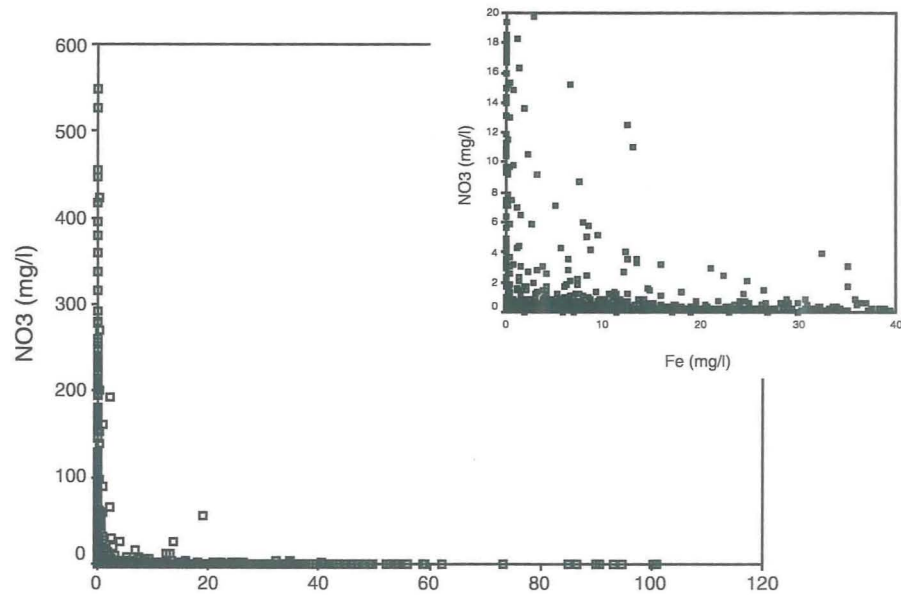
Appendix B   Manual user

The file TNOCLASS_NL1.xls (Excel 97) contains the whole classification. The file contains three spreadsheets:
- the first spreadsheet called "original" contain the original values of the data set,
- the second spreadsheet called "corrected" contains the whole data set (like in spreadsheet original) but some transformations have been achieved. New variables are also calculated
- the third spreadsheet called "classification" includes calculations of parameters used for the classification and provides the water types.

If you wish to use the excel file to determine the water types of your groundwater analyses, the following indications should be read attentively. Shaded columns in spreadsheets represent data that are indispensable to perform the calculations (with Excel and Wateq) and to determine water types.

1. Spreadsheet "original"
The format of the spreadsheet "original" must be respected otherwise the calculations performed on the other spreadsheets will not refer to the right variables. Check also that the concentrations of your variables are similar to those in spreadsheet "original".
Signs "<" indicating that concentrations are lower than detection limit must be replaced by the half of the detection limit. It must be checked that blank cases (missing values) are not replaced by zero.

2. Spreadsheet "corrected"
The spreadsheet "corrected" copies the data from the spreadsheet "original" and transforms some of them:
- Al concentrations are converted in mg/l
- N concentrations in NH_4^+, NO_2 and NO_3 are converted in NH_4^+, NO_2 and NO_3 concentrations respectively
- Ptot concentrations have been used to calculate PO_4 concentrations.

It must be checked that all variables used for the classifications have the right concentrations in spreadsheet "corrected". If not, they must be corrected on this page.
On the left side of the spreadsheet, variable SO_4F is calculated (column BX) for the redox level determination and new variables (from columns BY to CK) are calculated to estimate cation exchange processes in brackish and salt groundwater.

2. Spreadsheet "classification"
This spreadsheet contains calculations of parameters used for the classification. It contains the following information:
- Columns A to G copy selected data from the spreadsheet "original" (well number, geological division etc.).

- Columns H and I contain the quality labels (Qlabel) and the saturation index of calcite. These data are generated using the pre- and post-processing subroutine of WATEQ4F developed at TNO (Venema, 2000).
- Columns from J to S contain calculations of the parameters used for the classification:

Column	Description
J	Selection of good analyses (code < 31000, see chapter 3)
K	Salinity
L	Saturation index of calcite
M	pH
N	Redox level
O	Assumption of pyrite oxidation coupled to nitrate reduction
P	OXC-ANTRO
Q	Freshening or salt water intrusion using Na^+ concentrations
R	Freshening or salt water intrusion using Mg^{2+} concentrations
S	Freshening or salt water intrusion using Na^+ **and** Mg^{2+} concentrations

- Columns T to Y contain the simplified parameters (reduction of classes, see chapter 5.1),
- Columns Z contain depth classes of groundwater samples (see chapter 5.3)
- Column AA contains the resulting water types.

Appendix C   Maps of water types in the Netherlands

The following maps are represented in appendix C:
- 2 maps representing the distribution of water types in fresh groundwater between 5 and 15 meters below surface level and between 15 and 30 meters,
- 1 map representing the distribution of water types in brackish and salt groundwater between 5 and 15 meters below surface level and between 15 and 30 meters,
- 4 maps representing the distribution of the 10 major water types in shallow and deep fresh groundwater with indication of pyrite oxidation and levels of OXC-ANTRO.

