HOVER

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Hydrogeological processes and Geological Settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems - HOVER

Deliverable 5.4

Assessment of attenuation patterns for a number of relevant European settings

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SUMMARY

The present document is deliverable D5.4 " Assessments of attenuation patterns for a number of relevant European settings" corresponding to the task 5.4 "Assessing the spatial extent and importance of denitrification" of the HOVER project "*Hydrogeological processes and Geological Settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems* ".

Work package 5 of the HOVER project aims to assess nitrate and pesticide travel times in saturated and unsaturated zones and, where possible, attenuation patterns for a number of relevant European settings for evaluating the efficiency of programme of measures.

The task 5.4 is centered on the denitrification aspects. After a presentation of the denitrification concept, the methods used in UK, England, Denmark, Netherland/Flanders and Cyprus are presented.
Based on this information completed by literature review a simple common approach is proposed to define the oxic, anoxic, mix and to map this information at large scale.
Pilot sites will be testing the method and results will be available in D5.5.

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1 INTRODUCTION

Nitrate is of major concern for groundwater in Europe as nitrate is causing failure to achieve good chemical status in 57% of groundwater bodies representing 72% of surface of GWB (EEA website, 2nd RBMP).

Groundwater systems in cultivated floodplains are vulnerable to nitrate contamination due to extensive fertilisation and the shallow depth of the groundwater. Since the beginning of the 90's and under the EU Nitrate directive important effort were made in order to decrease the nitrate pressure on the water resources. Today a great part of the point source were solved. However the diffuse pressure of nitrate remains important in various areas and the transfer time of water and associated pollutant from soil to groundwater may also explain some still quite high NO_3 concentrations in groundwater and increased trends (see report D6.3).

Denitrification process is important as it allow a decrease of N concentration in water. This natural processes can be used in order to maintain or obtain high quality water for example building wetlands or keeping the geochemical conditions allowing this process. In the pressure-impact studies it is necessary to know where denitrification occurs in order to correctly evaluate the location of the main pressure and to differentiate dilution to denitrification. This is important as denitrification is not a permanent processes and anthropogenic activities may lead to the decrease of the denitrification process and subsequently a drastic increase of NO_3 concentration in groundwater?

Within the floodplain environment, mainly alluvial and fluvio glacial aquifers, riparian areas, characterised by significant exchanges between surface water and groundwater, are a favourable site for nitrate removal through denitrification.
In hard-rock aquifer with lithology rich in Fe, Mn, organic matter and pyrite such as in Britany in France the denitrification is also a very important processes permitting keeping groundwater bodies in quite good chemical status while intense agriculture activities, such as pig

Two challenges will be tackled in this report, identification of denitrification processes in groundwater and mapping this information at large scale.

2 CONCEPTS OF DENITRIFICATION IN GROUNDWATER

The denitrification phenomenon is complex with different interrelationships between rivers, wetlands, the unsaturated zone and the saturated zone as shown in the illustration below and is characterised by:

- parameters related to the transfer with the flow rate in the aquifers, the rate of diffusion and degradation of nitrate ;
- indicators such as water levels in the wells or boreholes; and concentrations in the groundwater of nitrate, iron, sulphates, dissolved oxygen in groundwater;
- oxidation-reduction conditions: groundwater confinement, presence of denitrifying bacteria, presence of organic matter;
- favourable mineralogical contexts with the presence of pyrite (sulphur) and biotite.
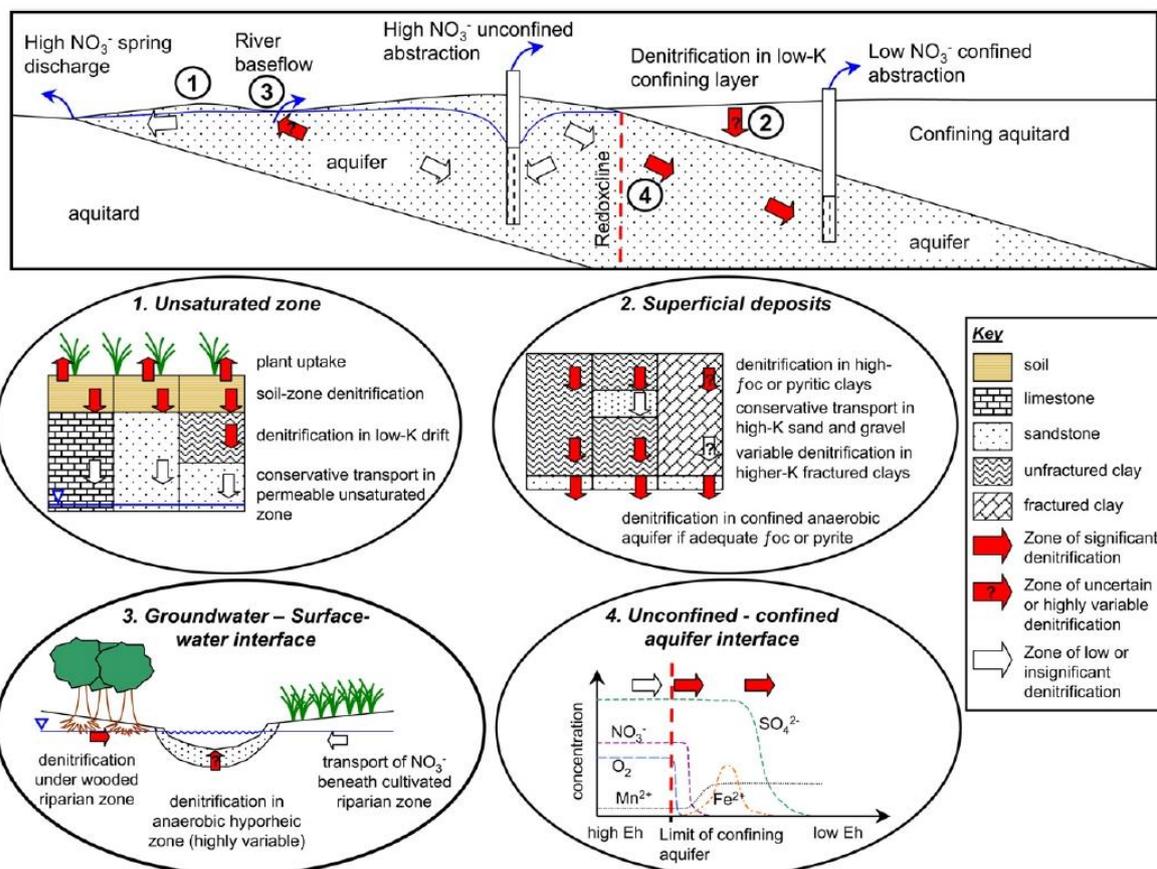
Figure 1: Conceptual model of denitrification occurrence in the subsurface environment. (Rivett et al., 2008).

2.1 Nitrogen cycle

Nitrogen (N) is a chemical element present in all living organisms. It is a constituent of many biomolecules such as proteins, DNA and chlorophyll. In addition to being present in the atmosphere in gaseous form (dinitrogen N_2 and nitrous oxide N_2O), nitrogen is present in the environment in various forms, both inorganic (mainly ammonium NH_4, nitrate NO_3 and nitrite NO_2) and organic (in living

organisms, humus and the various degradation products of organic matter). Nitrogen passes from one form to another through many processes often linked to the activity of micro-organisms that use it for their energy needs and growth.

Nitrogen is very abundant in the atmosphere in the form of N_2 (78%); it can be assimilated by certain bacteria during the fixation process. However, atmospheric nitrogen is not readily available to living organisms, and is therefore often a limiting factor in primary production. Also, in cultivated areas, a large amount of nitrogen is provided by chemical fertilizers in mineral form and by soil improvers in organic form. In organic form, nitrogen is decomposed by soil micro-organisms; it is transformed into NH4 by the process of mineralization. From its NH_4 form, it is transformed into nitrite and then into nitrate by certain bacteria in oxygenated condition, this is the nitrification process. Nitrogen in the form of nitrate NO_3 is very mobile in soils due to its negative charge which opposes the negative charge of the clay-humus complex in the soil. It is therefore easily carried away by leaching and can thus reach groundwater and then surface water. Finally, nitrogen in nitrate form (in soils and/or groundwater) can also return to the atmosphere as N_2O and N_2 during the denitrification process.
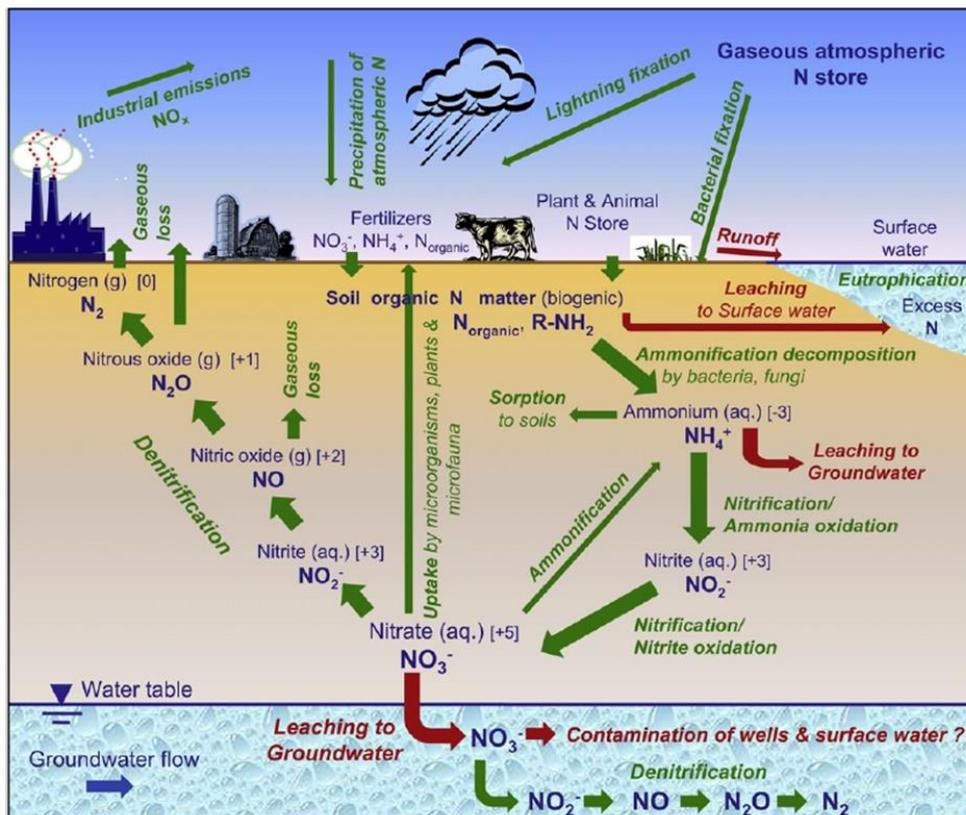

Figure 2: The nitrogen cycle and its influence upon the water environment (Rivett et al., 2008)

2.2   Denitrification principles

Under the term denitrification were grouped the natural biological or chemical processes that lead to the consumption of nitrate. Denitrification is the reduction of nitrate to a gaseous species, it involves an exchange of electrons and for this reason it must be associated with an oxidation reaction.

Denitrification organisms are ubiquitous in surface waters, soils and groundwater. They are facultative anaerobic (capable of aerobic and anaerobic respiration) heterotrophic (requiring organic matter) bacteria that obtain their energy and carbon from the oxidation of organic matter (Rivett et al., 2008).

This phenomenon is permanent in groundwater and in some permanently saturated wetlands, and temporary in soils and wetlands alternating oxidation/reduction. Thus, the drainage of wetlands leads to a decrease in denitrification potential. In aquifers, the site of complex biological denitrification reactions is located in the upper part of the reducing zone.

The first mechanism of denitrification is the reduction of nitrate coupled to the oxidation of the organic matter (CH_2O).

$$5\,CH_2O + 4\,NO_3^- + 4\,H^+ \rightarrow 2\,N_2 + 5\,CO_2 + 7\,H_2O$$
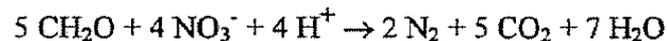
This processes is linked to heterotrophic bacteria. This the most discussed/presented process as it mainly exist in the subsurface (sediments, wetlands, …) and soils. However another denitrification process exists, more common in groundwater, due to denitrification coupled to the oxidation of sulphide minerals. This reactions can be described as:

$$5\,FeS_2 + 14\,NO_3^- + 4\,H^+ \rightarrow 7\,N_2 + 10\,SO_4^{2-} + 5\,Fe^{2+} + 2\,H_2O$$

The reaction with sulphates is possible due to the action of an autotrophic bacteria: *Thiobacillus denitrificans*.

In nature, nitrate is the most oxidized form of the nitrogen cycle. It is reduced in the environment by two distinct biological pathways that occur in anoxia or anaerobia. The first pathway, assimilative, leads to the formation of ammonium, which is the main chemical form of nitrogen that can be directly assimilated by living organisms. The second pathway, dissimilative, uses nitrate as a respiratory oxidant and produces energy in the form of a membrane potential that can be converted into ATP. In both cases, the key step in the process is the reduction of nitrate (NO_3) to nitrite (NO_2) catalysed by an enzyme known as nitrate reductase.

The assimilation pathway is mainly known in plants, algae and fungi. At the bacterial level, it has been demonstrated in cyanobacteria.
For the dissimilatory pathway, the reduction of nitrate to nitrite is the common step of 2 different processes. In its narrowest sense, denitrification refers to the disappearance of nitrate by respiration. The end product of the reduction is molecular nitrogen N2. Two gaseous reduced intermediate products are also present in the cycle of reducing nitrite to molecular nitrogen: nitric oxide or nitrogen monoxide (NO) and nitrous oxide (N_2O). All steps in the reduction of nitrate to molecular nitrogen are energy-producing.
The second process is known as dissimilatory nitrate reduction to ammonia. The latter is not necessarily assimilated and can be released as NH_3 gas.

Different processes may take place at the same time as denitrification, such as dilution/water mixing, which may mask the impact of denitrification on nitrate concentration in groundwater.

2.3 Elements contributing to denitrification processes

COD: Dissolved Organic Carbon

Organic carbon is one of the most important factors in heterotrophic denitrification. It plays a direct role as substratum (source of energy and carbon) for bacteria and non-directly (in soils) as aerobic micro-organisms are consuming C leading to the decrease of oxygen content in the media. Some studies were showing that the Thiobacillus denitrificans can use as source of energy the following different sulphur compounds: sulphur, sulphides, pyrites, iron sulphide and thiosulphate.

Presence *of pyrite and biotite* in the environment, in the aquifer formation.

In various geological context widely represented in Europe, basement aquifers (granite, schist, micaschists, gneiss), limestone aquifers, alluvial aquifers, the key element of denitrification is the presence of an electron donor: pyrite or organic matter. Pyrite is a common mineral. The organic matter can be part of the geological formation or can be contributed by water together with nitrates.

Presence of *nitrogenous substratum* (NO_3, NO_2, NO, N_2O) as final electron accepting

The main oxidoreduction in natural water is the organic matter degradation by bacteria and other mrcroorganisms using the organic matter for their respiration. When the oxygen will be entirely consumed, the bacteria will use other oxidizer such as nitrate, manganese, iron, sulphates.
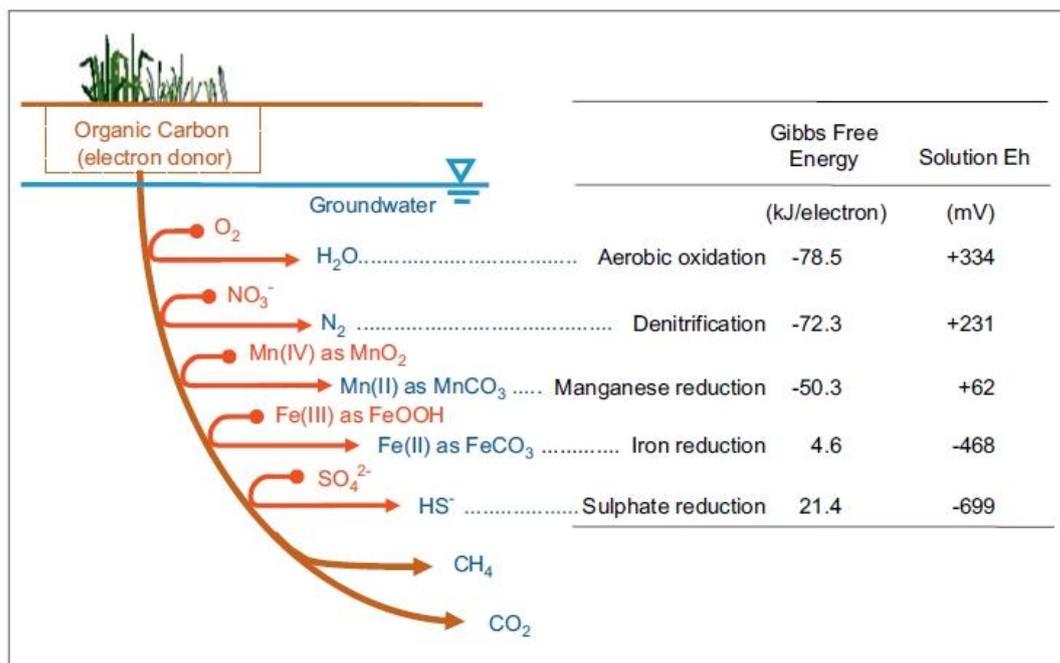
Figure 3: Thermodynamic sequence of electron acceptors for oxidation of organic carbon in the saturated zone (extract from Rivett et al., 2008, adapted from Korom, 1992).

Dissolved Oxygen

The partial pressure of oxygen is fundamental in the syntheses and regulation of the denitrification. However it is difficult to evaluate the threshold value above which the denitrification process may not occur. In the soils, the denitrification depends on the degree of humidity which affect the aeration and anoxia level. Denitrifying activity increase with the part of the porosity occupied by water. Humidity variations in soils, linked to rainfall events leads to pulses functioning.

pH

The optimal pH for denitrification depends mainly on the bacteria involved in the denitrification process. A wide range of pH allowed denitrification however pH between 7 and 8 seems optimum.

Temperature

Denitrification is possible in between 5°C and 60°C. An exponential increase of the denitrification cinetic is observed in between 5°C and 30°C. Higher than 30°C, a few variation is observed. The influence of temperature is also depending on bacteria involved in the denitrification process.

2.4 Scale changes in denitrification studies: from microscopic to macroscopic

Denitrification studies concerned various scales, from microscopic to aquifer (figure 4).
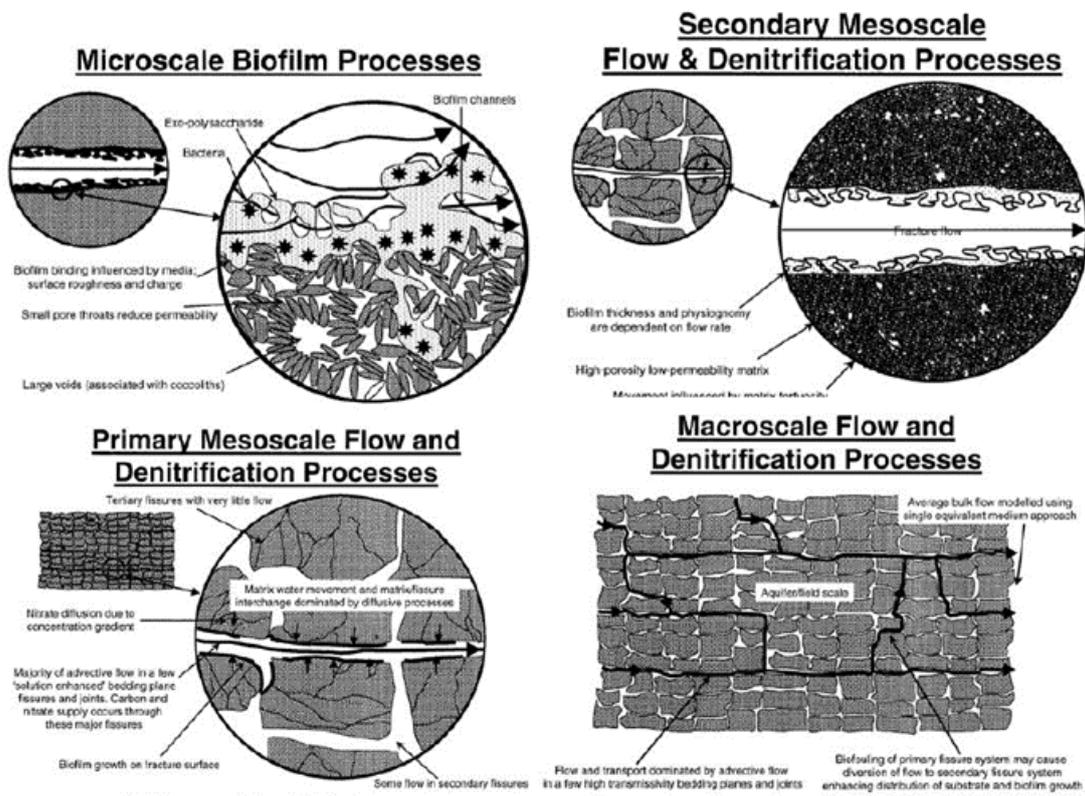
Figure 4 : Definition of representatives scales (from Tompkins et al., 2001)

Denitrification varies in space and also in time so in order to propose de EU scale representation it is necessary to make some scientific assumption from biogeochemical understanding to borehole/well and up to aquifer/groundwater body.

2.5 References

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3   CASE STUDIES

3.1   CASE STUDY ENGLAND

3.1.1   Denitrification concept considered

There have been a number of studies of denitrification in groundwater in England at the local and regional scale, as reviewed by Rivett et al. (2007) and Stuart (2018). However, national scale assessments are required as they can provide a screening tool to assess the likelihood of denitrification for different hydrogeological settings in the context of potentially polluting activities. Whilst detailed statistical methods (Blicher-Mathiesen et al., 2014; Højberg et al., 2017; Koch et al., 2019; Wilson et al., 2020) have been developed for these national scale assessments, these can be challenging to apply where borehole metadata are limited. In England, limitations include lack of information on borehole construction (depth, aquifer penetrated, screened section) and variation in sampling frequency and regime. In light of this, there is a need for a simplified approach to mapping **denitrification potential at the national scale** which uses semi-quantitative methods without the need for further extensive data collection.

Here we report the work of Stuart et al. (2018), which uses a semi-quantitative scoring method to map denitrification potential at the national scale in England. This research was also briefly reported in D5.2.

3.1.2   Description of the study carried out and outputs

3.1.2.1   Study area and overarching approach

This study was undertaken at the national scale in England (Figure 5). In England based on previous local and regional scale literature reviews (Stuart, 2018), two conceptual models of where denitrification potential may be significant have been identified: (1) where aquifers are confined by low permeability bedrock formations, and (2) where aquifers are confined by low permeability quaternary deposits. These conceptual models are shown in Figure 6.

The overarching approach used in this study is as follows. First, the location and geometry of aquifers are mapped where confined by either low permeability bedrock or quaternary deposits. Each confined aquifer zone was then assigned both a redox and a confidence score based on qualitative assessment of key indicator species in national databases of groundwater quality held by the environmental regulator for England.   Quantitative redox scores were then derived for a subset of individual monitoring points with sufficient parameters measured. Finally, the quantitative monitoring point scoring was overlain on the qualitative aquifer-level scoring as combined map product for use by environmental regulators. Herein we present the methodology in detail.
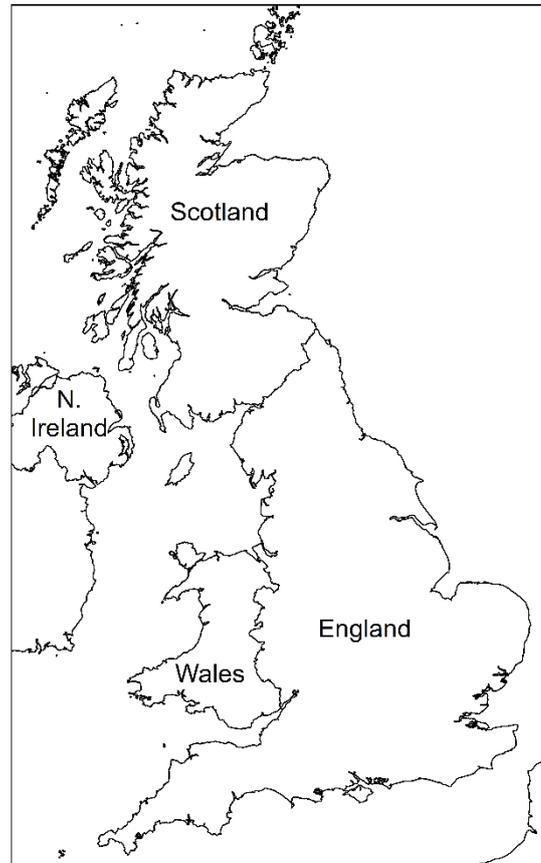
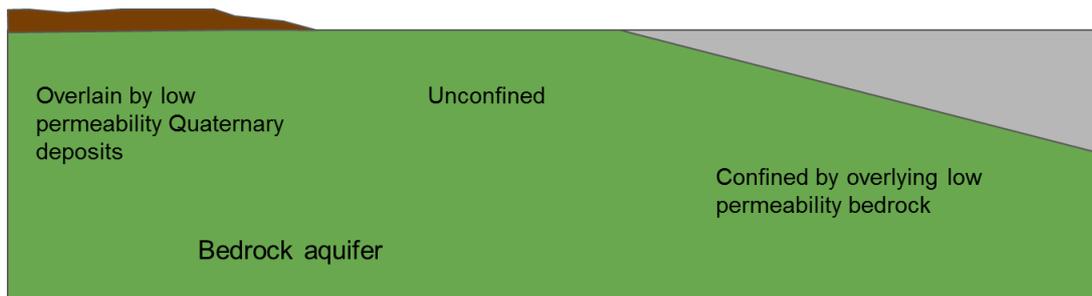Figure 5 Location of England in the United Kingdom

Figure 6 Conceptual model of aquifer settings where denitrification may occur in England

3.1.2.2 Mapping confined aquifers

Aquifers confined by bedrock formations were mapped using the BGS 3D geological model of Great Britain (Mathers et al., 2014). Aquifers were represented by the surface projection of their subcrop (below surface extent) with a depth cut-off of 400 m below the surface defining the base of the usable aquifer. This depth is consistent with other approaches to defining the base of aquifers such as guidance for EU Water Framework Directive implementation by the UK Technical Advisory Group (2012).

Polygons were constructed from the limit of subcrop (subcrop/outcrop boundary) and the point where the horizon top dips below the Terrain minus 400m surface. A triangulated surface is fitted to key borehole markers using discrete smooth interpolation to derive an unfaulted surface. A polyline is then created at the intersection between the geological surface and the Terrain minus 400m surface. Finally, a polygon is created between the outcrop/subcrop line and the intersection line. An example of the triangulated surface for the subcrop of the Great Oolite is shown in Figure 7.

Aquifers confined by low permeability quaternary deposits were mapped using the recharge classification of Griffiths et al. (2011). Griffiths et al. (2011) divide the quaternary into a series of domains based on recharge attenuation. The two least permeable classes LL (predominantly till) and LM (lacustrine deposits and peat) were used to delineate areas where bedrock aquifers are likely to be confined by low permeability quaternary deposits. This is consistent with previous work used to delineate areas not receiving nitrate in recharge by Ascott et al. (2015); Wang et al. (2012).
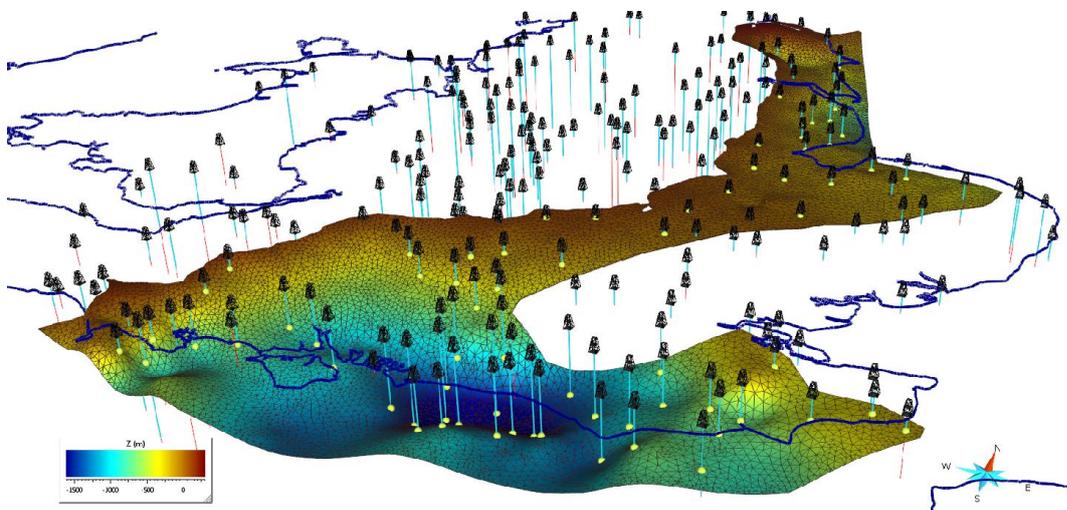

Figure 7 Fitting of triangulated surface for the subcrop of the Jurassic Great Oolite Group

3.1.2.3 Qualitative scoring of confined aquifers

To derive qualitative scores for each confined aquifer, a bespoke set of thresholds for classification of the spectrum of low redox conditions was developed as shown in Figure 8. These thresholds were derived from the approach of McMahon and Chapelle (2008) and publications summarised by Stuart (2018) which show that denitrification in the three main aquifers of England consistently occurs when DO <0.4 mg/L, NO_3 generally <1, Fe >100 µg/L Mn>4 µg/L.

Groundwater quality data from 4,291 boreholes were extracted from the national environmental regulator databases. Each borehole was attributed to an aquifer (either unconfined, confined by bedrock or confined by low permeability quaternary deposits). A temporal average of each indicator concentration value for each point was taken for the whole data period. For each confined aquifer zone, the data for both the unconfined and confined zones were overlaid on the confined zone polygon to determine which threshold values would provide sufficient discrimination of potential redox conditions within the data. The distribution of concentrations in aquifers with confirmed low redox confined zone water quality from the literature articles summarised in Stuart (2018) which do not depend on Environment Agency monitoring data were primarily used to inform this assessment. An average threshold value was derived for each indicator as shown in Table 1.

Figure 8 Low-redox thresholds used for analysis of groundwater monitoring data

Group	Indicator parameter	Thresholds used in this method	McMahon and Chapelle, 2008
N-species	TON (mg/L)	≤1	≤0.5
	NO_3-N(mg/L)	≤1	≤0.5
	NO_2-N (mg/L)	≥0.1	
	NH_4-N (mg/L)	≥0.3	
Trace metals	Fe total (µg/L)	≥500	
	Fe dissolved (µg/L)	≥100	≥100
	Mn total (µg/L)	≥500	
	Mn dissolved (µg/L)	≥100	≥50
	Ni total (µg/L)	≥10	
	Ni dissolved (µg/L)	≥10	
O and S species	DO (mg/L)	≤1	≤0.5
	DO (%)	≤10	
	SO_4 total (mg/L)	≤1	
	SO_4 dissolved (mg/L)	≤0.5	≤0.5
	S (mg/L)	≥0.02	
Doc and pH	pH insitu	NA	
	pH lab	NA	
	DOC (mg/L)	≥3	

Each confined zone polygon was attributed a low redox score, confidence score, and final potential score as shown in Table 2. For each parameter in Table 1, the patterns of concentrations were evaluated visually using data points with values meeting the threshold criteria in Table 1 separately coloured and plotted on the confined and unconfined zones for each aquifer. For each parameter a low redox score was assessed as Yes, No, Possibly and Insufficient data, and a combined assessment for low redox as Yes or No was subsequently assigned for each confined zone polygon.

For each confined zone an assessment of the confidence in low redox score was derived using monitoring point coverage (Table 2). For aquifers confined by bedrock, the confidence indicator was derived by comparing the total area of the zone with the area in the zone covered by monitoring points manually calculated as a concave hull. For aquifers confined by quaternary deposits, the complexity of the quaternary deposits meant it was not possible to use this approach and so a qualitative visual estimate of coverage was used instead (High, Medium or Low). For each confined zone polygon a final denitrification potential score was derived based on both the low redox score and the confidence score.

Figure 9 Denitrification potential scoring in confined aquifers from combination of monitoring data and confidence from aquifer coverage

Low redox in confined zone supported by monitoring data	Confidence from coverage	Potential
Yes	High	High
Yes	Medium	High
No	High	Low
No	Medium	Low
Yes	Low	Not classified (NC)
No	Low	Not classified (NC)

3.1.2.4 Quantitative scoring of monitoring points

The methodology for qualitative scoring of aquifers detailed in section 3.1.2.3 provides a simple approach to assessing the likely potential for denitrification to occur at the aquifer scale. There is likely to be significant variability in denitrification potential within a given aquifer confined zone. As a result there is a need for a more detailed quantitative evaluation of the denitrification potential of individual monitoring points where data are of suitable quality. Selected indicators were used to assess denitrification potential for individual site data (Table 3) based on the polygon-level assessments used for the confined zones. Here we used TON <1 mg/L, NH4>0.3 mg/L, Fe_dis >100 µg/L and Mn_dis >100 µg/L. To allow for missing data the number of indicator measurements at each site was included in the assessment. Only sites with measurements for all four indicators meeting the criteria were assessed as having High denitrification potential. Sites with 3 indicators meeting the criteria were classed as Medium. All sites with 2 or fewer indicators were classed as Not classified NC. Sites where aquifers are unconfined were included to potentially allow sites in this zone where autotrophic denitrification was occurring to be identified.

Figure 10 Denitrification potential confidence from monitoring data for individual points

No of indicators with measurement	Number of indicator values meeting threshold	Confidence
4	4	High
4	3	Medium
3	3	Medium
4	2 or fewer	Low
3	2 or fewer	Low
2 or fewer	-	Not classified (NC)

3.1.2.5   Development of map products

For each aquifer, shapefiles were developed which integrate the three layers developed in this methodology: (1) Denitrification potential of aquifer zones confined by bedrock, (2) denitrification potential of aquifer zone confined by low permeability quaternary deposits, (3) denitrification potential of individual monitoring points. These were combined into a map product using ArcGIS ArcMap where individual layers can be switched on depending on the context. For brevity, here we report the map product for the Chalk, which is the most important aquifer in England. The reader is referred to Stuart et al. (2018) for details of the combined map product for other confined aquifers.

3.1.2.6   Results

Table 4 shows the low redox score, confidence score and derived final denitrification potential scores for aquifer zones confined by bedrock or low permeability quaternary deposits. The confined zones of the Palaeogene, Chalk, Upper and Lower Greensand, Corallian, Oolite, Permo-Triassic sandstones and the Carboniferous have high denitrification potential with confidence provided by a good coverage of monitoring data. For the remaining bedrock aquifers with defined confined zones, Lias, Zechstein and Dinantian, monitoring data does not support the presence of broad scale denitrification potential. Particularly for the Zechstein, this may be an artefact of data coverage, so confidence is low and this has not been classified. Other aquifer groups (Crag, Palaeogene, Lower Cretaceous, Mercia Mudstone) with monitoring data which suggests denitrification potential but do not have confined zones defined in this research have not been included.

For aquifers confined by low permeability quaternary deposits the picture is different. As shown in Table 4 aquifers in areas of Crag, Chalk, Permo-Triassic sandstones, Zechstein and the Carboniferous confined by low permeability quaternary deposits have denitrification potentials confirmed by a good coverage of monitoring data. Aquifers with medium confidence of denitrification potential are also shown in red. Monitoring data for the Palaeogene, Upper and Lower Greensand, Oolite and Older rocks do not confirm the presence of denitrification at the broad scale. Areas with low confidence in the assessment due to insufficient monitoring data are shown in grey, the Corallian, Lias and Dinantian.

Figure 11 Denitrification potential for subcrop bedrock aquifers and aquifers confined by low permeability quaternary deposits

Aquifer group	Denitrification potential in subcrop bedrock				Denitrification potential in outcrop overlain by low permeability quaternary deposits			
	Subcrop polygon defined	Low redox in confined zone supported by monitoring data	Confidence from coverage	Potential	Outcrop with low permeability quaternary deposits	Low redox below quaternary supported by monitoring data	Confidence from coverage	Potential
Crag	No	NA	Low	NC	Yes	Yes	High	High
Palaeogene	No	Yes	Medium	High	Yes	No	Medium	Low
Chalk	Yes	Yes	High	High	Yes	Yes	High	High
Upper Greensand	Yes	Yes	High	High	Yes	No	Medium	Low
Lower Greensand	Yes	Yes	High	High	Yes	No	Medium	Low
Lower Cretaceous	No	Yes	Medium	High	No	NA	None	NC
Corallian	Yes	Yes	High	High	Yes	No	Low	NC
Oolite	Yes	Yes	High	High	Yes	No	Medium	Low
Lias	Yes	No	Low	NC	Yes	No	Low	NC
Permo-Triassic	Yes	Yes	High	High	Yes	Yes	High	High
Zechstein (Mag Lmst)	Yes	No	Medium	Low	Yes	Yes	High	High
Carboniferous	Yes	Yes	High	High	Yes	Yes	Medium	High
Dinantian (Lower Carb)	Yes	No	Low	NC	Yes	Yes	Low	NC
Devonian	No	NA	Low	NC	No	NA	None	NC
Older	No	NA	Low	NC	Yes	No	Medium	Low

The resulting denitrification potential for individual monitoring points (covering both confined and unconfined aquifer settings) using the scoring approach in Table 3 are summarised in Table 5. The majority of sites are shown to have low potential with about 14% having High or Medium potential.

Figure 12 Summary of individual monitoring point denitrification potential

No of sites	Denitrification potential
92	High
352	Medium
2424	Low
213	Not classified
3081	

Figure 8 shows an example of the combined map product for the Chalk. Individual monitoring points with high and medium denitrification potential map well to the areas of subcrop and low-permeability quaternary deposits.
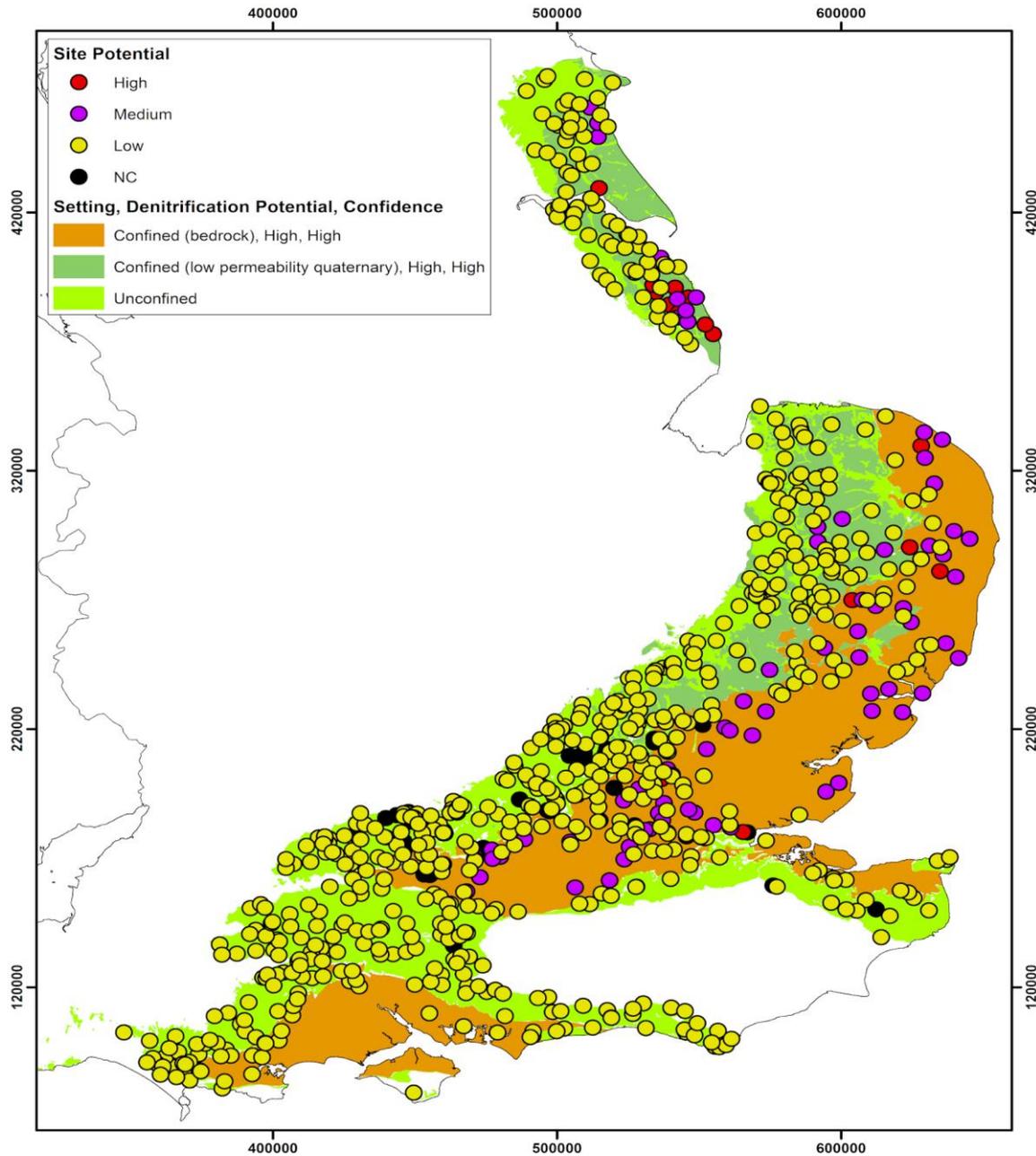

Figure 13 Combined map of denitrification potential for the Chalk

3.1.2.7 Evaluation of the approach used in this study

The outputs developed in this study provide useful information on the 3D nature of the subsurface, in particular the location and geometry of confined aquifers. The overview at the aquifer scale of the potential for denitrification to occur, in addition to presentation of individual monitoring points, can be used as supporting lines of evidence in assessing the risk of nitrate impact on groundwater quality in England for example as part of the groundwater Nitrate Vulnerable Zones designation process.

The approach developed is advantageous as it can be applied using national groundwater quality databases and does not require detailed information on groundwater flow, depth of sampling and other metadata. As a result, this approach could be applied in areas where there are groundwater quality monitoring databases but limited information from which to establish which part of the aquifer is being sampled.