The different water type names are described below:

Fresh watertypes:

Watertype	Groundwater description
F-eq6S	Fresh, eq or supersat. with respect to calcite, pH>6, S-red.
F-eq6Fe	Fresh, eq or supersat. with respect to calcite, pH>6, Fe-red.
F-eq6N	Fresh, eq or supersat. with respect to calcite, pH>6, N-oxic
F-s6S	Fresh, subsaturated with respect to calcite, pH>6, S-red.
F-s6Fe	Fresh, subsaturated with respect to calcite, pH>6, Fe-red.
F-s6N	Fresh, subsaturated with respect to calcite, pH>6, N-oxic
F-s5S	Fresh, subsaturated with respect to calcite, pH 4.5-6, S-red.
F-s5Fe	Fresh, subsaturated with respect to calcite, pH 4.5-6, Fe-red.
F-s5N	Fresh, subsaturated with respect to calcite, pH 4.5-6, N-oxic
F-s4N	Fresh, subsaturated with respect to calcite, pH<4.5, N-oxic

Brackish and salt watertypes:

Watertype	Groundwater description
S-eq6S	Salt/brackish, eq or supersat., pH>6, S-red.
S-eq6Fe	Salt/brackish, eq or supersat., pH>6, Fe-red.
S-eq6N	Salt/brackish, eq or supersat., pH>6, N-oxic
S-s6S	Salt/brackish, subsaturated with respect to calcite, pH>6, S-red.
S-s6Fe	Salt/brackish, subsaturated with respect to calcite, pH>6, Fe-red.
S-s6N	Salt/brackish, subsaturated with respect to calcite, pH>6, N-oxic
S-s5S	Salt/brackish, subsaturated with respect to calcite, pH 4.5-6, S-red.
S-s5Fe	Salt/brackish, subsaturated with respect to calcite, pH 4.5-6, Fe-red.
S-s5N	Salt/brackish, subsaturated with respect to calcite, pH 4.5-6, N-oxic
S-s4N	Salt/brackish, subsaturated with respect to calcite, pH<4.5, N-oxic

Fresh Water Types at a Depth of 5 - 15 meters below Surface Level

Fresh Watertypes at Depth 5-15 m
- F-eq6S
- F-eq6Fe
- F-eq6N
- F-s6S
- F-s6Fe
- F-s6N
- F-s5S
- F-s5Fe
- F-s5N
- F-s4N

Locations with Salt/Brackish Water
- × 5 - 15 m

Geology
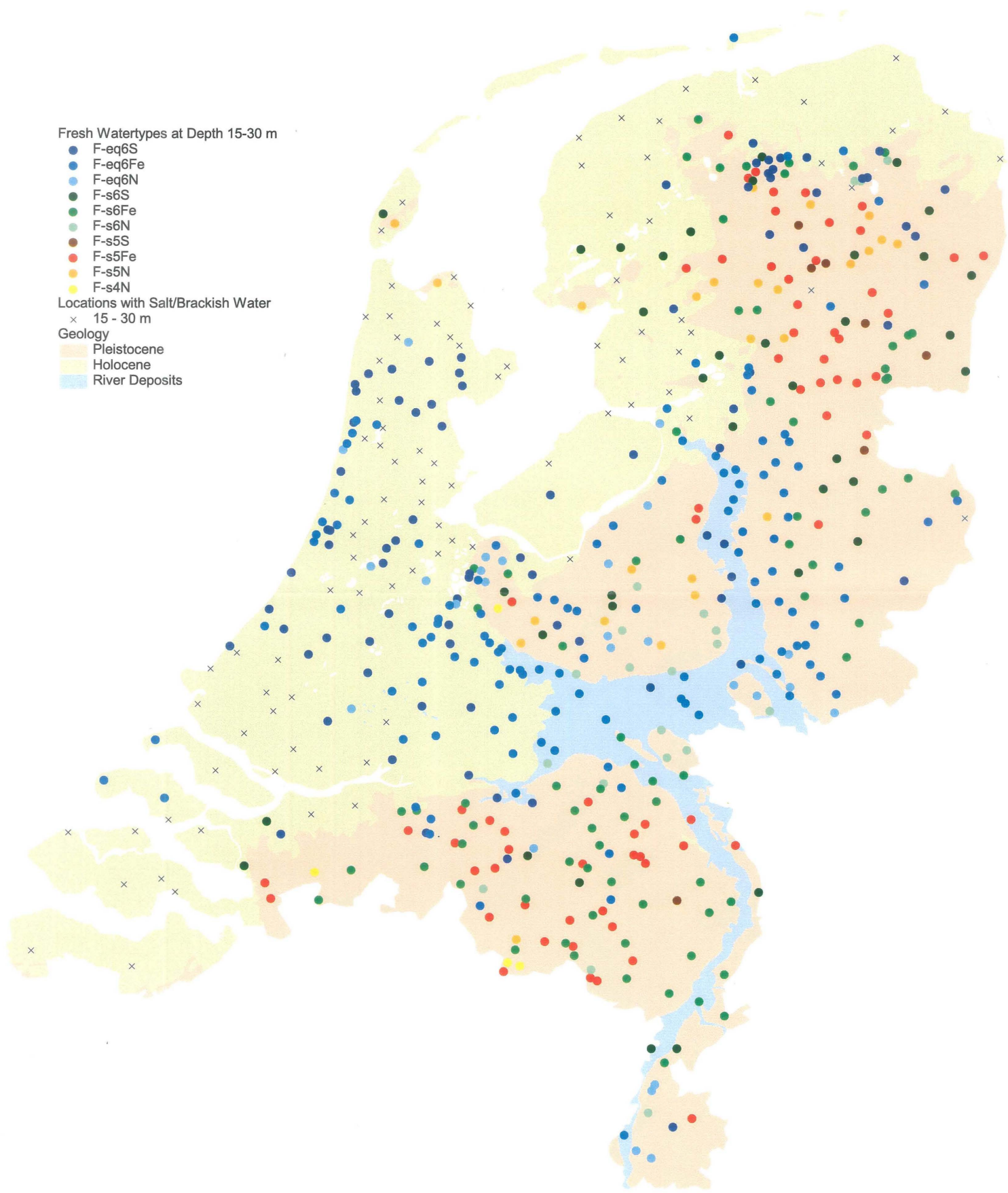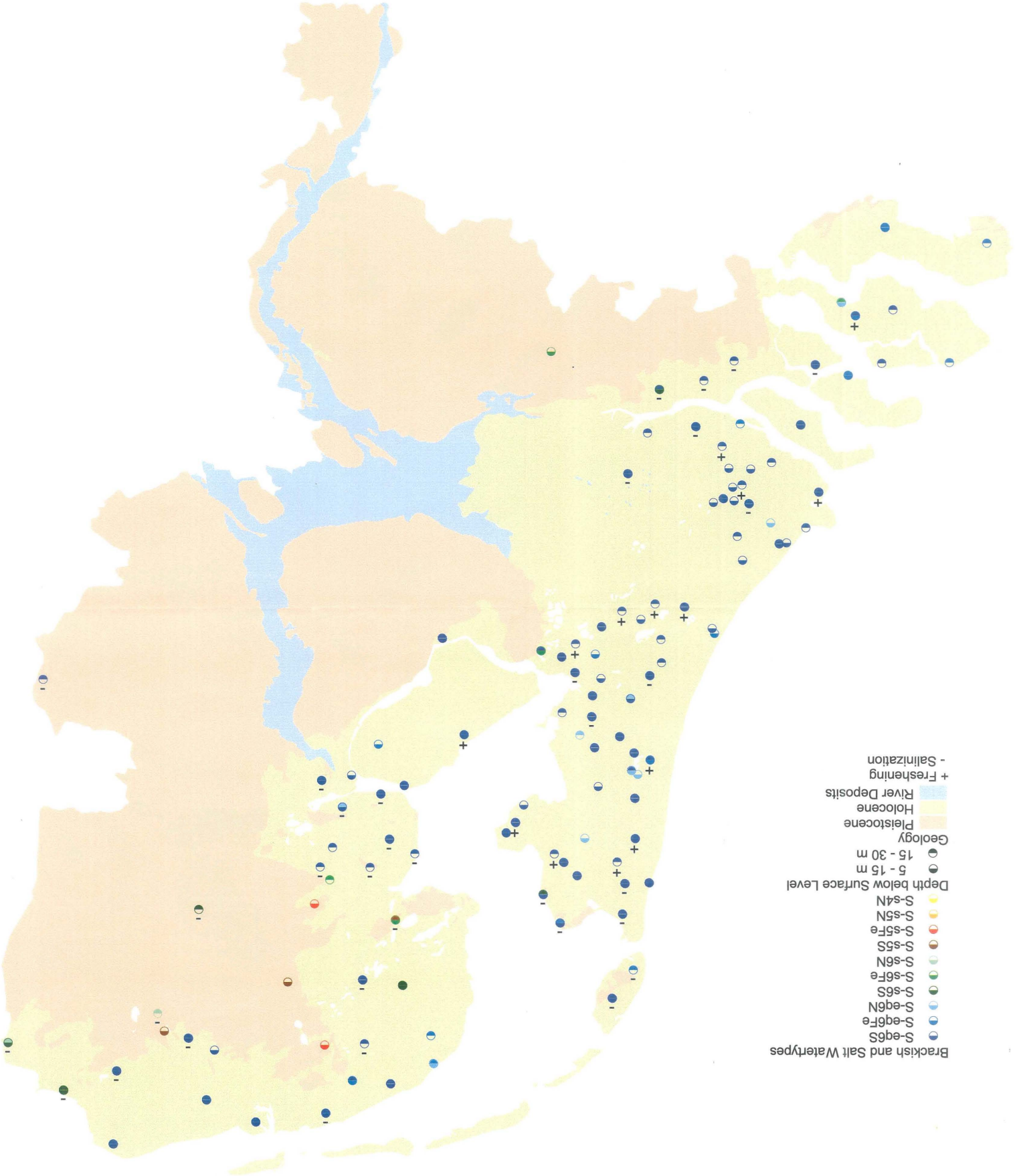