There are a number of limitations to the approach developed. The maps were derived from 1:625,000 scale geological mapping, with further aggregation of formations resulting in some multi-layered aquifers being treated as single units. Consequently, the maps cannot be used at the local or site scale. The choice of indicator species used was focused towards heterotrophic denitrification. Other nitrate attenuation processes (e.g. autotrophic denitrification and dissimilatory nitrate reduction to ammonia (DNRA)) are likely to result in different patterns of indicator species.

The methodology developed in this study provides qualitative indications of denitrification potential at the scale of the aquifer (where confined by bedrock or quaternary deposits), with a quantitative assessment of data from individual monitoring points overlain to aid interpretation. The approach does not give any indication of the depth at which denitrification is occurring, or the rate of nitrate removal.

3.1.3 References

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3.2 CASE STUDY FRANCE

3.2.1 Denitrification concept considered

Denitrification potential at national scale

3.2.2 Description of the study (studies) carried out and outputs

2 methods (approaches) were used in France at national scale:
- a decision tree
- statistical analysis : k-means classification

Determination of denitrification potential -> from monitoring points to hydrogeological unit

A simplified tree decision adapted from Hinkle and Tesoriero (2014) to French data available in ADES database.
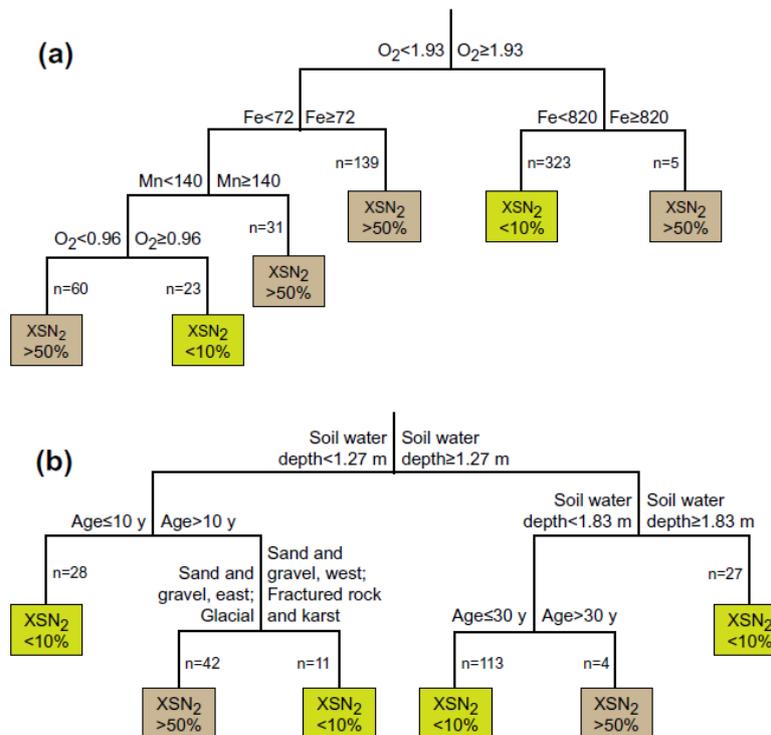

Figure 14 : Classification tree models for %XSN$_2$ [percent of NO$_3$ occurring as XSN2] for groundwater ambient-monitoring sites (extract from Hinkle and Teseriero, 2014).
(a) Explanatory classification tree model. Explanatory variables are measured redox indicator species (field O2; Mn and Fe). Accuracy on building data subset: 87% (n = 581); testing subset, 87% (n = 291).
(b) Predictive classification tree model. Predictive variables are apparent age, predicted depth to seasonally high water table in soil horizon (from Wolock, 1997), and principal aquifer group. Accuracy on building data subset: 82% (n = 225); testing subset, 79% (n = 113). [Number of sites from the building dataset on each tree node are indicated with ''n=''. ''Age'' = apparent age; ''Soil water depth'' = predicted depth to seasonally high water table in soil horizon; O$_2$: mg/L; Mn, Fe: µg/L. In (a) n = 872 because 5 of the 877 groundwater ambient-monitoring sites did not have O$_2$ data. In (b), n = 338

because 8 of the 346 age-dated groundwater ambient-monitoring sites did not have data for predicted depth to seasonally high water table in soil horizon.]

For the territory of metropolitan France, a recent studies exist at French national level to assess and characterize the pressure-impact of nitrate use (Gourcy et al, 2017). This work was difficult to achieve as there is no geological and hydrogeological and agro-pedo-climatic homogeneity at the French metropolitan territory and Corsica.

As an illustration of this heterogeneity, below is the map of simplified hydrogeological formations at the French metropolitan territory. The map (Figure 1Figure 15) represent the first aquifers that can be affected by nitrate and pesticides pressures.
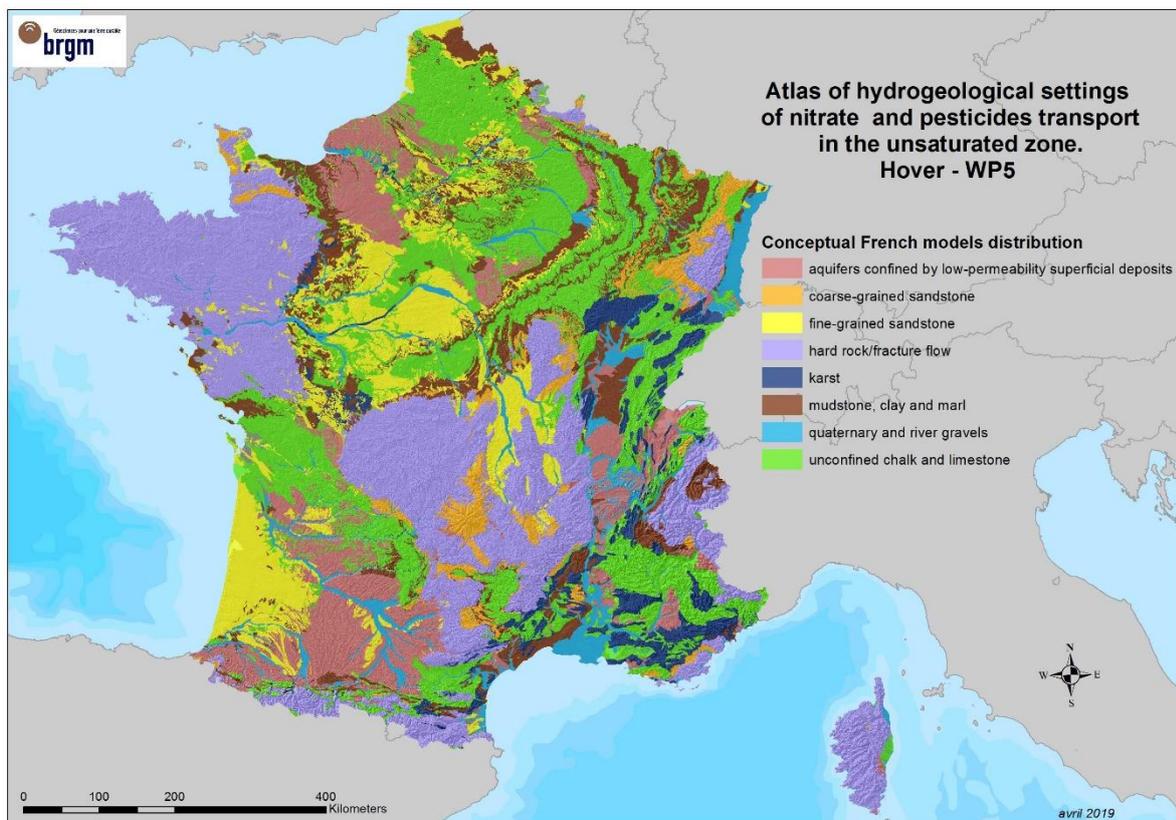

Figure 15: Main types of aquifer and no-aquifer formations identified as concerned by the nitrate and/or pesticides problematic in metropolitan France and Corsica.

In Gourcy et al. (2017), the method applied at the French metropolitan territory and Corsica for pressure-impact analysis of nitrate on groundwater is described. A classification tree method has been used, modified from Hinkle and Tesoriero, 2014. The following data has been taken into account: data extracted from the ADES database; physico-chemical parameters (dissolved oxygen content and redox potential); concentrations in elements sensitive to redox processes (Fe, Mn) and measured regularly in groundwater (Figure 16).
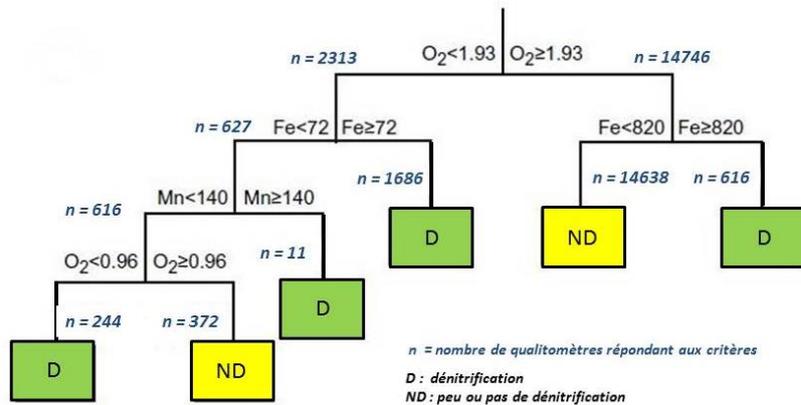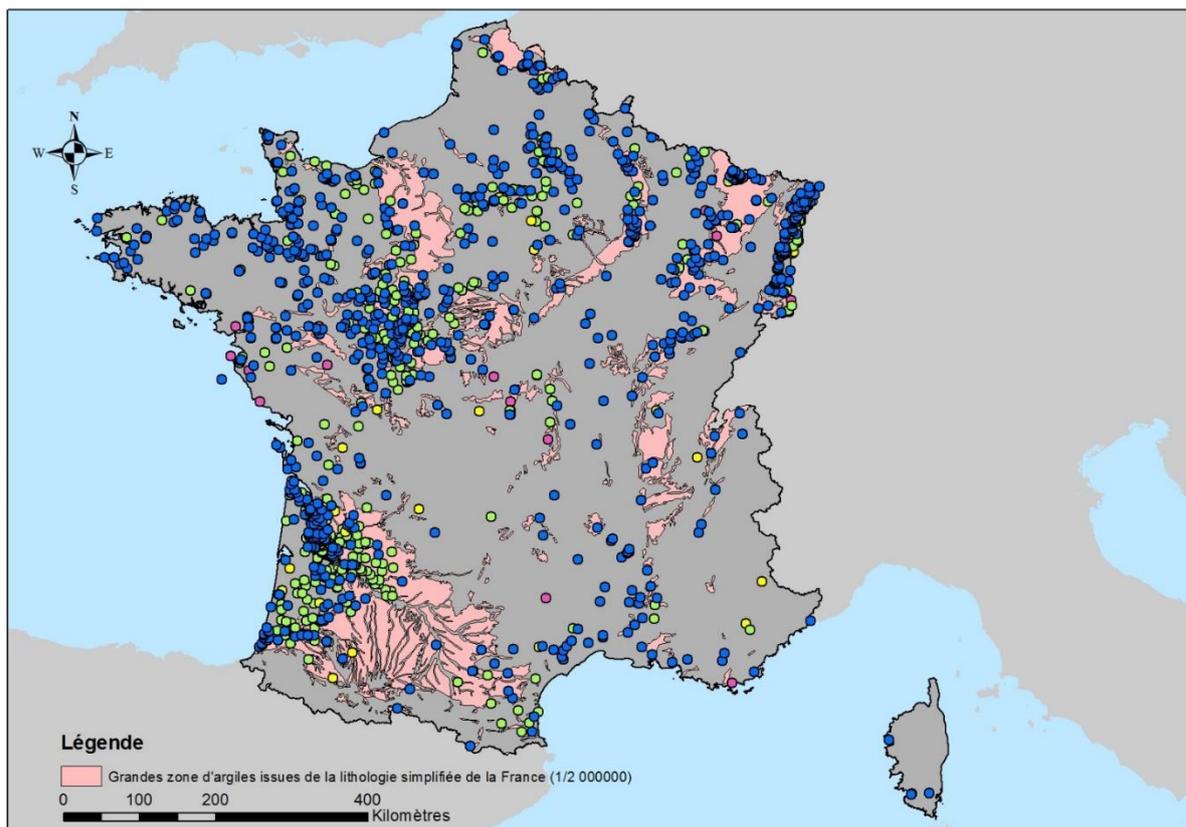
Figure 16: *Classification tree applied to all the quality measurements in 2015 (modified according to Hinkle and Tesoriero, 2014). The locations of four different types of samples that have indication for denitrification (the green D's) are plotted as D1 to D4 (extract from* Gourcy *et al, 2017).*

Légende

Grandes zone d'argiles issues de la lithologie simplifiée de la France (1/2 000000)

0   100   200   400
Kilomètres

● D1 : concentration en O2> ou = 2 mg/l
● D2 : concentrations en O2< 2 mg/l et en Fer > ou = 72 µg/l
● D3 : concentrations en O2< 2 mg/l ,en Fer < 72 µg/l, Mn > ou = 140 µg/l
● D4 : concentrations en O2< 2 mg/l ,en Fer < 72 µg/l, Mn > ou = 140 µg/l et O2< 1 mg/l

Figure 17: Location of points capturing potentially denitrified groundwater (from Gourcy et al., 2017). Points with no signs of denitrification are not shown on this map.

The results indicate 1532 water points likely to denitrify on the French metropolitan territory and Corsica (Figure 17). Their location is indicated by the map presented below. Areas with indications for denitrification include areas dominated by alluvial sands, clays and marls and marly limestones/chalk.

In order to develop the map of the groundwater denitrification potential areas of the metropolitan territory and Corsica, we used only the 1 529 boreholes and wells identified using the classification tree method. The main difficulty in this type of mapping is spatializing and aggregating point data at the scale of work units. One of the proposals made is to calculate the percentage of points likely to denitrify within each work unit (Figure 18).
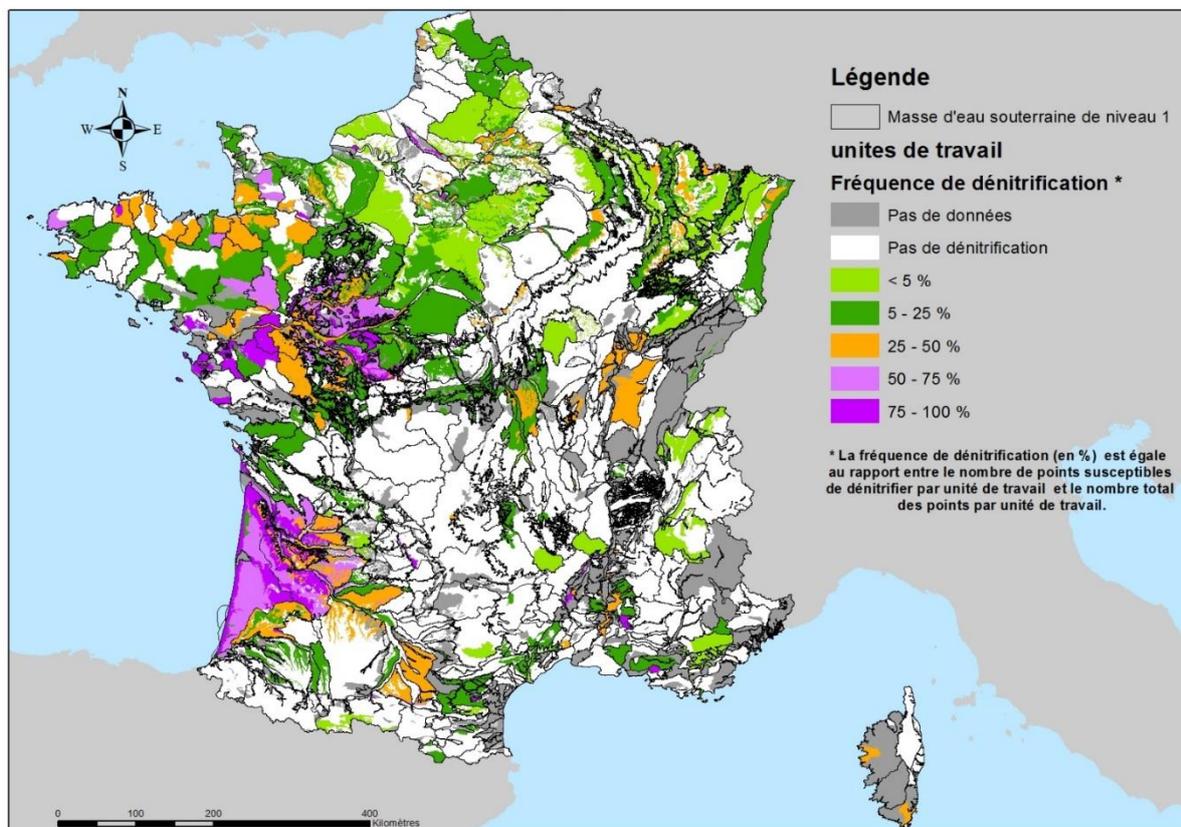

Figure 18: Percentage of denitrification potential per homogeneous hydrogeological unit (from Gourcy et al., 2017).

3.2.3 Test of the HOVER proposed method for the same area(s)

3.2.4 References

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Hinkle S.R., Tesoriero A.J., 2014. Nitrogen speciation and trends, and prediction of denitrification extent, in shallow US groundwater. Journal of Hydrology, 509, pp. 343-353.

3.3   CASE STUDY NETHERLANDS /FLANDERS

3.4   Introduction

3.4.1   *Monitoring networks and datasets*

The monitoring network that forms the basis for this study is the combined groundwater quality monitoring network of the provinces of Noord-Brabant and Limburg in the Netherlands, which was introduced in the Deliverable 5.2 of the HOVER project.

Figure 3.19 Monitoring wells available in the Dutch case study

For this current deliverable, the dataset was extended over the border with the adjacent Flanders province in Belgium, evaluating the data which is publicly available through the DOV-website (https://www.dov.vlaanderen.be/). The datasets of the Dutch provinces of Noord-Brabant and Limburg and the Belgium province of Flanders are used systematically for compliance and surveillance monitoring for the EU WFD. Compilation of the combined dataset was part of a combined effort with the GeoERA project RESOURCE under WP3 H3O-PLUS.

The Netherlands and adjacent Flanders are characterized by shallow water tables and unconsolidated deltaic deposits; the altitudes in the pilot area ranges between -5 and 50m above mean sea level. The South part of the Netherlands and the northern part of Flanders are along the largest producers of agricultural products worldwide, and are characterized by intensive livestock farming that yields high agricultural pressure on groundwater since the 1970's. The Dutch government introduced strict regulations of the application of manure and fertilizer since 1985 when the Dutch Manure Law was enacted. The EU Nitrates Directive of 2000 further strengthened the Dutch and Belgian laws, and action programs for reducing nitrate leaching to groundwater have been in place since. At the peak of the applications of nitrogen in 1985, nitrate concentrations in shallow groundwater easily reached 500 mg/l, but a clear trend reversal was demonstrated for dry agricultural areas on sand (Visser et al. 2007). Still, concerns grow over pesticide leaching and the new threats imposed by emerging contaminants such as antibiotics (Kivits et al. 2018).

3.4.2   The Dutch Sand-Meuse monitoring network

Starting in 1984 dedicated monitoring networks were setup to monitor the quality of groundwater. The National Monitoring Network (LMG) consists of about 100 observation wells in the pilot region. From 1992 onward, this network was complemented by another 120 wells of the Provincial Monitoring Networks (Broers 2002, Broers & van der Grift 2004). Together these networks are now incorporated in the Monitoring Network for the WFD in the Sand-Meuse region, which is the data that will be used for this pilot study. All mentioned networks consist of dedicated multi-level observation wells with standardized well completions and standard monitoring depths of 10, 15 and 25 m below surface level. The multi-level wells have screen lengths of 1 or 2 meters and a diameter of 2-inch that allows for sampling with submersible Grundfos pumps. The wells have all been sampled for $^3H/^3He$ during campaigns in 2001, 2008/2009 and recently in 2017/2018. Until 2009 only wells under agricultural lands and sandy soils were age dated, while in 2017/2018 this dataset was complemented including wells in wetter sandy areas, in areas with clayey soils and in urban areas and nature reserves (Kivits et al, 2019). Using $^3H/^3He$ age dating, information is obtained about saturated zone travel times and groundwater ages, which enables the data produced to be used for forensics of past land use inputs.

3.4.3   The Flemish Nitrate Monitoring Network

The Flemish Nitrate Monitoring network ('freatisch grondwatermeetnet') as set up in 2003 in order to improve understanding of the quality of the upper 50 m of groundwater and to test compliance against the EU Nitrates Directive and the EU Groundwater Directive. The 2100 monitoring wells in the network were specifically designed for this task and consist of multi-level observation wells (e.g. Snellings, et al. 2008). They are sampled twice a year or more often on a broad range of solutes including nitrate and pesticides. The network design is special as it intentionally placed observation well screens on both sides of the NO_3-Fe redox cline (Eppinger 2008). Thus, it enables a precise determination of the redox transition from nitrate containing water to iron-reduced water with no nitrate. The deepest screen is always placed in the Fe redox zone. A higher number of wells were installed in areas with higher risks of nitrate leaching towards deeper groundwater, thus enabling a better estimate of the exceedance frequency of nitrate thresholds in high risk zones. The network was extended with extra monitoring locations in nature reserves in 2007. The network has not been age dated, but the special design makes it very interesting to study the process of denitrification at the regional scale.