- Pleistocene
- Holocene
- River Deposits
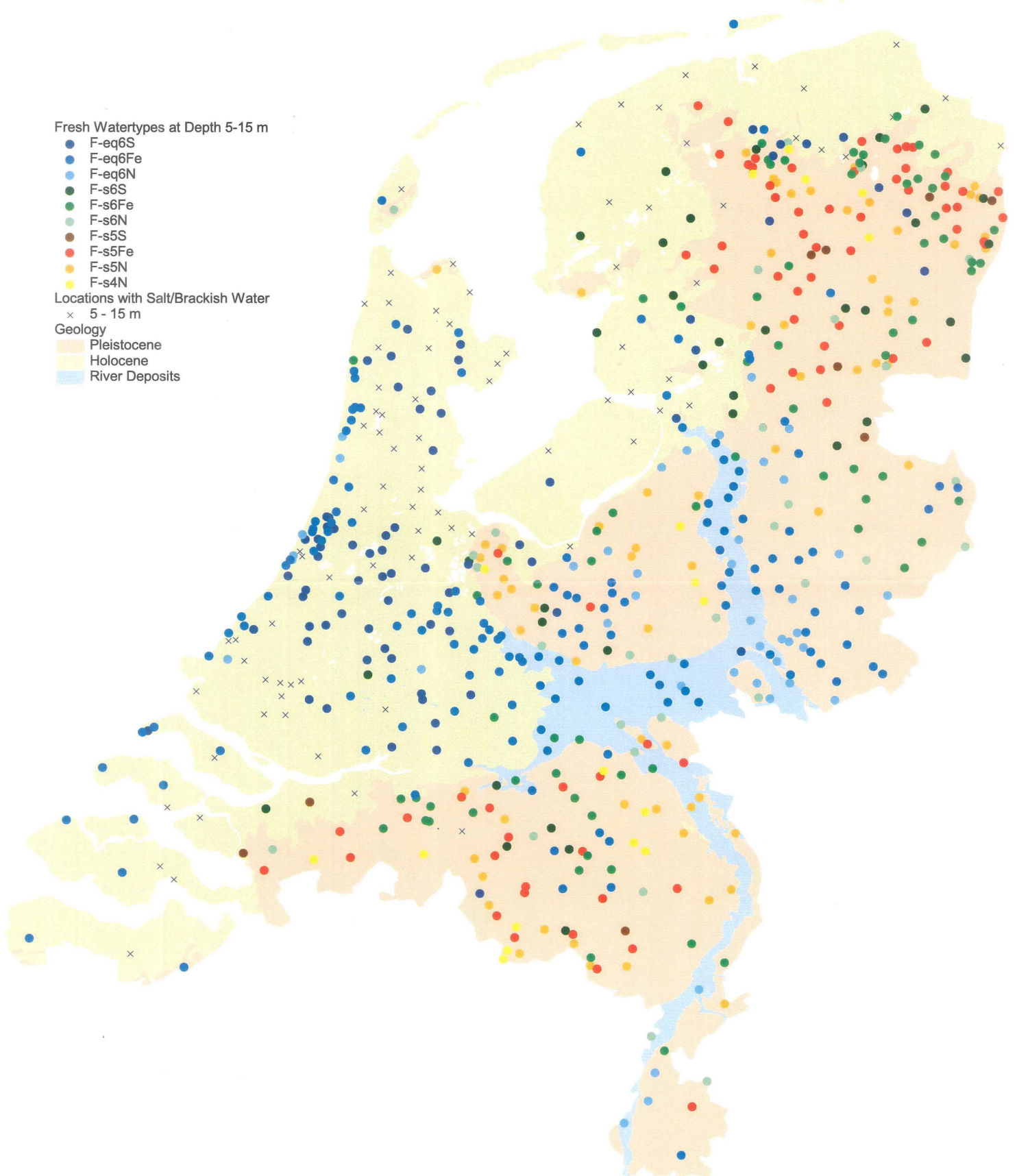
0   10   20   30   40   Kilometers

Netherlands Institute of Applied Geoscience TNO
- *National Geological Survey*

# Fresh Water Types at a Depth of 15 - 30 meters below Surface Level

Fresh Watertypes at Depth 15-30 m
- F-eq6S
- F-eq6Fe
- F-eq6N
- F-s6S
- F-s6Fe
- F-s6N
- F-s5S
- F-s5Fe
- F-s5N
- F-s4N

Locations with Salt/Brackish Water
- × 15 - 30 m

Geology
- Pleistocene
- Holocene
- River Deposits

0 10 20 30 40 Kilometers

Netherlands Institute of Applied Geoscience TNO
- *National Geological Survey*

Brackish and Salt Water Types at Depths of 5 - 15 and 15 - 30 meters below Surface Level

Brackish and Salt Watertypes

- S-eg5
- S-eg6Fe
- S-eg6N
- S-s6S
- S-s6Fe
- S-s6N
- S-s5S
- S-s5Fe
- S-s5N
- S-s4N

Depth below Surface Level

- 5 - 15 m
- 15 - 30 m

Geology

- Pleistocene
- Holocene
- River Deposits
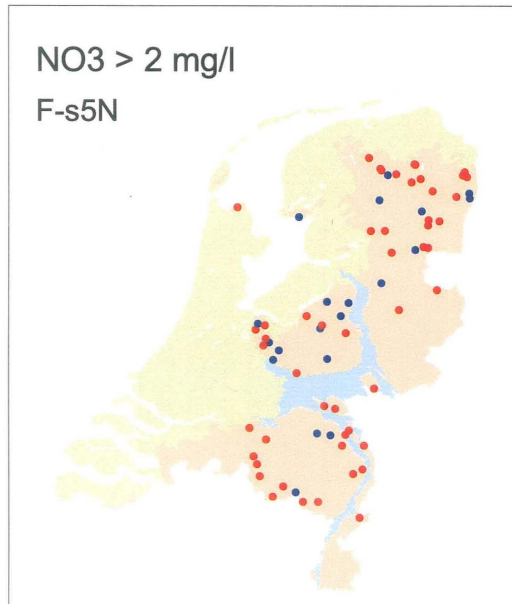
+ Freshening
- Salinization

0 10 20 30 40 Kilometers

Netherlands Institute of Applied Geoscience TNO
- National Geological Survey

TNO

Redox level in Fresh Water Type F-eq6

Shallow: 5-15 m

Deep: 15-30 m
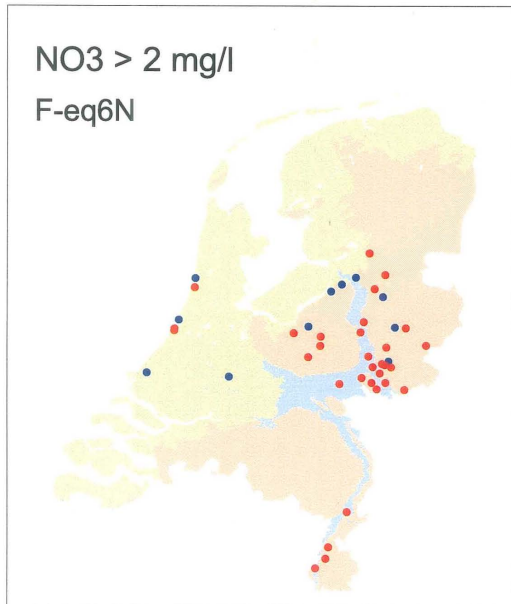
NO3 > 2 mg/l

F-eq6N

Oxidation Capacity
- 🔴 high OXC
- 🔵 low OXC

Geology
- Pleistocene
- Holocene
- River Deposits

* Pyrite Oxidation

NO3 > 2 mg/l

F-eq6N

Fe-red.

F-eq6Fe

Fe-red.

F-eq6Fe

S-red.

F-eq6S

S-red.