3.4.4   Aims of the work

For our common Dutch/Flemish pilot area, we aim:
1. to assess the spatial extent and importance of denitrification,
2. to evaluate the temporal and spatial patterns of nitrate and selected pesticides in relation to redox processes, and
3. to link advective travel times and time lags for nitrate and the pesticides.
4. Evaluate the redox decision tree with extra measurements of H_2S, CH_4 and N_2.

For the first aim we collected the available data and deduced the depth of denitrification, linking this to the geological formations in the subsoil. For the second aim, we analyse patterns of nitrate and sulfate and a selection of pesticides in relation to redox status of the groundwater. For the third aim, we link up with the results described in deliverable D5.3 where the advective time lags have been assessed and describe the contamination patterns in relation to both redox status and advective travel times. For the analysis of redox status, we applied an existing and using well established redox decision tree, which validity we test using extra data on gas compositions, namely H_2S, CH_4 and N_2.

3.5 Denitrification concept considered

3.5.1 General concept and data availability

Often, groundwater exhibits a typical redox sequence starting with oxygen-rich infiltration water and redox process consuming electron donors on the way through the (reactive) subsurface (Figure 1.2). Because water in recharge area ages with depth, this redox sequence can often be observed in concentration-depth profiles showing the redox sensitive solutes in water. The most distinguishable redox transition in groundwater under farmlands is the transition from water with substantial amounts of nitrate to water with substantial amounts of Fe (II); this transition in generally denoted as the NO_3/Fe redox cline (e.g. Postma et al. 1991, Zhang, 2009).
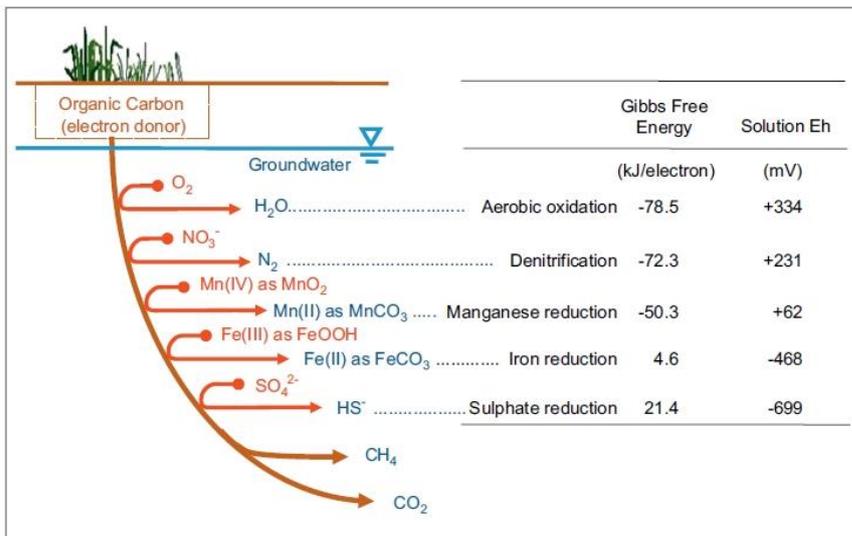

Figure 3.20 Thermodynamic sequence of electron acceptors for oxidation of organic carbon in the saturated zone (extract from Rivett et al., 2008, adapted from Korom, 1992).

In the Netherlands and Flanders, the depth and set-up of the groundwater quality monitoring networks allow for assessing these redox changes with depths, as multi-level wells are available (see Figure 3.21). Especially, the Flemish network is efficient, as it was designed having these redox transitions in mind. The Brabant and Limburg monitoring networks have the advantage that all monitoring screens have been age dated (which was reported in HOVER deliverable 5.3) and the Brabant networks has the additional advantage of a survey of gas compositions in 2017 and 2018 yielding measurements of the redox sensitive species N_2, H_2S and CH_4. We will use these data sources to realize the aims set for this chapter, assessing the depths of ongoing and complete denitrification and the linkages between contaminants and the redox status of the groundwater. Our dataset will show that for our pilot area, the depth of complete denitrification is relatively shallow.
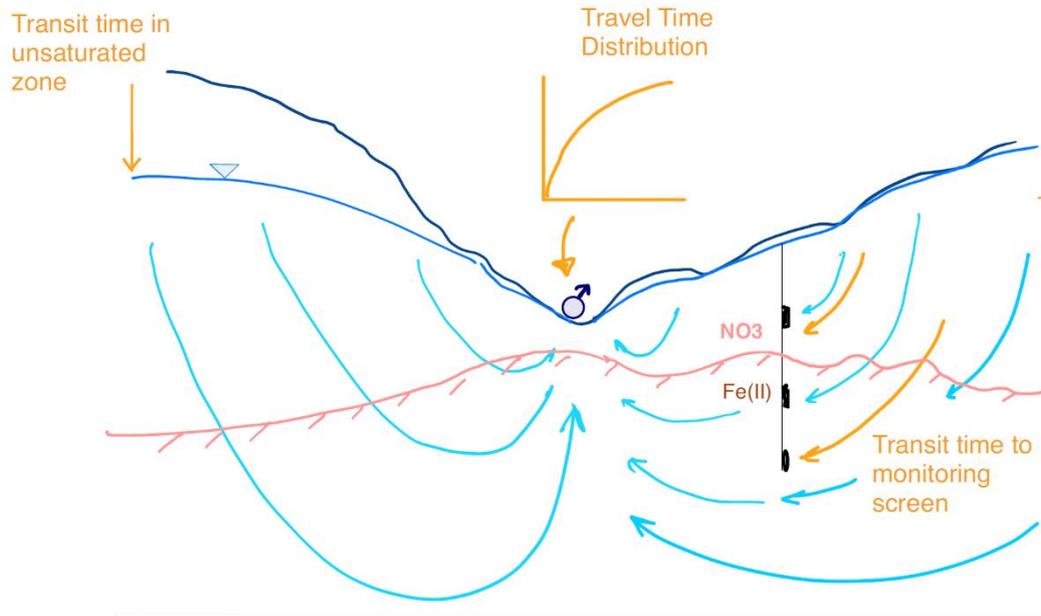
Figure 3.21 Conceptualization of groundwater flow, advective time lags and redox transformations. Multi-level wells allow for independent determination of the groundwater age - depth profiles and determination of redox transition with depth.

3.5.2   Linkage between advective time lags and denitrification

Information about travel times in the saturated and unsaturated zones is derived from age dating using $^{3}H/^{3}He$ (Visser et al. 2007; Visser et al. 2019). Unsaturated zone travel times are typically short due to the shallow depths of the water tables in the region. Age-depth profiles are available for different types of land use and are used to facilitate trend detection and assessment of chemical status for these land uses (Figure 3.22). The figure shows that there is a clear age-depth gradient for most areas in Brabant and Limburg, which means that older water from previous infiltration periods is found deeper than recently infiltrated water. This hampers the direct interpretation of redox transitions in the subsurface, as the solute inputs may have changed with time, as we know they did, influencing the concentrations and redox processes as well. (e.g. Broers 2004; Broers & van der Grift, 2004; Visser et al. 2007).
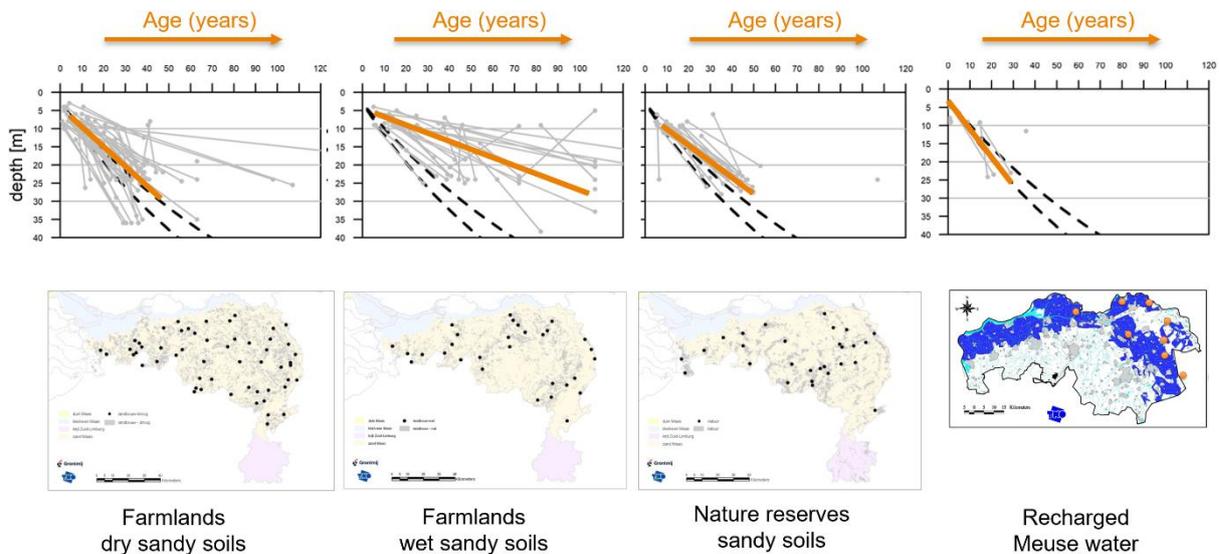
Figure 3.22 Age-depth profiles for different land use types in the pilot area. Grey lines connect shallower and deeper monitoring screens, visualizing the age-dept relation for the individual screens. The orange line suggests the median age-depth relation for the area type as a whole.

3.5.3   Redox classification tree

As most datasets do have a complete set of macro-chemistry and the main redox sensitive ions (O_2, NO_3, NO_2, Fe Mn, SO_4 and sometimes CH_4) we applied a classification tree using these redox sensitive species. The gases H_2S and N_2 are not typically measured but would give additional information that is not always available (see section 3.7 for details). The classification tree that we apply here is particularly useful for large datasets. Figure 3.23 shows the redox decision tree used to identify the redox class of groundwater samples. The classification is based on Graf Pannatier et al (2000), who created it for the Dutch National Monitoring network (LMG), but with some recent changes in order to make it more generally useful for multiple datasets.

The following data has been taken into account nitrate, chloride, iron, manganese, sulphate, oxygen and methane. Nitrate concentration is the first criterion used to access the redox level whereby a distinction is made between groundwater with a nitrate concentration higher or lower than 2 mg/l. If nitrate >2 mg/l, groundwater can either be classified as Mix, Mn-reduced, oxic/suboxic. Groundwater in the class 'Mix' contains both iron and nitrate above 2 mg/l. Mn-reduced groundwater contains manganese, for which a threshold of 0,5 mg/l is used to distinguish between oxic/suboxic water and Mn-reduced water. The division between oxic and sub-oxic water is then made using a threshold of 2 mg/l O_2, but we often denote the class to be oxic/suboxic as the O_2 measurements are not always reliable as they need to be measured in the field with a well-calibrated oxygen meter. For groundwater with nitrate concentrations lower than 2 mg/l, a distinction is then made between fresh and brackish groundwater (threshold Cl=200 mg/l), because sulphate concentrations are naturally higher in brackish and salt groundwater (e.g. Yu et al. 2018). Sulphate, iron, manganese and methane are the following parameters used to identify the redox level in groundwater. 'Sulfur-reduced' groundwater contains less than 5 mg/l sulphate and less than 1 mg/l methane. If methane is higher, groundwater is classified as 'Methanogenic'. If groundwater contains sulphate, groundwater can be classified as 'sulfur-reduced/methanogenic', 'Fe-reduced' or 'Mn-reduced'. The distinction between 'Sulfur-reduced/methanogenic' and 'Fe-reduced' is made on the basis of methane concentration

when available. The classification tree is made operational in the Groundwater Quality Viewer of the Netherlands ('Grondwaterkwaliteit in Beeld'; https://www.grondwatertools.nl/gwatlas/?language=en).

This classification scheme has recently also been implemented in the GeoERA version of the database that will be used within GeoERA project RESOURCE WP3 to map redox in the groundwater viewer for the transboundary Roer Valley aquifer. For HOVER, we will use it to identify depth and locations where denitrification is happening.

```
                                    NO₃ > 2 mg/l

                Fe < 0.5 mg/l                                    Cl < 200 mg/l

        Mn < 0.5 mg/l (d)      Mix              SO₄ > 5 mg/l                    SO₄F > -0.2

    O₂ > 2 mg/l (a)   Mn-reduced      Fe < 0.5 mg/l      CH₄ < 1 mg/l (b)    Fe < 0.5 mg/l    CH₄ < 1 mg/l (b)

  Oxic   Suboxic   Mn > 0.5 mg/l (f)   CH₄ < 1 mg/l (c)  Sulfur-reduced  Methanogenic  Mn > 0.5 mg/l (e)  Fe-reduced  Sulfur-reduced  Methanogenic

        Mn-reduced  CH₄ < 1 mg/l (c)  Fe-reduced  Sulfur-reduced    Mn-reduced  Fe-reduced
                                                  methanogenic

                Fe-reduced  Sulfur-reduced
                            methanogenic
```
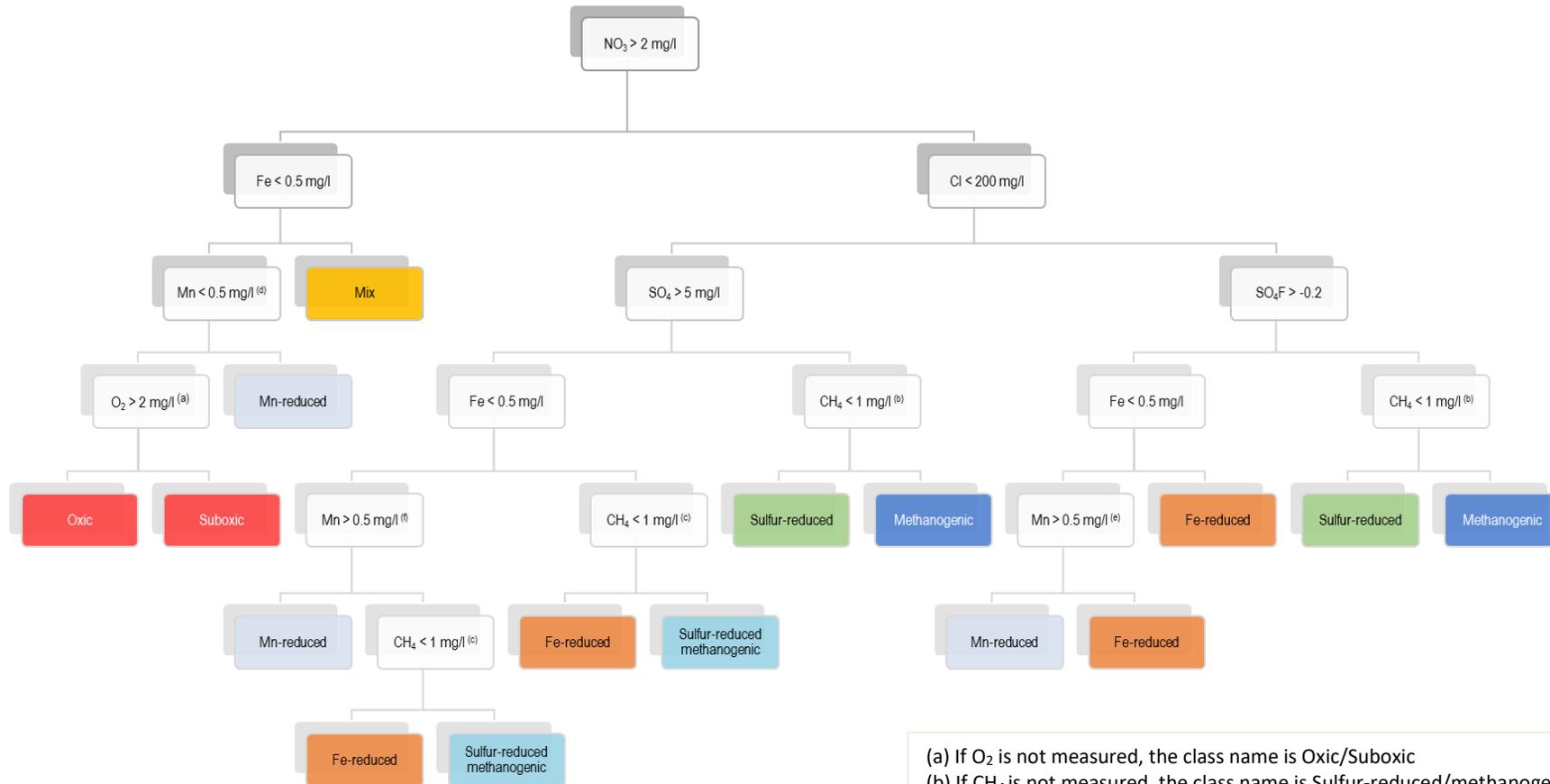
(a) If O_2 is not measured, the class name is Oxic/Suboxic
(b) If CH_4 is not measured, the class name is Sulfur-reduced/methanogenic
(c) If CH_4 is not measured, the class name is Fe-reduced
(d) If is not measured, the class name is Oxid of Suboxic (depends on O_2)
(e) If Mn is not measured, the class name is Fe-reduced

Figure 3.23 Redox classification tree. Diversion to left = "yes", diversion to right = "no"

3.5.4   Evaluation of the classification tree

In this section, we make use of the data that was collected within the WFD monitoring network for the Sand-Meuse groundwater body. A validation of the dataset for the purpose of redox classification is provided in Appendix A of this deliverable (section 0). We applied the classification tree of Figure 3.23 to this dataset, which helps to get an oversight of the concentration ranges in the redox classes that we defined.

Figure 3.24 shows the distribution of 6 redox influenced indicators for the 5 distinguished redox classes. Clearly nitrate is dominantly present in the Oxic/Suboxic class but has substantial concentrations in the Mn-reduced and Mix classes as well. This is also reflected in the nitrate/nitrite ratio, which indicates that some nitrate reduction may occur already in waters that are classified as Oxic/Suboxic, Mn-reduced and Mix. Manganese is present in all redox classes but shows the highest median in the Mn-reduced class which is determined by the Mn threshold of 0.5 mg/l in the classification tree for this class. By definition, iron only occurs in the classes Mix and Fe-reduced with the highest concentrations in the Fe-reduced class. Iron appears to be present in the S-reduced/methanogenic class as well, which means Fe-sulfide precipitation is not complete in those samples. Sulfate concentrations are below <5 mg/l in the S-reduced class by definition and show the highest concentrations in the Fe-reduced water, but significant sulfate is also present in the Oxic/Suboxic class. The latter is in correspondence with the known SO_4 loads in infiltrating water under farmlands. The high sulfate concentrations in Fe-reduced water are linked to additional sulfate that is produced during the process of pyrite oxidation coupled to nitrate reduction (Zhang et al. 2009). A small number of counts of sulfate > 75 mg/l are present in the S-reduced/methanogenic class; these represent brackish samples with indications for sulfate reduction following the SO4F criterion of the classification tree.

As most available datasets did not include measurements of the gases CH_4, H_2S or N_2, we evaluated the effects of these kinds of measurements in section 3.7.
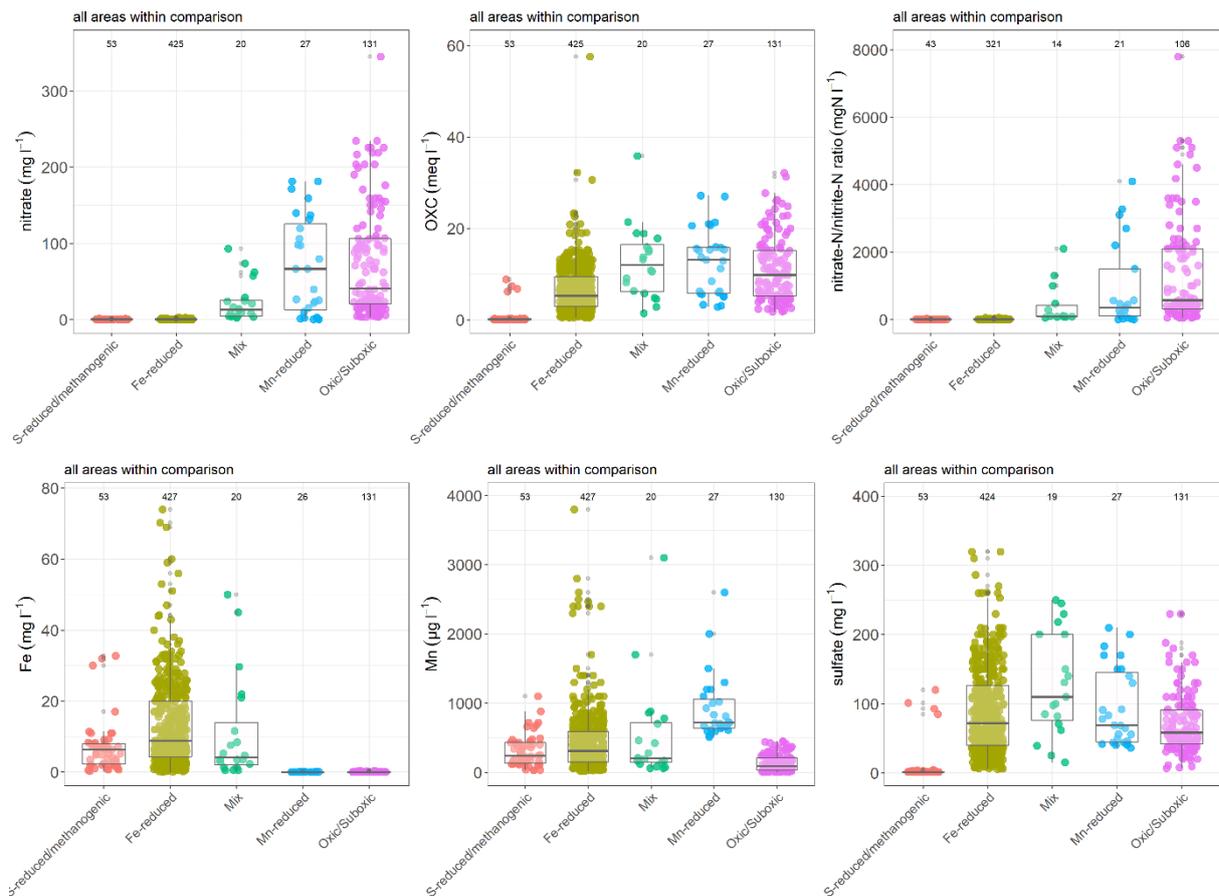
Figure 3.24 Jitters and boxplots of nitrate (mg/l), OXC (meq/l), nitrate-nitrite ratio (mgN/l), iron (mg/l), manganese (µg/l) and sulfate (mg/l) per redox class for all areas within comparison (agriculture, nature, urban areas, areas influenced by Meuse and discharge areas)

3.6   Mapping the total depth of denitrification in relation to geology

We analysed the data in the Flemish and Dutch monitoring networks to estimate the depth at which denitrification processes operate and linked it to the hydrogeological build-up of the pilot areas. The work profits from previous work done in the H3O-projects (Deckers et al. 2014, https://www.grondwatertools.nl/h3o) that yielded a harmonized hydrogeological 3D map of the transboundary area.