F-eq6S

0   30   60   90   Kilometers

TNO Netherlands Institute of Applied Geoscience TNO
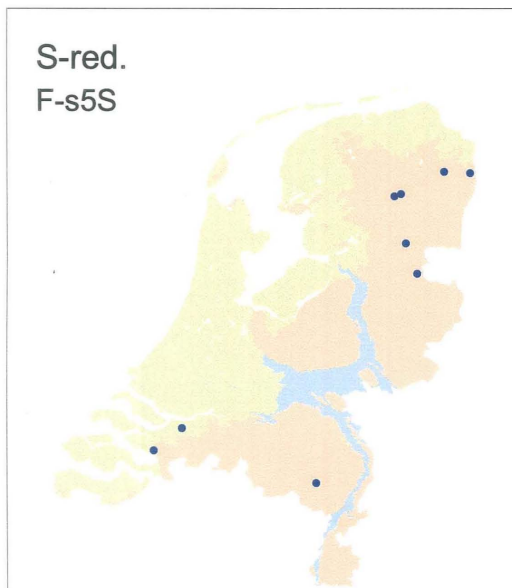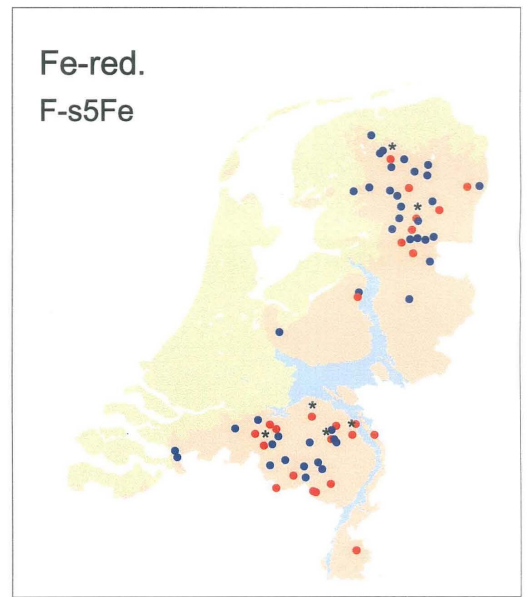*- National Geological Survey*
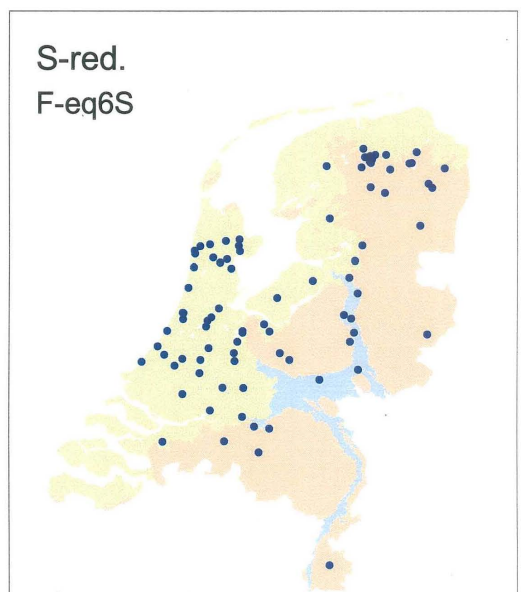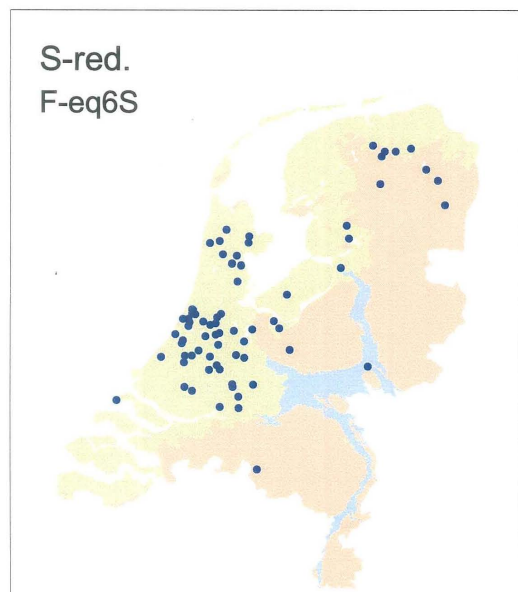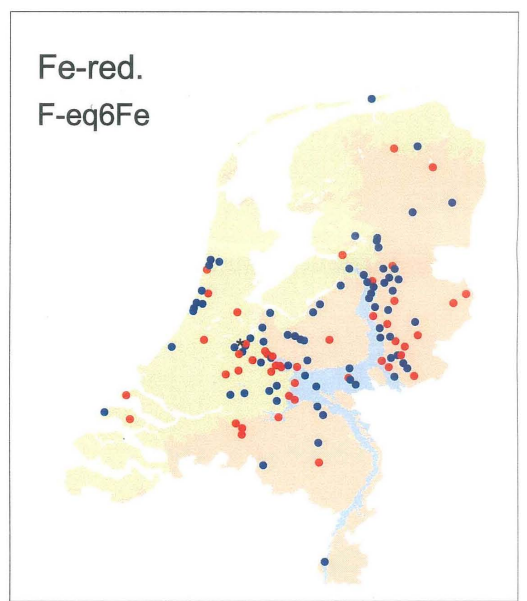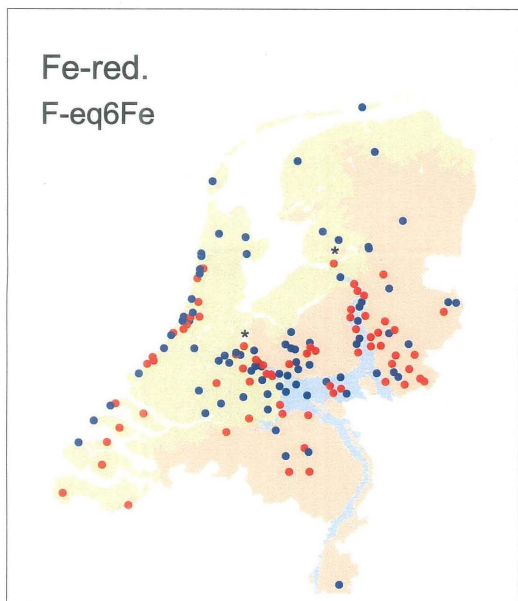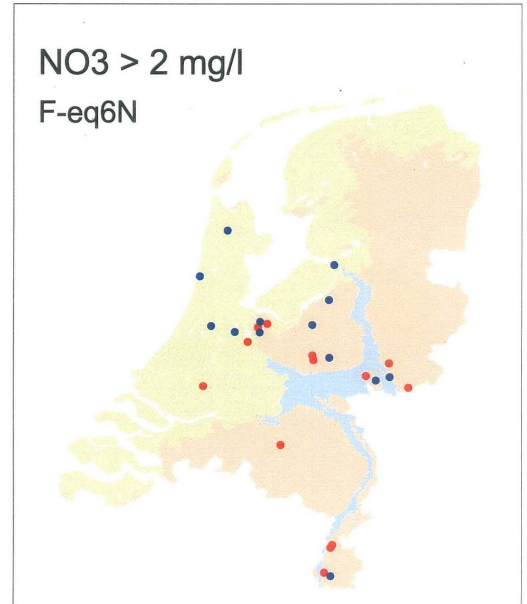
Redox level in Fresh Water Type F-s6

Shallow: 5-15 m

Deep: 15-30 m
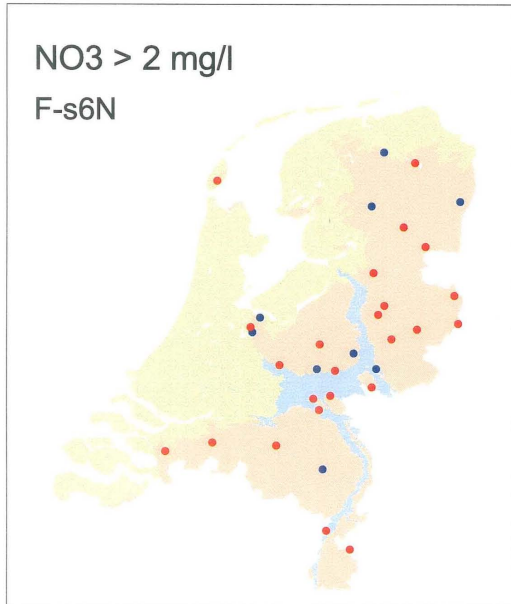
NO3 > 2 mg/l

F-s6N

Oxidation Capacity
- 🔴 high OXC
- 🔵 low OXC

Geology
- Pleistocene
- Holocene
- River Deposits

* Pyrite Oxidation

NO3 > 2 mg/l

F-s6N

Fe-red.

F-s6Fe

Fe-red.

F-s6Fe

S-red.

F-s6S

S-red.

F-s6S
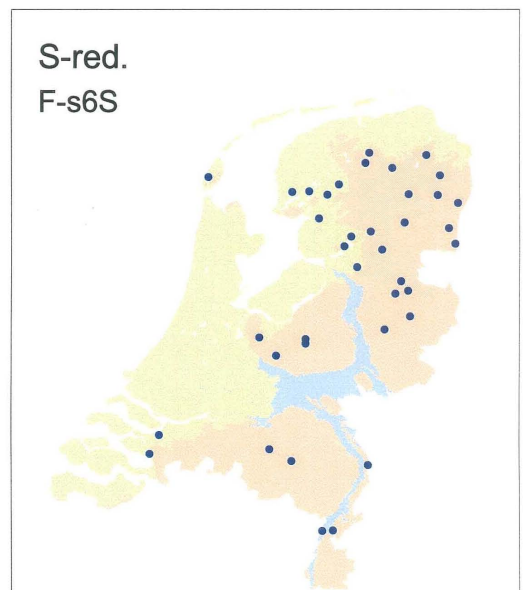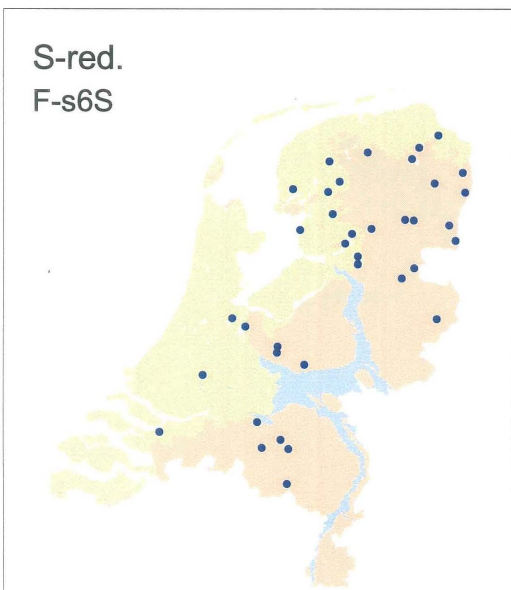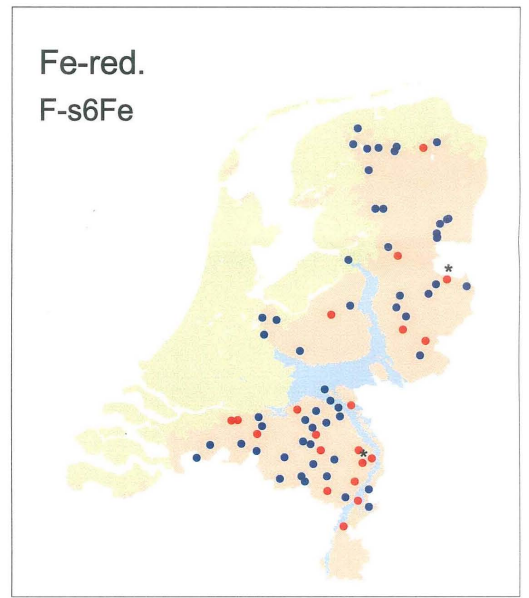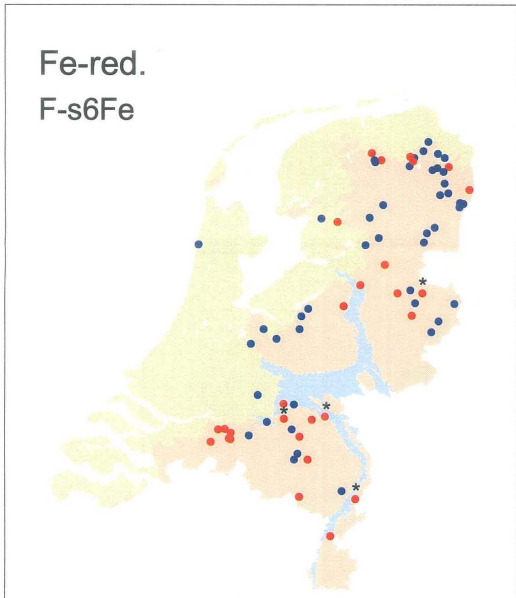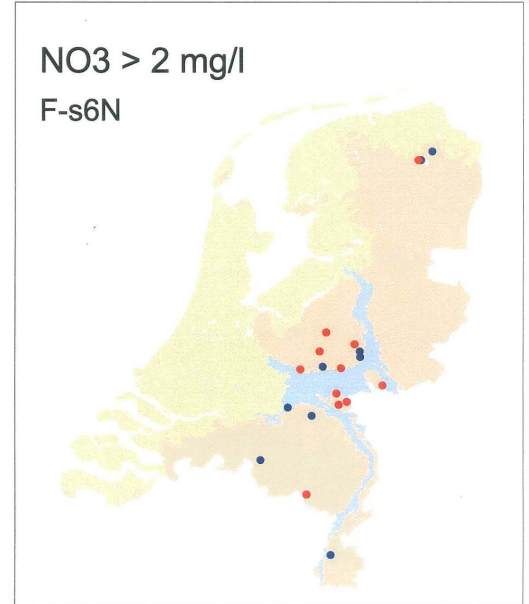
0   30   60   90   Kilometers