3.6.1   Evaluation of depth plots

A first step in the approach was to compare the concentration-depth profiles of a number of redox sensitive solutes for the Dutch and Flemish datasets. These comparisons were made for 5 shallow geological formations. We describe two of those, further information is available in the Appendix B (Section 0).

The Boxtel Formation consists of Pleistocene eolian fine sands and sandy to loamy fluvioperiglacial deposits, the Beegden Formation consists of fluvial sand and gravel deposits from the Meuse river. The Boxtel Formation typically overlays the Beegden Formations, except for the current river valley of the Meuse (see Figure 3.21). For the analyses of this section we concentrated on the part of the wells that

appear under farmlands, as those wells exhibit the most clear and understandable depth patterns as a result of the continuous inputs on nitrogen through farming. The analysis is performed on the average concentration in a monitoring well screen over the period 2005-2020.
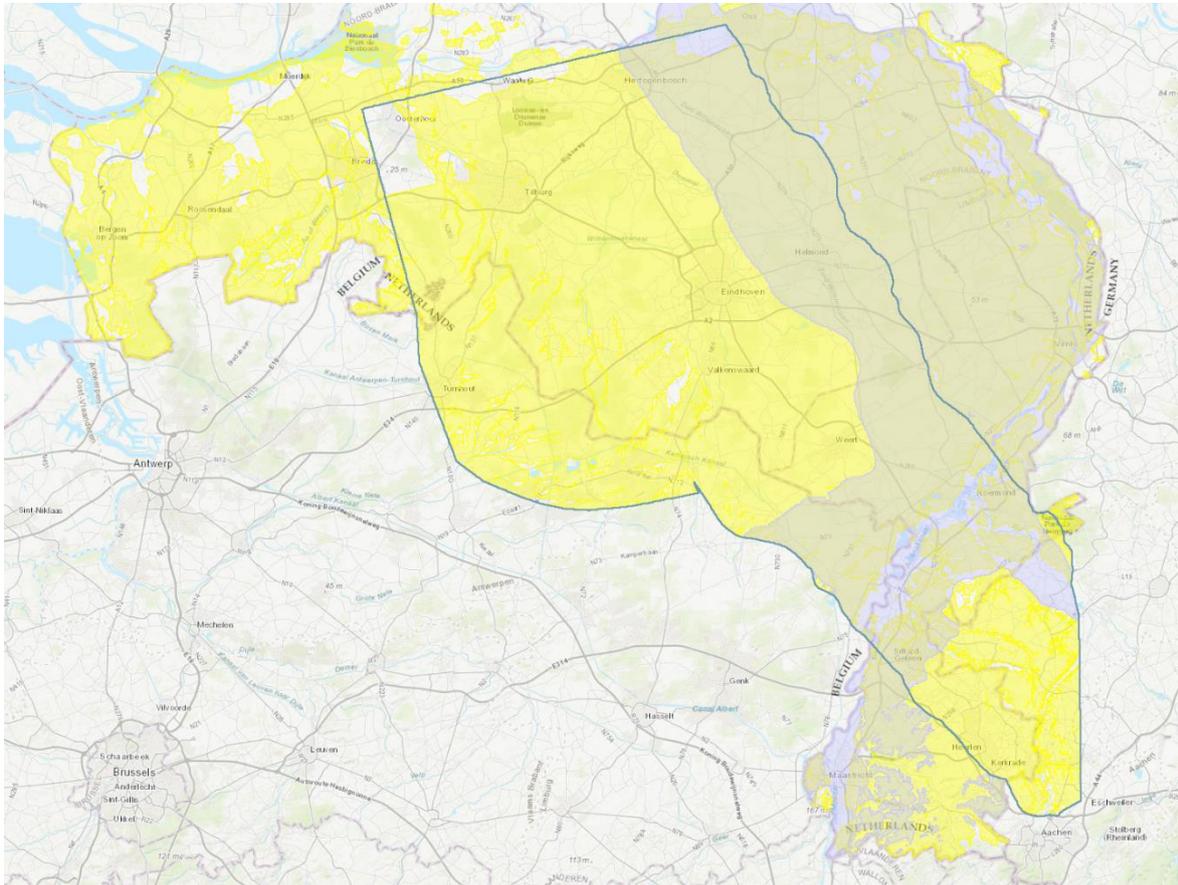

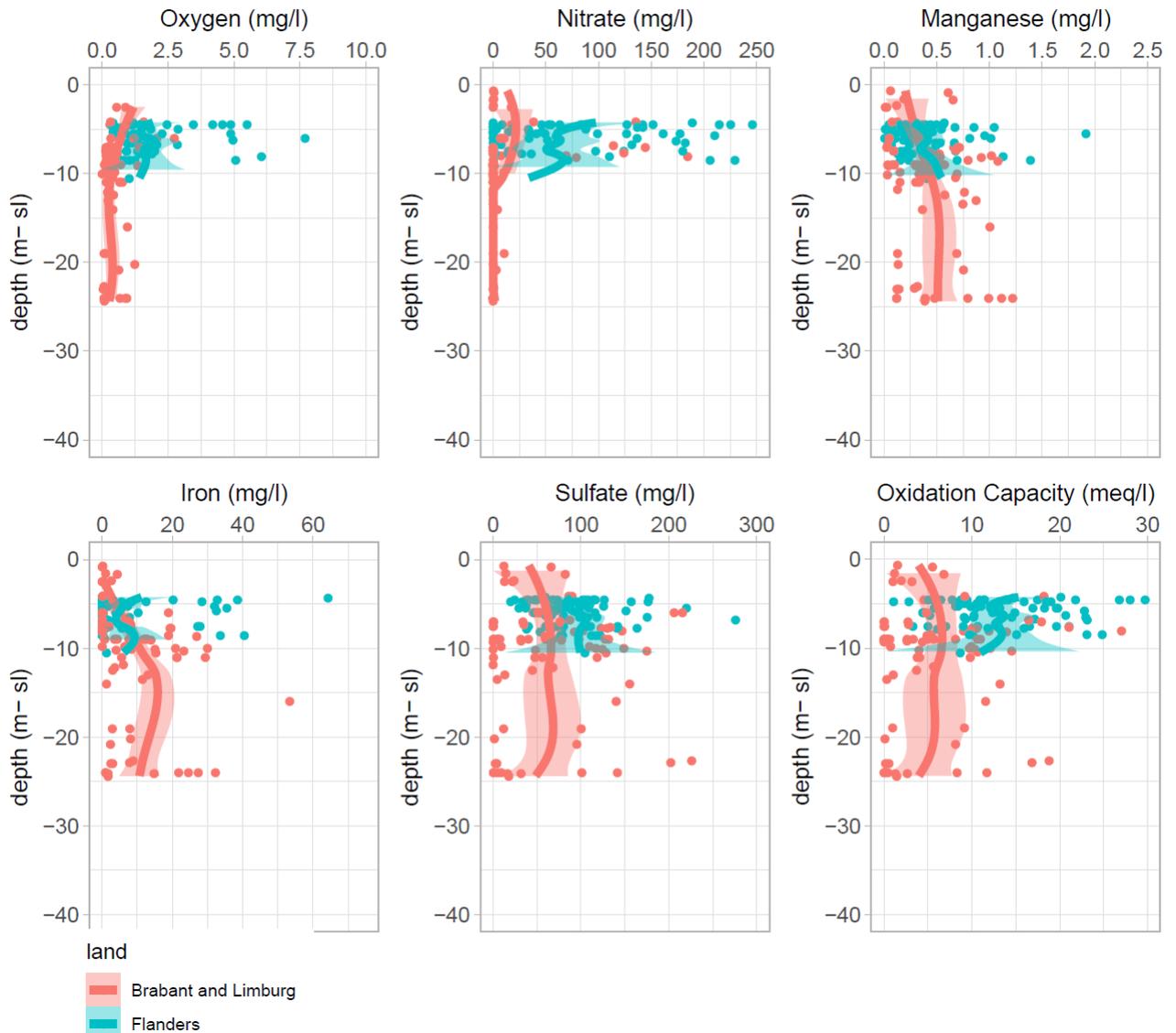Figure 3.21 Map of the extent of the Boxtel and Beegden Formations (Boxtel in yellow, Beegden in purple)

Figure 3.22 Concentration-depth profiles for agricultural areas in the Boxtel Formation (bx2). Concentrations are averages per monitoring screen over the period 2005-2020

The concentration-depth plots for the Boxtel Formation reveal that nitrate is completely absent from a depth of 10m and more (see Figure 3.22). In the first ten meters of the subsoil, nitrate concentrations up to 250 mg/l were observed, with typically higher concentrations in the Flanders wells than the Dutch wells. Even in the first ten meters, quite a number of waters with measurable Fe(II) are present, especially in the Flanders part of the study area. This suggest that locally the NO_3/Fe redox cline is present at shallow depth. In the Dutch part of the area, there is a clear increase of Fe(II), indicating that denitrification and solution of Fe-hydroxides starts locally at about 4m depth and is complete around 10m depth for the whole area. The OXC and sulfate profiles for the Dutch part indicate that the deeper water is as much influenced by farming activities and leaching of NO_3 and sulfate as the shallow water, meaning that denitrification is responsible for the decrease of NO_3 with depth. We attribute the difference between the Boxtel profiles in the Netherlands relatively to Flanders to the

difference in topographical situation; the Dutch wells are mainly concentrated in the Roer Valley Graben, at lower positions in the landscape, where loamy deposits are general.
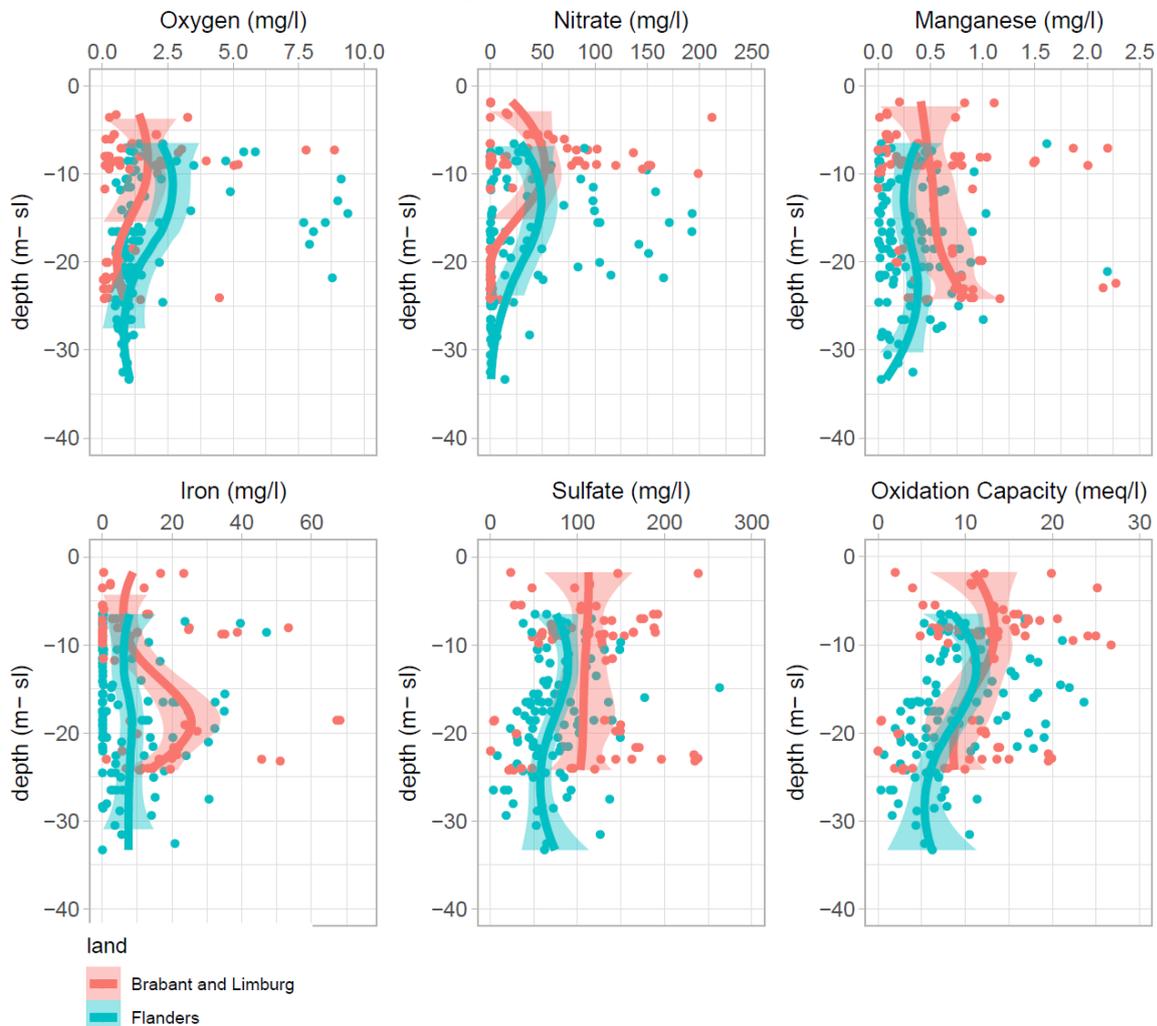
Beegden Formation

Figure 3.23 Concentration-depth profiles for agricultural areas in the Beegden Formation. Concentrations are averages per monitoring screen over the period 2005-2020

The concentration-depth plots for the Beegden Formation generally reach deeper than the Boxtel plots as the Formation is present at larger depth and with larger thickness (Figure 3.23). In the Beegden Formation, nitrate clearly travels further with depth than in the Boxtel Formation, especially in the Flanders part of the study area. The LOWESS smooth for Flanders suggests that the overall highest concentrations in Flanders appear around 15 m depth, compared with 9 m depth in the Netherlands part. Nitrate concentrations up to 200 mg/l were observed, but water lacking nitrate is present at similar depths. The oxygen profiles follow the nitrate profiles, confirming the differences between the two countries. The patterns of Fe(II), sulfate and OXC differ for the two countries, with a clear peak in Fe(II) at around 20 m depth in the Dutch part and overall higher manganese, sulfate and OXC. We attribute the differences between Flanders and the Netherlands to differences in topographical position, however differences in reactivity of the subsoil may play a role as well (see also section 3.6.3).

Obviously, a large amount of scatter is present in the dataset, which reflects local differences in solutes inputs, hydrogeological position and possible the reactivity of the subsoil. In the next sections, we will investigate the spatial aspects of the redox transitions, generally for the whole pilot area and specifically for the geological formations.

3.6.2   Map of total denitrification depth

Using the classification tree that was introduced in section 3.5.3, we assigned all samples for the redox class. For our data analysis, we chose the period 1970-2020 and for as many observations wells as possible given the current dataset, assuming that the redox transition does not change in time very fast (e.g. Van der Aa et al. 2003, Fraters et al. 2009).

Figure 3.24 serves as an example of the approach, here illustrated using the data from all wells under farmlands in the Beegden Formation for the period 1970-2020. Before that, the redox classes were translated into numbers: 1 = oxic/suboxic = 1, manganese reduced = 2, mixed water = 3, Fe-reduced = 4, S-reduced/methanogenic = 5. For the Flemish part a transition from class 2 (Mn-reduced) to class 3 (mixed water) is evident from the LOWESS smooth in the sixth plot of Figure 1.8. In the Dutch dataset both oxic/suboxic and Fe-reduced waters are obvious above 10 m depth and Fe-reduced water dominates at larger depths.
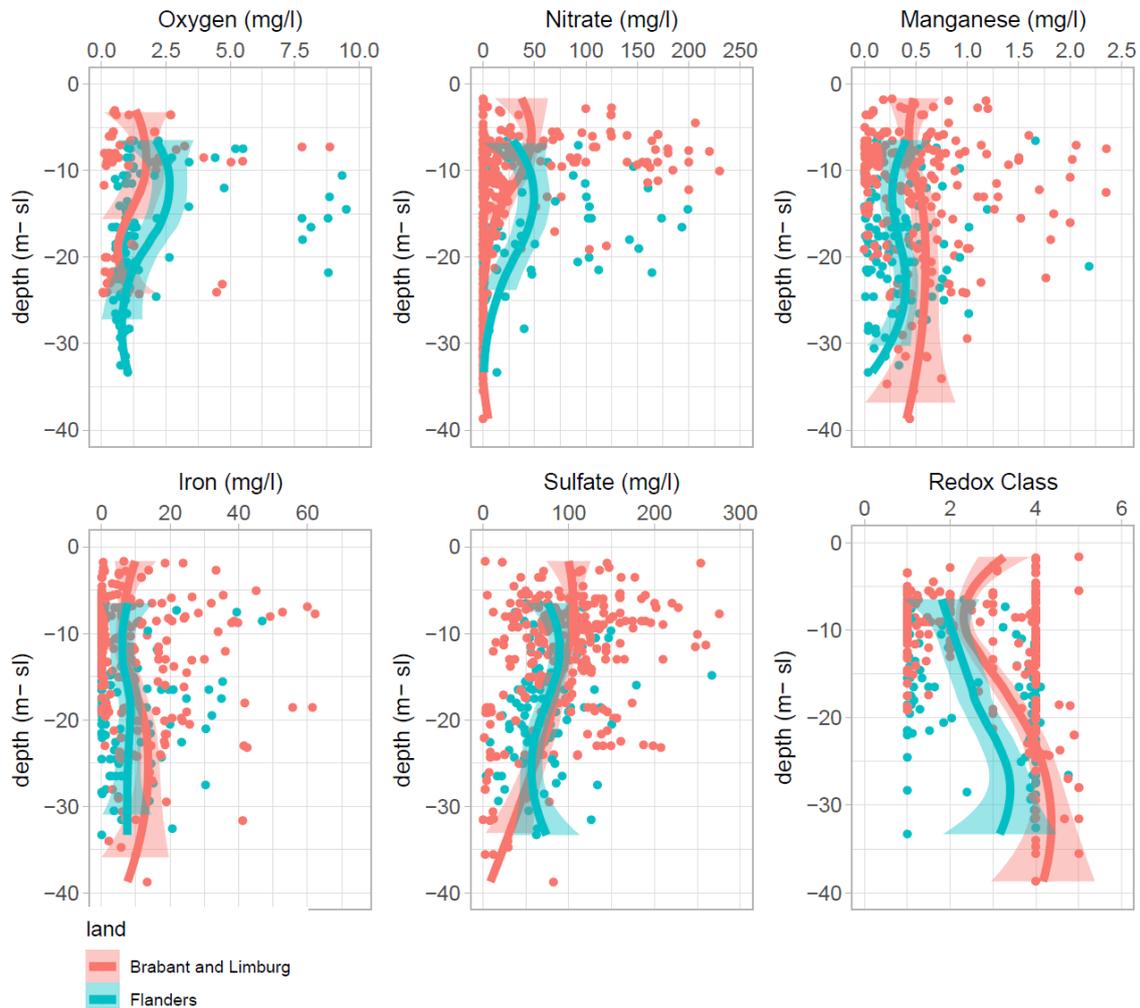
Beegden Formation

Figure 3.24   Redox classification tree applied at the concentration-depth plots. Concentration-depth profiles for agricultural areas in the Beegden Formation. Concentrations are averages per monitoring screen over the period 1970-2020. Redox classes: 1 = oxic/suboxic, 2=manganese reduced, 3=mix, 4- Fe-reduced, 5= S-reduced/methanogenic

We subsequently used the classification of redox class in Figure 3.23 to arrive with the depth of complete denitrification, which we defined as follows:

1. For all monitoring screens we averaged the redox class over the time period 1970-2020 (as denoted by 1 to 5 as described in the previous section)
2. For all multi-level wells, we derived the order of redox classes with depth
3. We put the threshold for complete denitrification at 3.5, meaning in between mixed water and Fe-reduced water
4. We determined between which two screens the transition from < 3.5 to > 3.5 occurred
5. We register the depth of the screen above that transition and the screen below
6. We registered the average depth of the transition by averaging the two depths of step 5
7. We registered the range of possible denitrification depth subtracting the 2 depths acquired at step 5.

Using this formal procedure, the depth of complete denitrification was determined for all monitoring wells that have screens above and below the transition zone. We used the ranges derived at step 7 to indicate the uncertainty of the measure (the precision). The results of all wells in the pilot area are shown in the map of Figure 3.25. We tested the sensitivity of the 3.5 threshold but found it to be rather insensitive.
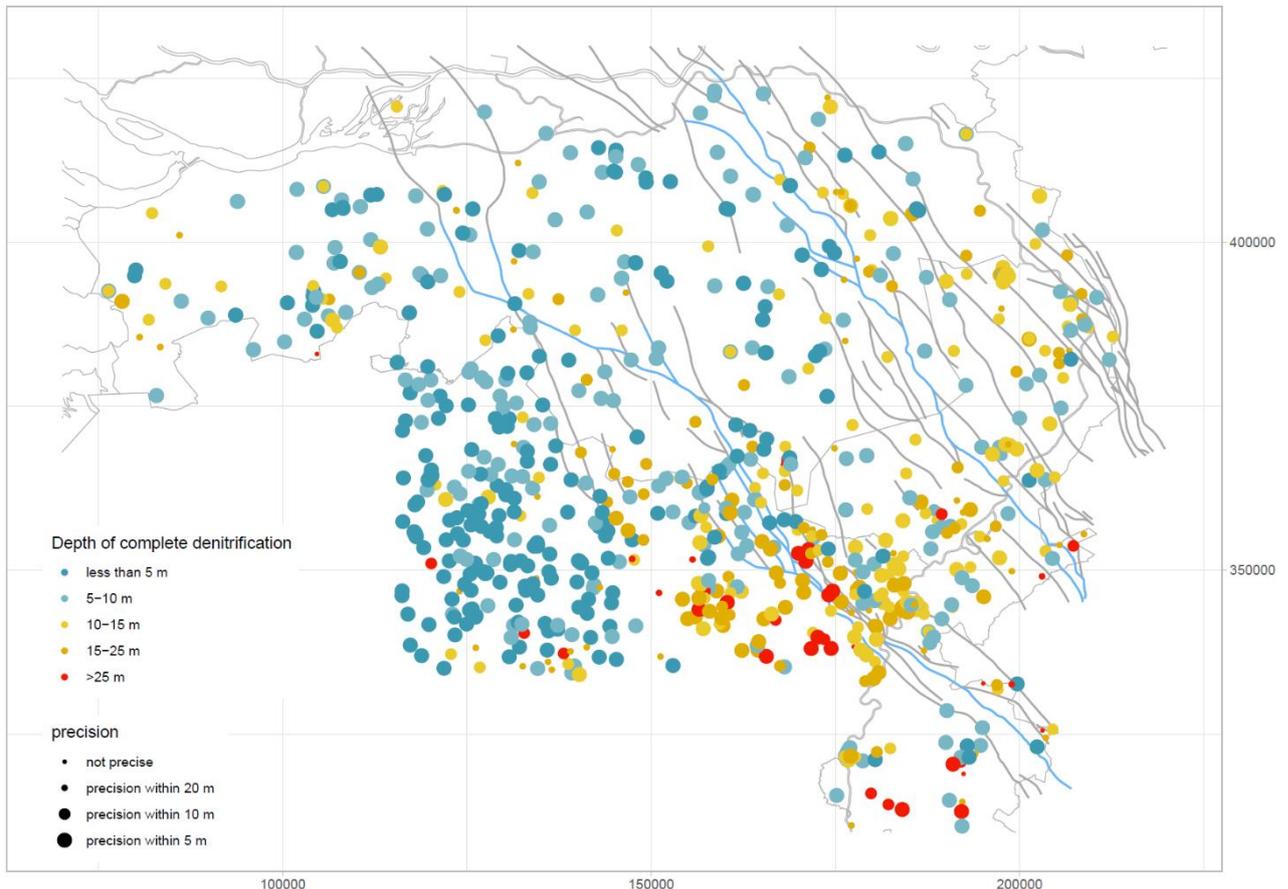

Figure 3.25 Map of the depth of complete denitrification, based on multi-level wells screens and monitoring data over the period 1970-2020

The map of Figure 3.25 shows large spatial variations of the depth of complete denitrification which we will further explore in the next sections. However, in general the result means that denitrification in the saturated zone in the Netherlands and Flanders pilot region appears at shallow depths, generally within the first 5-25 meters of the subsoil, and sometimes a bit deeper. This is not a general finding, although we know that similar patterns exist in Denmark and probably in other lowlands worldwide.

3.6.3   Denitrification depth in relation to geological Formations

Using the total dataset shown in Figure 3.25, we now evaluate the results per geological formation, to analyse how much the stratigraphical position and the reactivity of the individual geological formations influences the patterns of denitrification. In general, the study area is characterized by deposits from the Rhine river (Sterksel, Kieseloolite), Meuse river (Beegden) and Belgian rivers (Stramproy), all overlain by eolian and fluvioperigacial deposits of the Boxtel Formation (Figure 3.26).
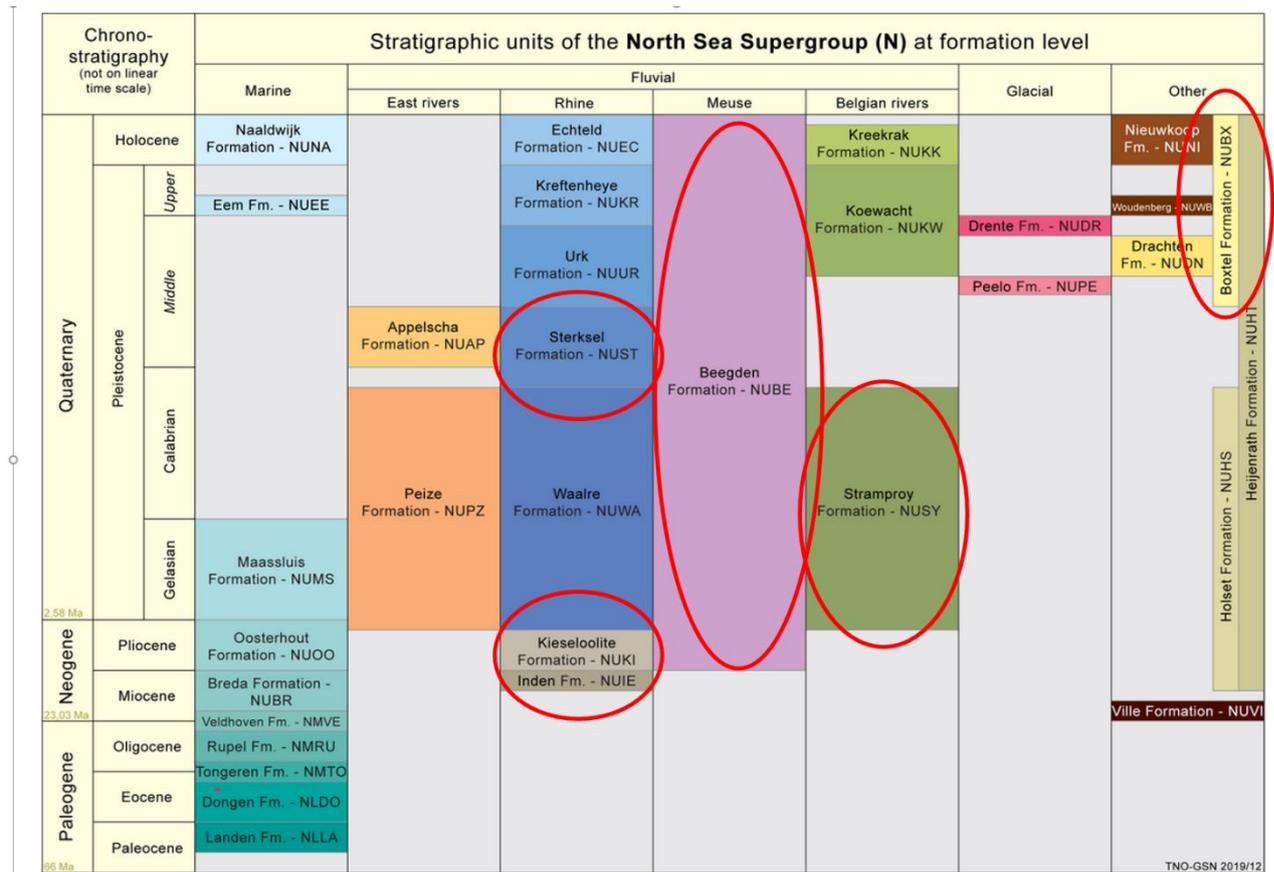
Figure 3.26   Stratigraphy of the upper Formations in the study area.

Boxtel Formation

Stratigraphically, the eolian sands and fluvio-periglacial deposits of the Boxtel Formation form the uppermost geological unit and it appears close to the surface. Still, most of the observations in the Boxtel Formations point to a very shallow depth of the nitrate-iron redox cline, mostly less than 10 m below surface (Figure 3.27). The shallow presence of the Fe/NO3 redox cline is in correspondence with the known reactivity of the Boxtel Formation in the Roer Valley Graben where the Formation reaches his maximum thickness with a sequence of sandy, loamy and peaty layers (Figure 3.28 and Figure 3.29Figure 3.28). Where the Boxtel Formation is developed less thick, the redox cline might be found at greater depths, which is the case in the southernmost part of the study area.

A shallow depth of total denitrification in the Boxtel Formation appears to be related to the thickness of the Boxtel Formation with shallower depth in area with great thickness of the (reactive) Formation (Figure 3.27 and Figure 3.28). Moreover, there is a relationship with the altitude of the surface level. Wells that reflect a deeper location of the NO_3/Fe redox cline are situated mostly in areas with higher surface elevation (Figure 3.30 and Figure 3.31).
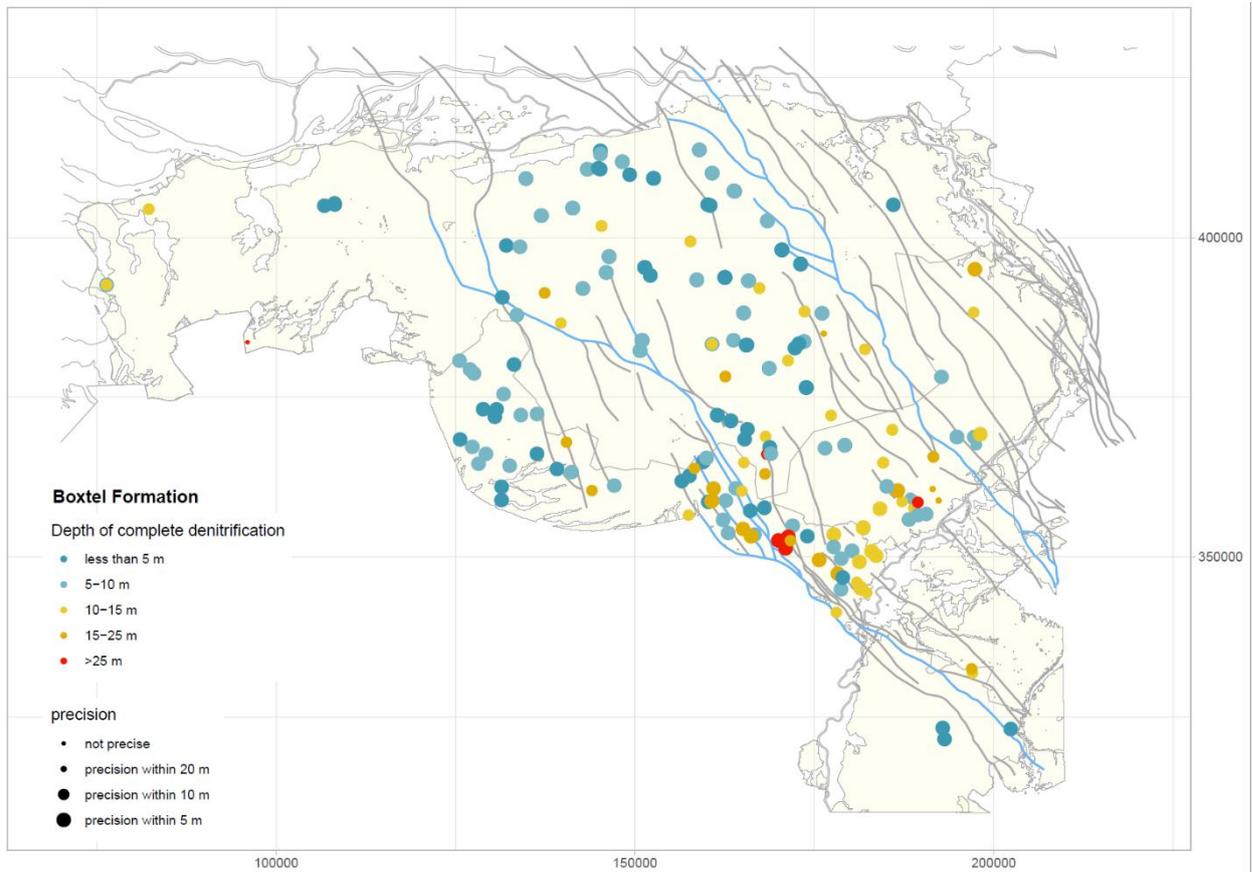
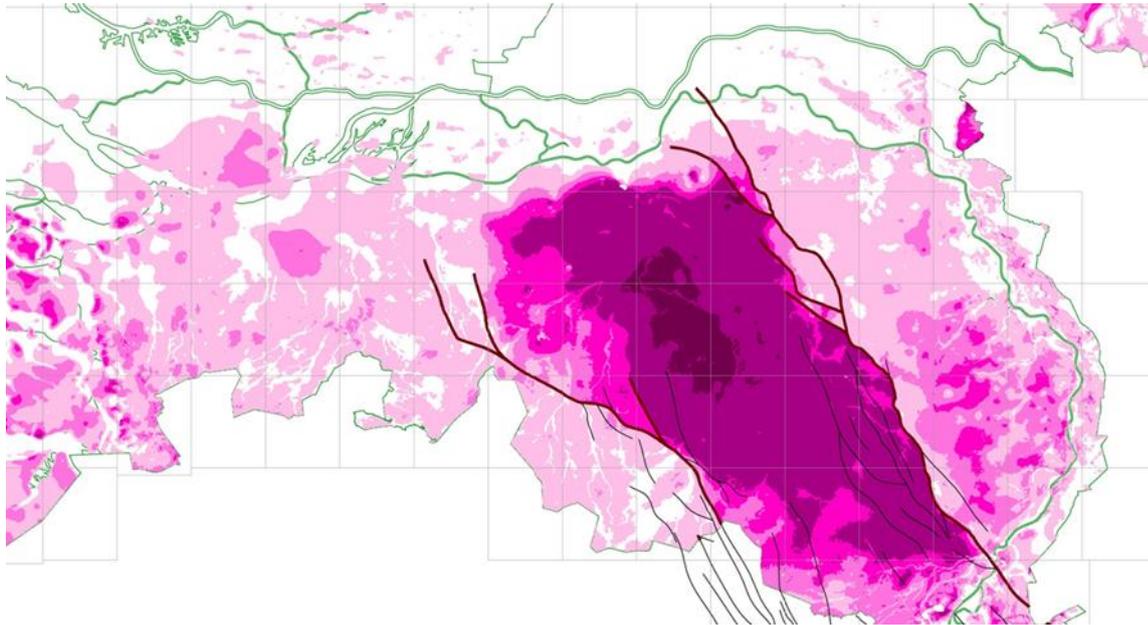Figure 3.27   Depth of total denitrification in the Boxtel Formation

Figure 3.28   Thickness of the Boxtel Formation in the Netherlands part of the study area. A thick sequence of eolian and fluvio-periglacial deposits is found in the Roer Valley Graben, and the Formation is known to be rich in organic contents in humic and peat beds that are present in the sequence.
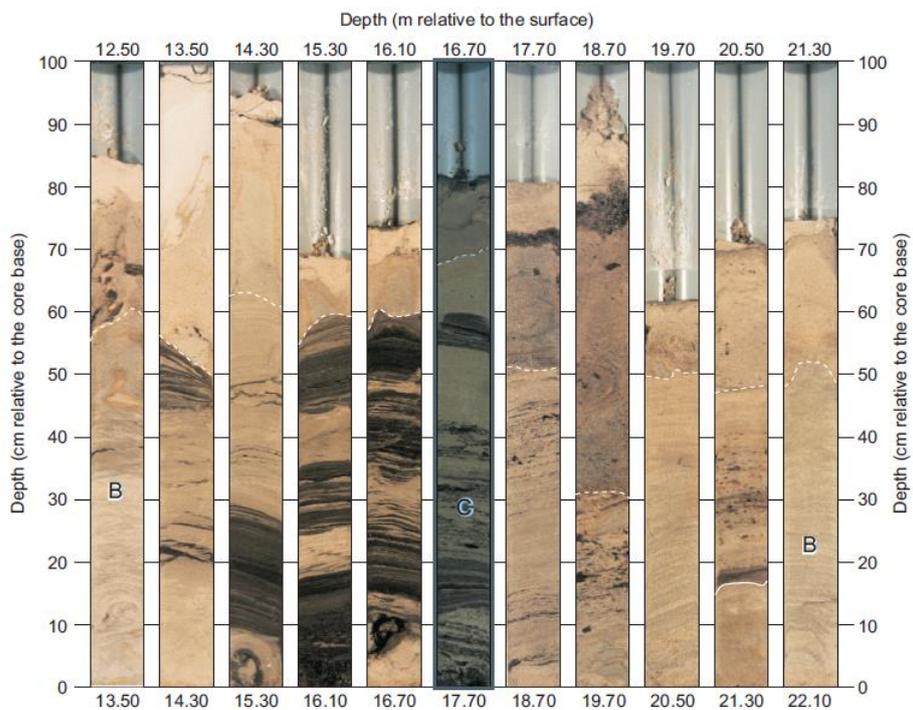

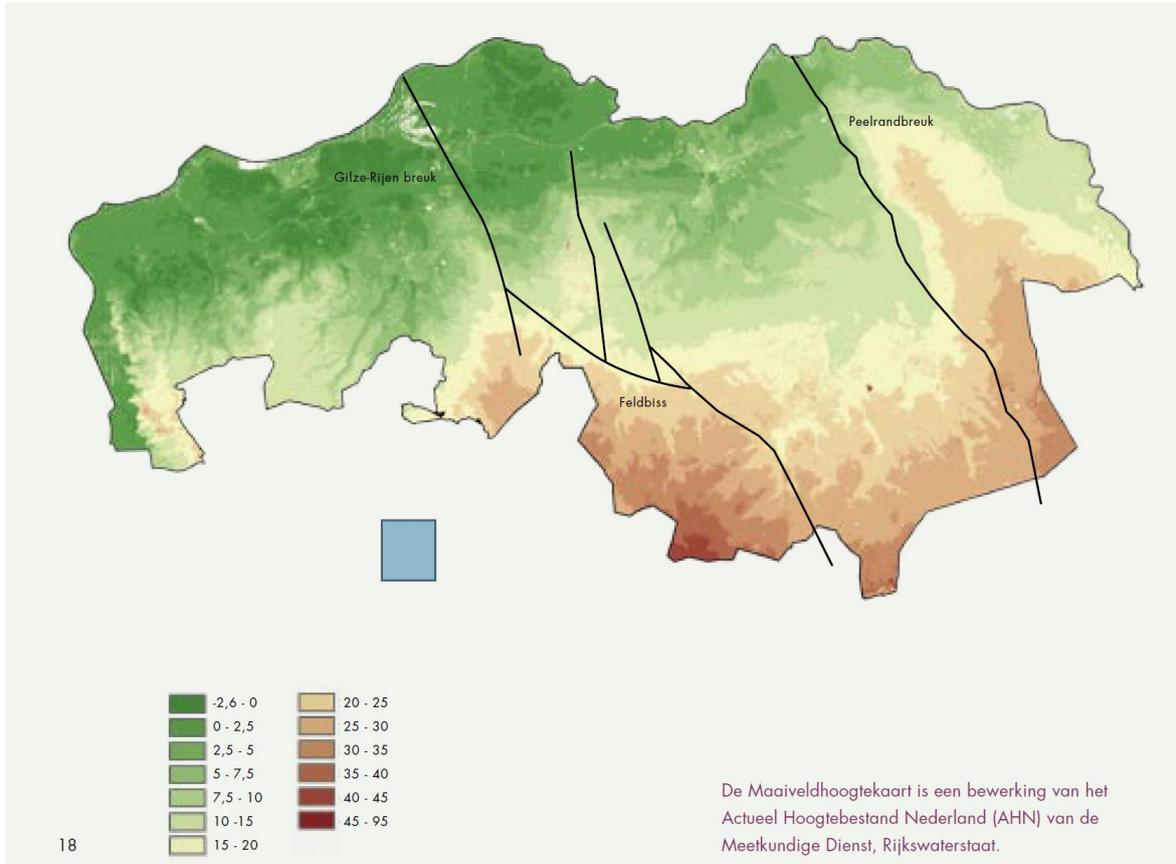Figure 3.29   A typical sequence of the Boxtel Formation at location 45D0154 (Schokker, 2003)