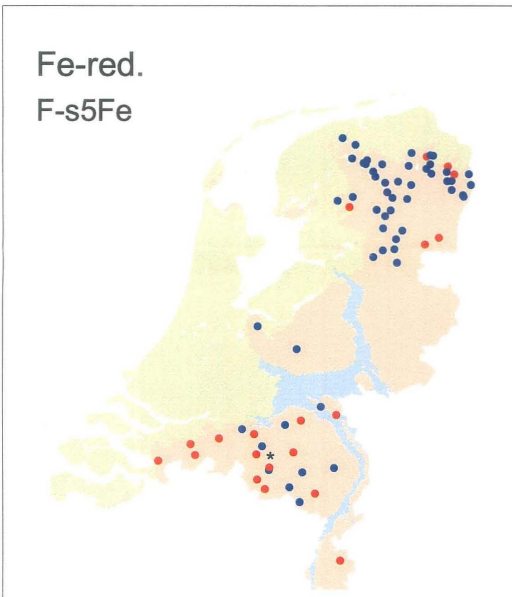**TNO** Netherlands Institute of Applied Geoscience TNO
- National Geological Survey

Redox level in Fresh Water Type F-s5

Shallow: 5-15 m

Deep: 15-30 m

NO3 > 2 mg/l

F-s5N

Oxidation Capacity
- ● high OXC
- ● low OXC

Geology
- � Pleistocene
- ▮ Holocene
- ▮ River Deposits

* Pyrite Oxidation

NO3 > 2 mg/l

F-s5N

Fe-red.

F-s5Fe

Fe-red.

F-s5Fe

S-red.

F-s5S

S-red.

F-s5S

0   30   60   90   Kilometers

TNO Netherlands Institute of Applied Geoscience TNO
- National Geological Survey
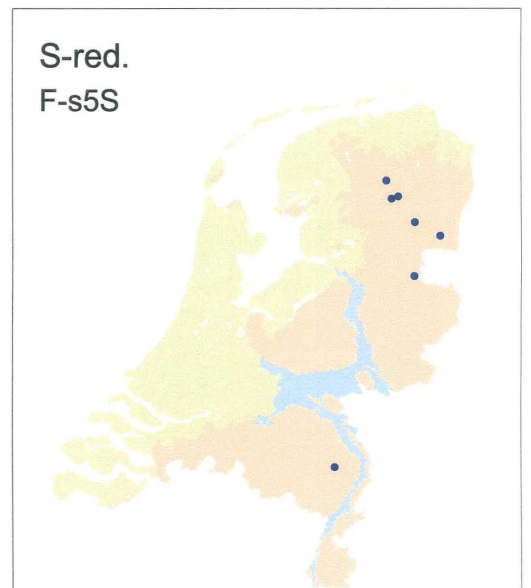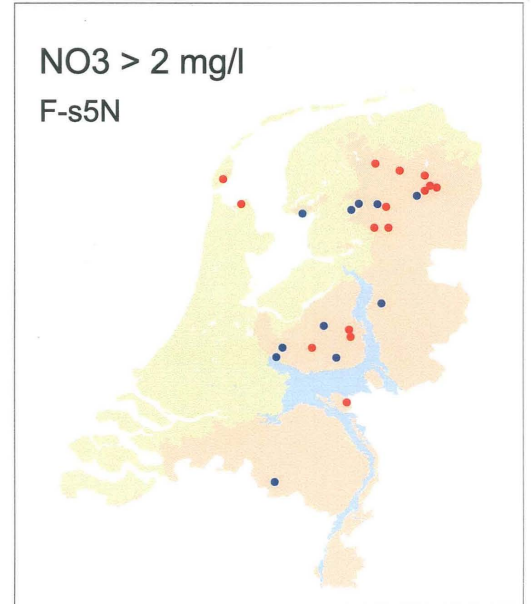
Redox level in Fresh Water Type F-s4

Shallow: 5-15 m

Deep: 15-30 m

NO3 > 2 mg/l

F-s4N

Oxidation Capacity
- ● high OXC
- ● low OXC

Geology
- Pleistocene
- Holocene
- River Deposits

* Pyrite Oxidation

NO3 > 2 mg/l

F-s4N

0   30   60   90   Kilometers

Netherlands Institute of Applied Geoscience TNO
- *National Geological Survey*