Figure 3.30 Altitude of surface level in the Noord-Brabant province and location of the main faults that determine the position of the Roer Valley Graben.
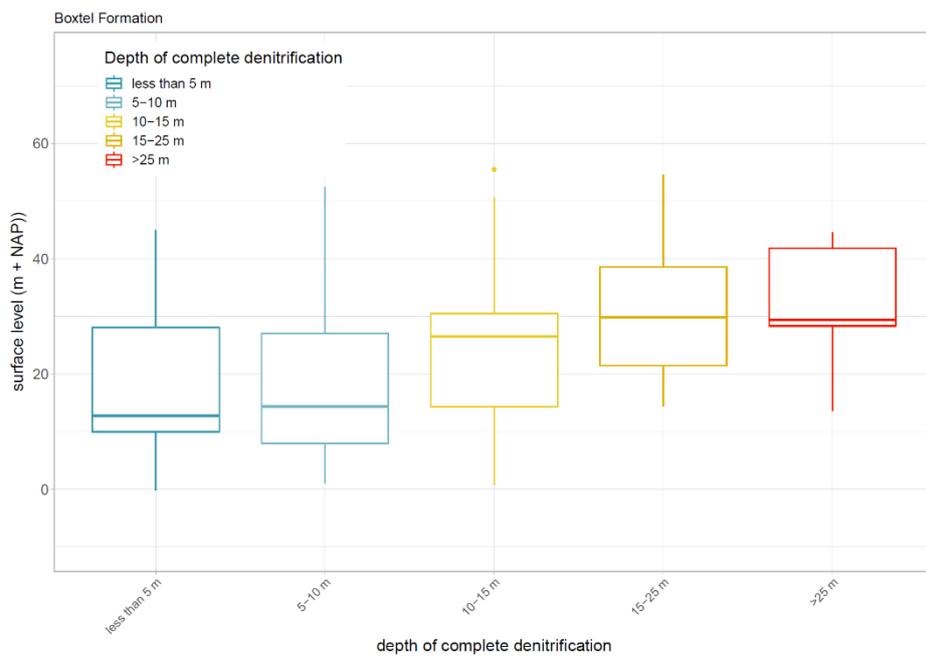

Figure 3.31 Relation between denitrification depth and surface level altitude for the Boxtel Formation
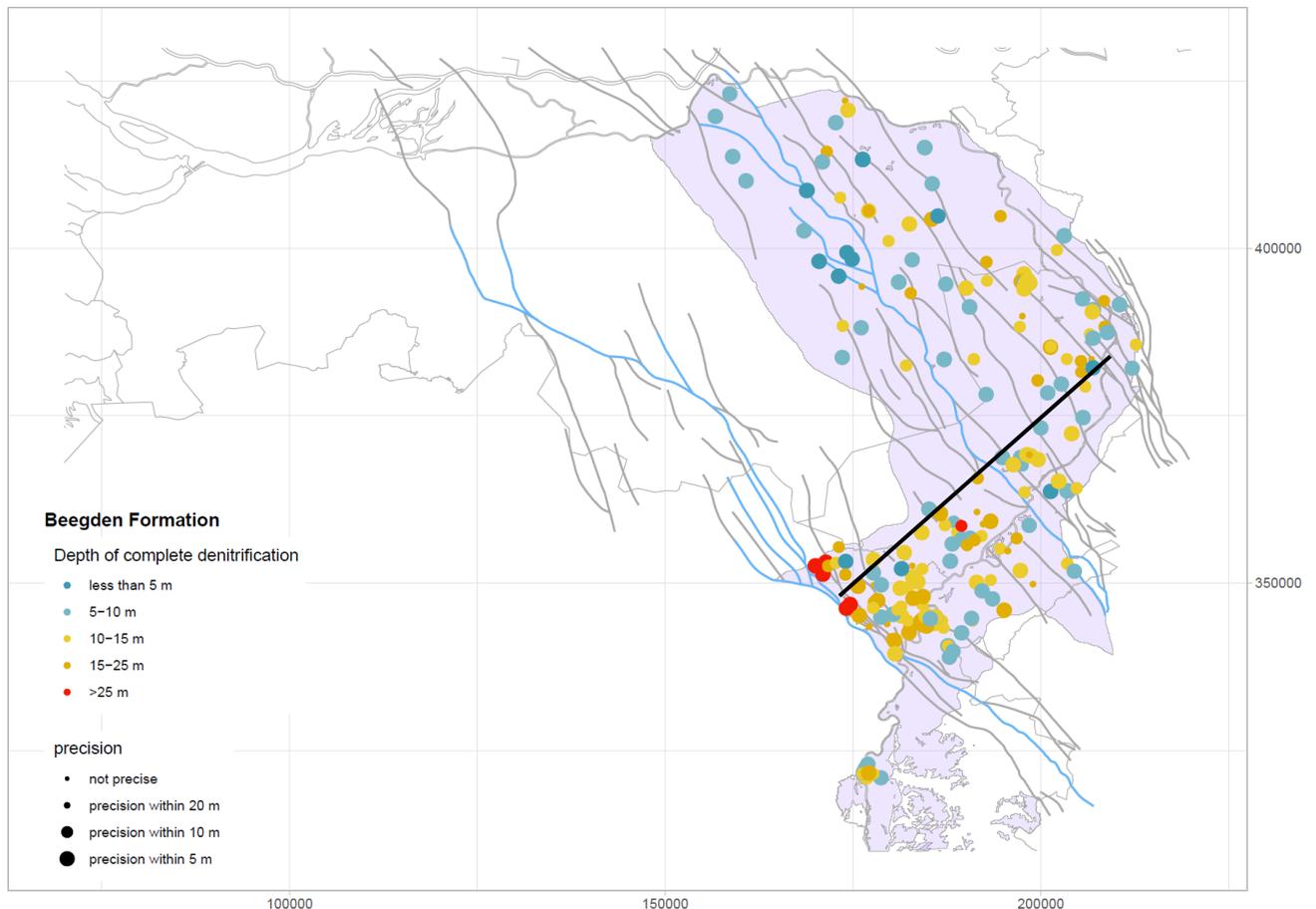
Beegden Formation

Figure 3.32 Depth of total denitrification in the Beegden Formation. Cross-section of Figure 1.20 marked in black

The Beegden Formation consists of moderately to coarse fluvial sands and gravels of the Meuse river. It is partly overlain by the Boxtel Formation, but the Boxtel cover is usually rather thin and not as developed as in the Roer Valley Graben. Figure 3.32 reveals that the depth of denitrification is typically larger than in the Boxtel Formation, with depth > 25 m especially in the southwest corner of the extension of the Formation. So, nitrate may travel up to 20 m depth or more in parts of the area with Meuse river deposits.

There is clear relation between the surface level of the well and the depth of total denitrification (Figure 3.33). The higher the elevation, the deeper the redox cline is positioned. We explain this by the longer history of leaching of oxidizing agents in the main recharge areas of the study area. Apparently, the reactive buffer of organic matter or sulfides in the subsurface may have been removed by the prolonged infiltration of water loaded with oxygen and/or small amounts of nitrate.

The general higher altitude in the Belgian part of the study areas therefore also determines the difference between the concentration-depth profiles that were observed in Figure 3.23. The cross-section of Figure 3.34 shows that the Beegden Formation (purple) is only overlain by a thin sequence of the Boxtel Formation (yellow) and overlays the Sterksel Formation (brown-reddish) and Stramproy Formations (light brown). The redox transition is either in the deeper parts of the Beegden Formation or the shallowest parts of the Sterksel and Stramproy Formations.
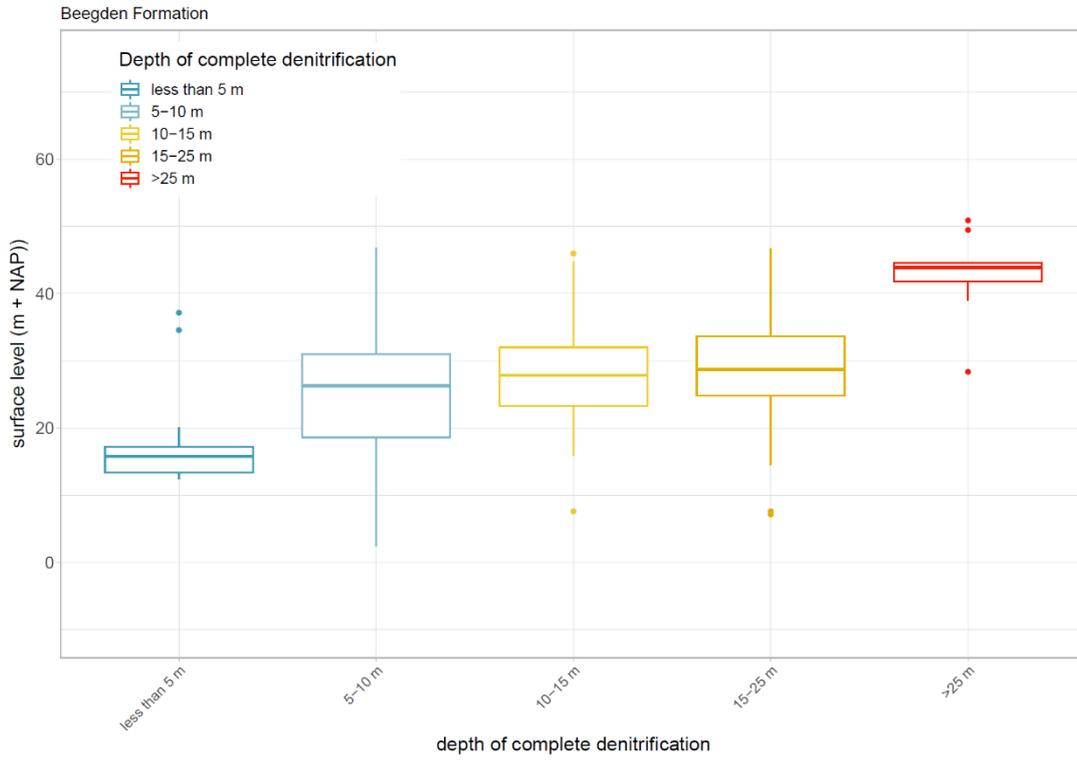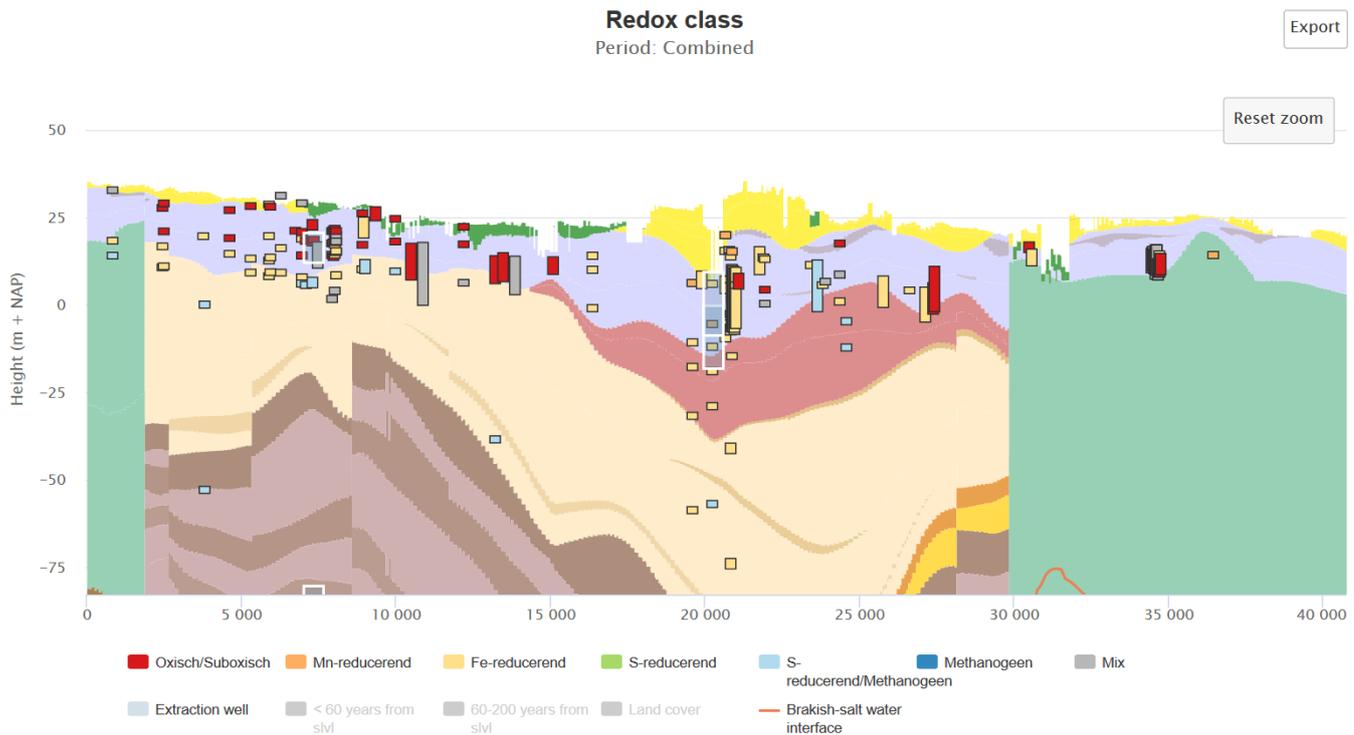
Figure 3.33 Relation between denitrification depth and surface level altitude for the Beegden Formation

Figure 3.34 Hydrogeological cross-section, showing the extension of oxic/suboxic water in the Beegden Formation (purple colour) and the transition to Fe-reducing water at larger depth.

Sterksel Formation

The fluvial deposits of the Rhine of the Sterksel Formation are mainly situated in the Roer Valley Graben and dominantly overlain by a rather thick sequence of the Boxtel Formation or by the Beegden Formation in the southeast part of the study area. This explains that the denitrification is often complete in the Sterksel Formation itself (Figure 3.35). The larger depth of denitrification is again found in the southernmost part of the study area, but denitrification depth > 25 m are seldomly observed and the precision of the determination is low.
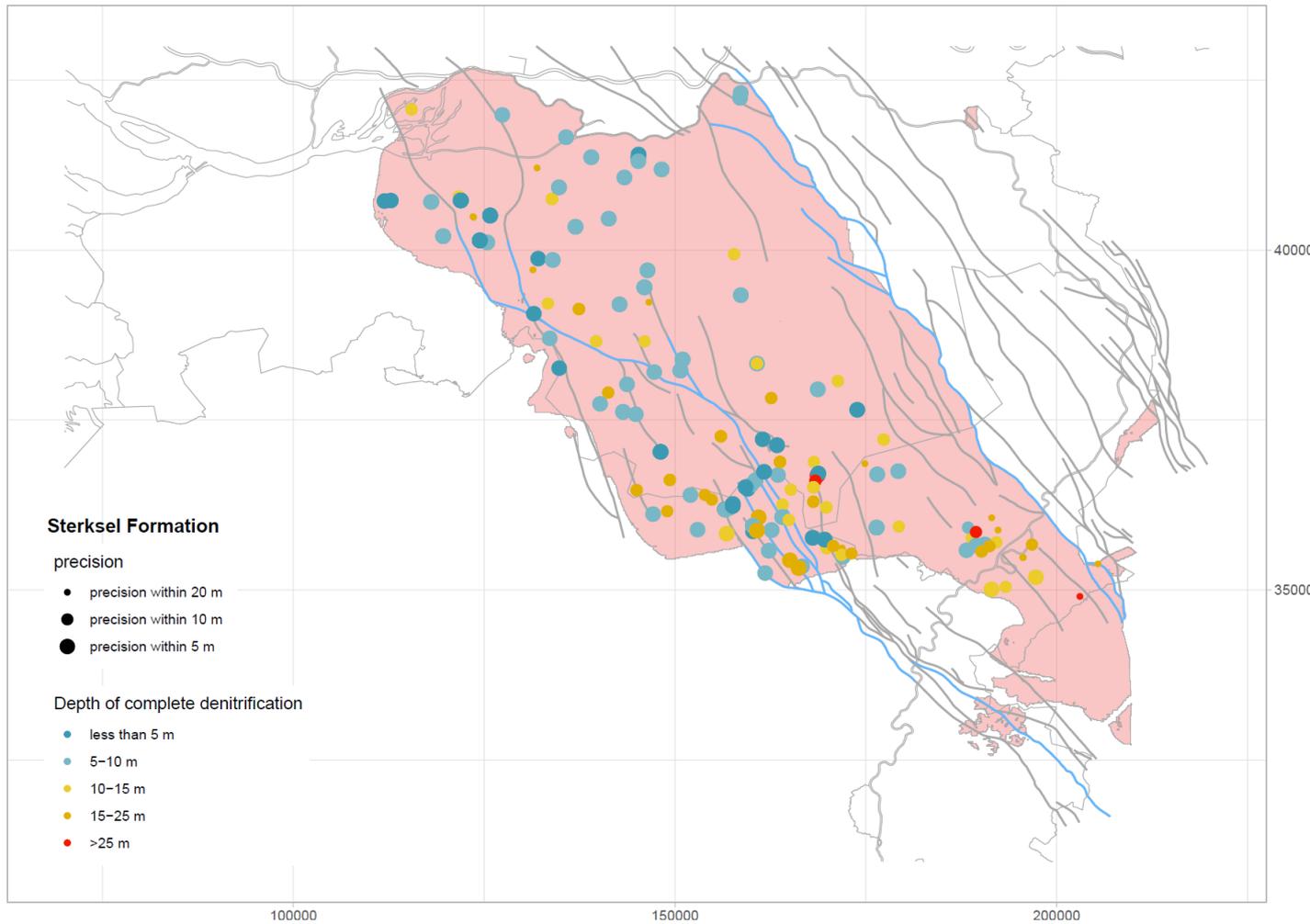
Figure 3.35   Depth of total denitrification in the Sterksel Formation.

Stramproy Formation

In most of the study area, the Stramproy Formation is overlain by the Sterksel Formation, which means that denitrification is often complete before the water enters the Stramproy Formation. Only were the Stramproy Formation having an outcrop (see Figure 3.37) there is nitrate leaching into it. Again, denitrification depth is mostly shallow and seldomly reaches 25 m depth, except for 3 "high-precision wells" in the southern part of the area (Figure 3.36).

Stramproy Formation

Depth of complete denitrification

- less than 5 m
- 5–10 m
- 10–15 m
- 15–25 m
- >25 m

precision

- not precise
- precision within 20 m
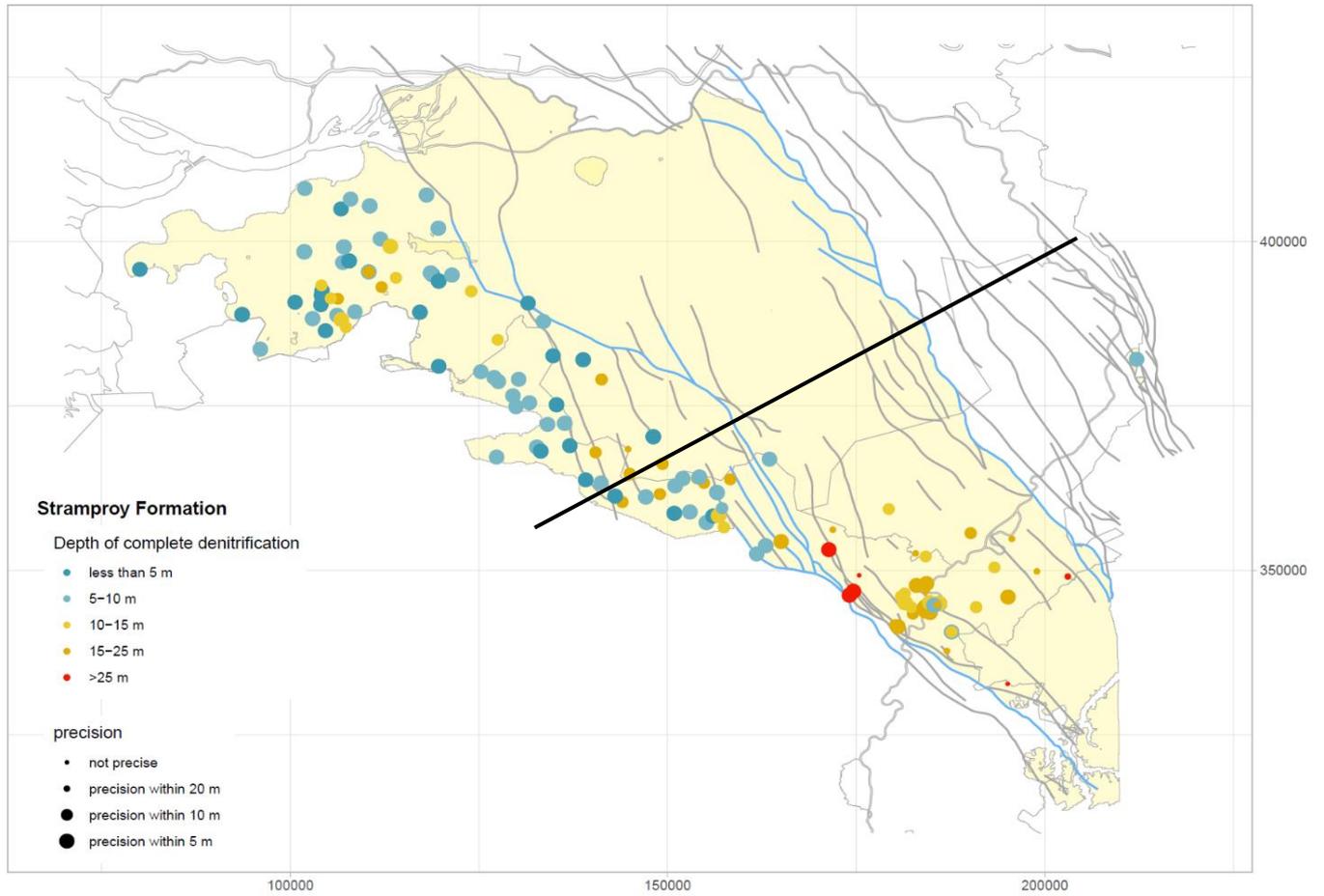- precision within 10 m
- precision within 5 m

Figure 3.36 Depth of total denitrification in the Stramproy Formation. Cross section of Figure 3.37 marked in black.
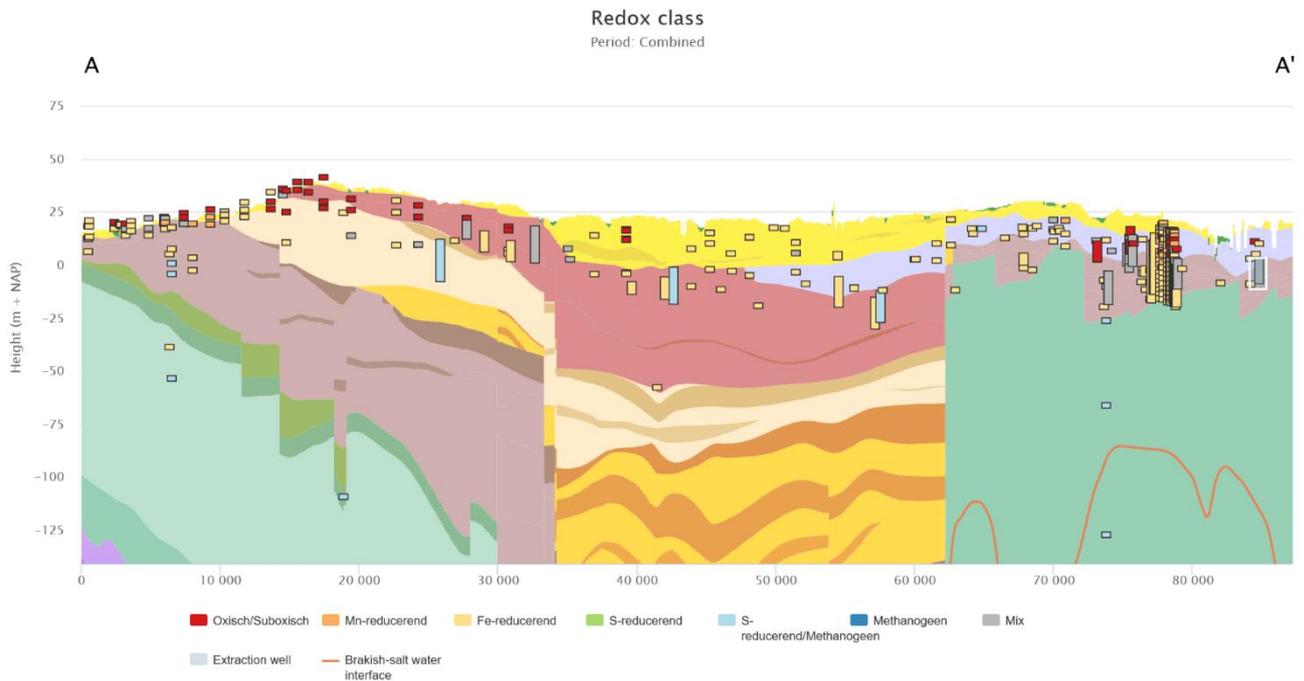
Figure 3.37 Hydrogeological cross-section, showing the extension of oxic/suboxic water in the outcrops of the upper parts of the Stramproy Formation (light brown colour) and the Sterksel Formation (brown-reddish). Denitrification happens shallow in the Boxtel Formation (yellow) and the Kieseloolite Formation (purple brown).

3.7 Refining the classification tree using additional gas determinations

Information about redox processes is additionally gained from chemical characterization using macro-parameters and the measurement of gases such as N_2, CH_4, H_2S etc., which help to deduce the redox transitions in the subsurface which indicate transformation processes affecting the fate of nitrate and possibly pesticides. Concentration of gases have been obtained during the 2017/2018 age dating campaign, using IsoFlasks sampling bags. H_2S was measured in the field using a field photo spectrometer.
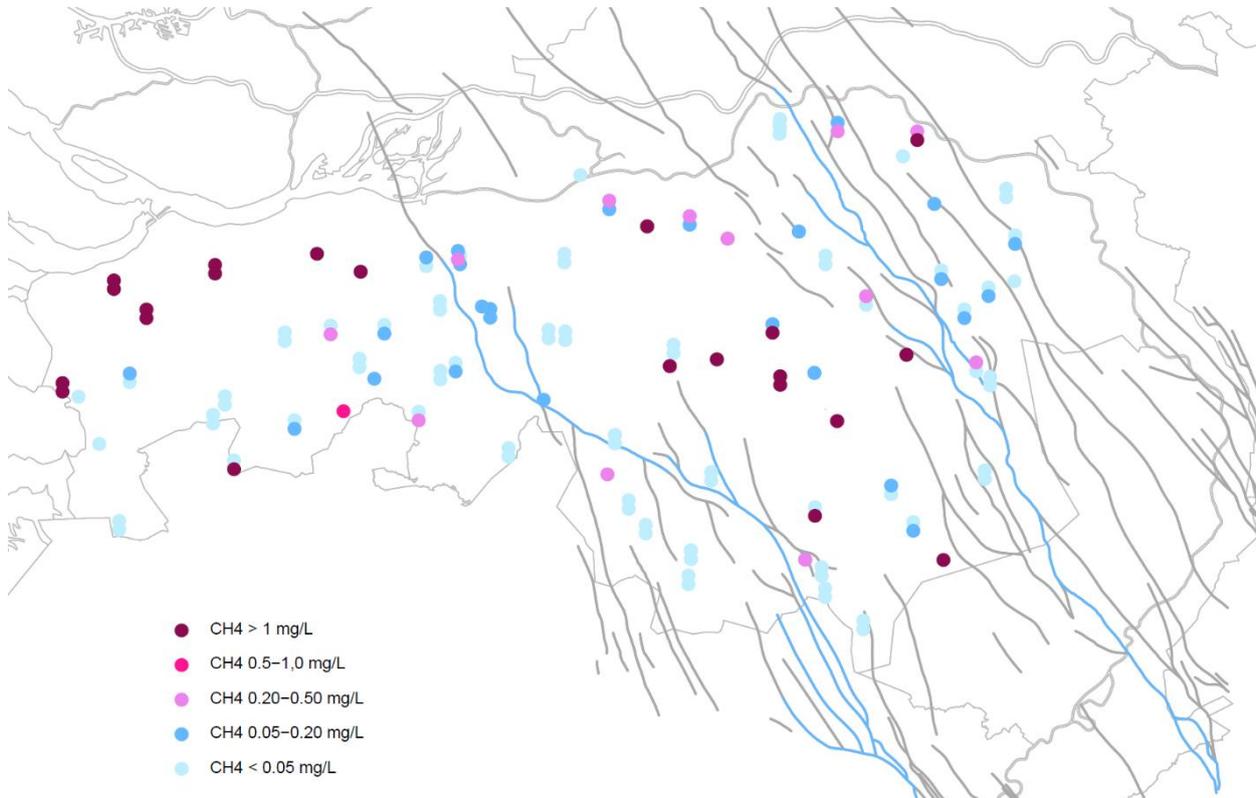
Figure 3.38 Map of CH$_4$ concentrations in monitoring screens at 10 and 25 m depth. The deeper screen is plotted just south of the shallower screen. Elevated methane is especially found in the centre of the Roer Valley Graben and the peri-marine north-western part of Noord-Brabant that is known for a marine clay cover

Up to now the collected gas data have not been interpreted for classifying groundwater according to redox status, as H2S, CH4 and N2 are not typically available in many groundwater quality datasets in the Netherlands. Therefore, classification tree which was discussed under Section 3.5.3 is particularly useful for large datasets, yielding the foundation for the interpretation as discussed in the last paragraphs.

The Noord-Brabant gas dataset is particularly suited to investigate the robustness of the decision tree and to refine the decision tree for datasets that also contain gas data. Thus, it may further support the interpretation of attenuating processes, such as sulfate reduction, denitrification and pesticide degradation. The measurements of H$_2$S and CH$_4$ may help to further refine the classification of Fe-reduced, sulfate-reduced and methanogenic water. The N$_2$ concentrations may help to further refine the divisions of oxic/suboxic water, manganese-reduced water and mixed waters, with higher dissolved N2 indicating that the process of denitrification determined the redox status.

Figure 3.38, Figure 3.39 and Figure 3.40 show the maps of the presence and concentrations of CH$_4$,H$_2$S and N$_2$ in the groundwater of the pilot area. In the next sections, we evaluated whether those additional measurements would alter the redox classification that were performed in the previous chapters.
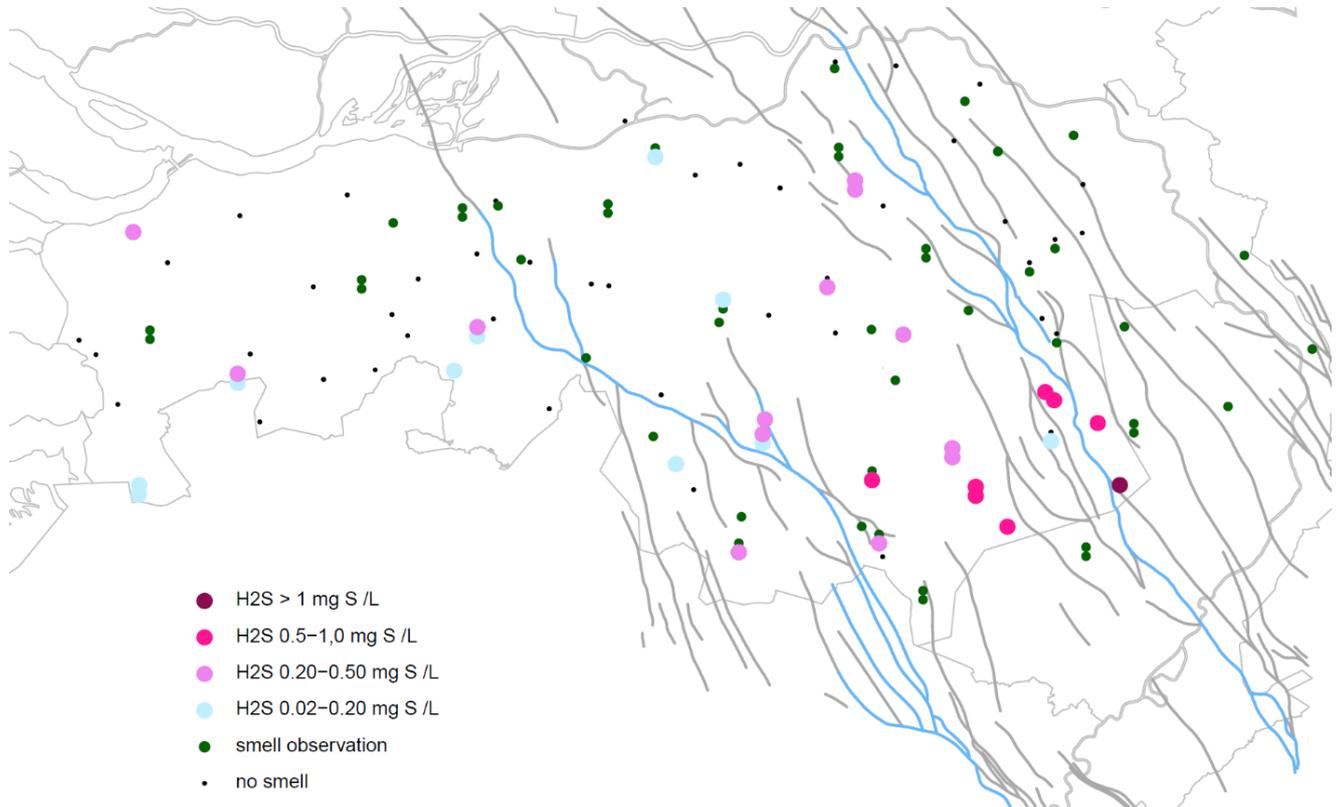
Figure 3.39 Map of H2S concentrations in monitoring screens at 10 and 25 m depth. The deeper screen is plotted just south of the shallower screen. Part of the monitoring wells of the provincial monitoring network were sampled in a previous study (Broers et al. 2015). Elevated H2S concentration were particularly found in the southern and south-eastern part of the Roer Valley Graben where organic rich fluvio-periglacial deposits of the Boxtel Formation are eminent.

- ● N2 > 40 mg/L
- ● N2 30 – 40 mg/L
- ● N2 25 – 30 mg/L
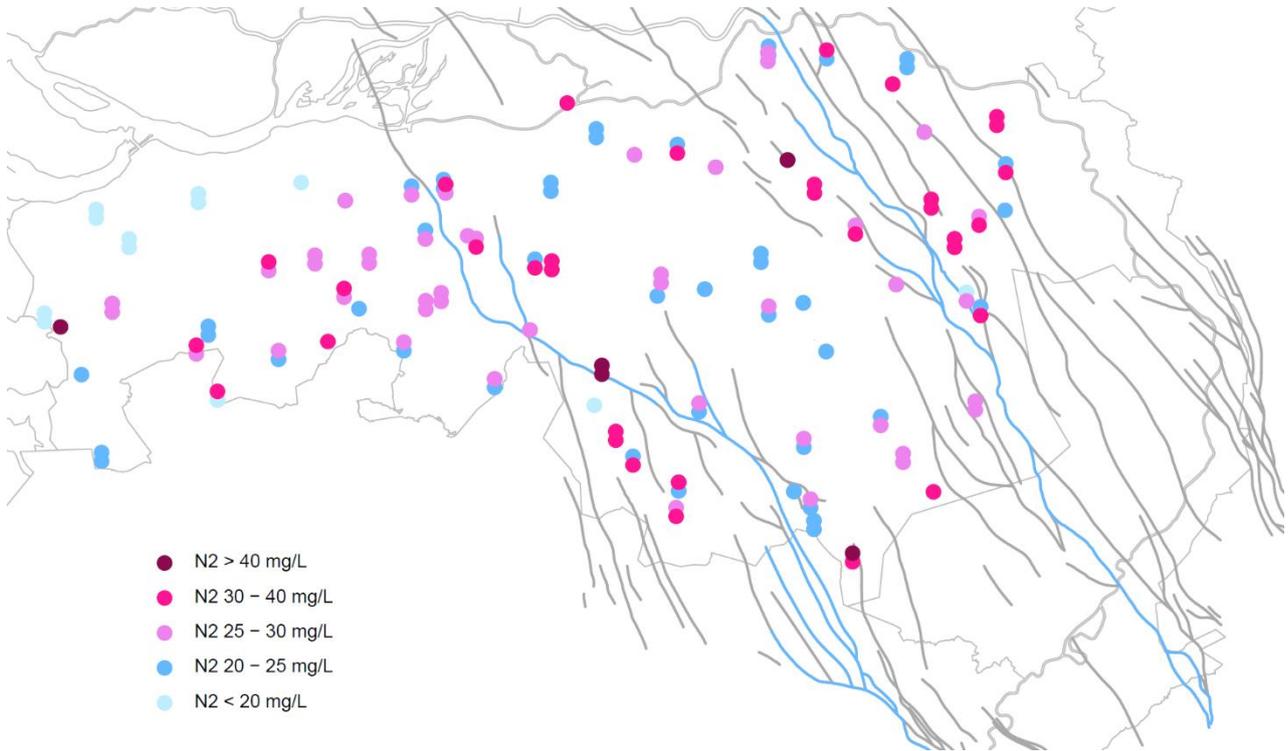- ● N2 20 – 25 mg/L
- ● N2 < 20 mg/L

Figure 3.40 Map of dissolved N_2 concentrations in monitoring screens at 10 and 25 m depth. The deeper screen is plotted just south of the shallower screen. Elevated N_2 concentrations occur in the sandy regions of Noord-Brabant, where denitrification has transferred nitrate into N_2 gas (Zhang et al. 2009, Visser et al. 2007)

3.7.1 CH₄ and H₂S and redox classification

Figure 3.41 shows the relations between H$_2$S, CH$_4$ and sulfate concentrations. Concentration of CH$_4$ > 1 mg/l correspond with sulfate concentrations of < 5 mg/l and sulfide concentration below 0.1 mg/l (with one exception). These relations confirm that sulfate reduction was complete in water that are above the CH$_4$ threshold of 1.0 mg/l that was used in the redox decision tree of section 1.2.2. The threshold effectively separates "sulfate-reduced" and "iron-reduced" waters from waters that underwent methanogenesis.
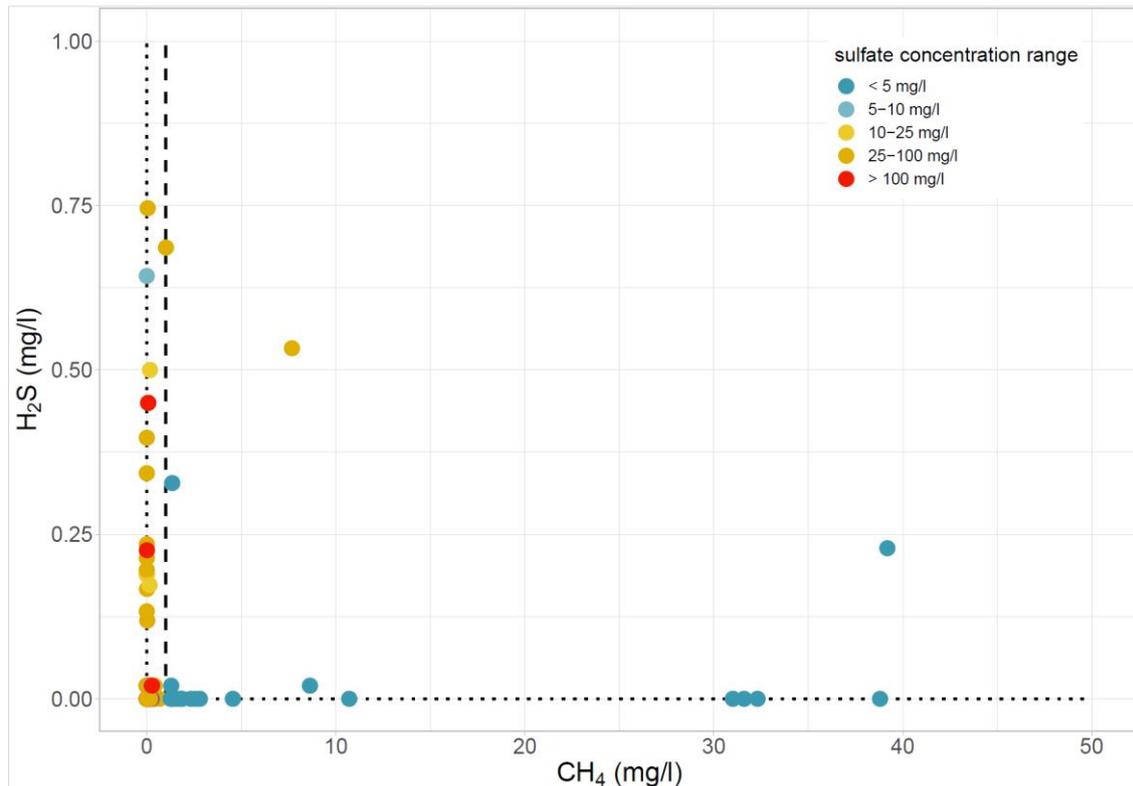

Figure 3.41   Relation between H2S and CH4 in the Brabant data set.

This figure also shows a large number of samples with significant concentrations of H$_2$S and no methane. The vast majority of these samples were characterized as "Fe-reduced" in the decision tree (Figure 3.42, lower panel). The presence of dissolved sulfide indicates an ongoing or past process of sulfate reduction in these waters of the Fe-reduced redox class. As is clear from Figure 3.42, centre panel, these samples contain significant concentrations of sulfate which indicates that the process of sulfate reduction is not complete (e.g. Yu et al., 2018 for a thorough discussion). Therefore, H$_2$S is a suitable indicator for an active process of sulfate-reduction even in cases where sulfate concentrations are still very high. Only measuring sulfate will not identify those waters with active sulfate reduction. As such, using the < 5 mg/l threshold in the classification tree for fresh water, only waters with completed sulfate reduction will be identified. For brackish waters, the classification tree uses the SO$_4$/Cl ratio to make that assessment (see Yu et al. 2018).
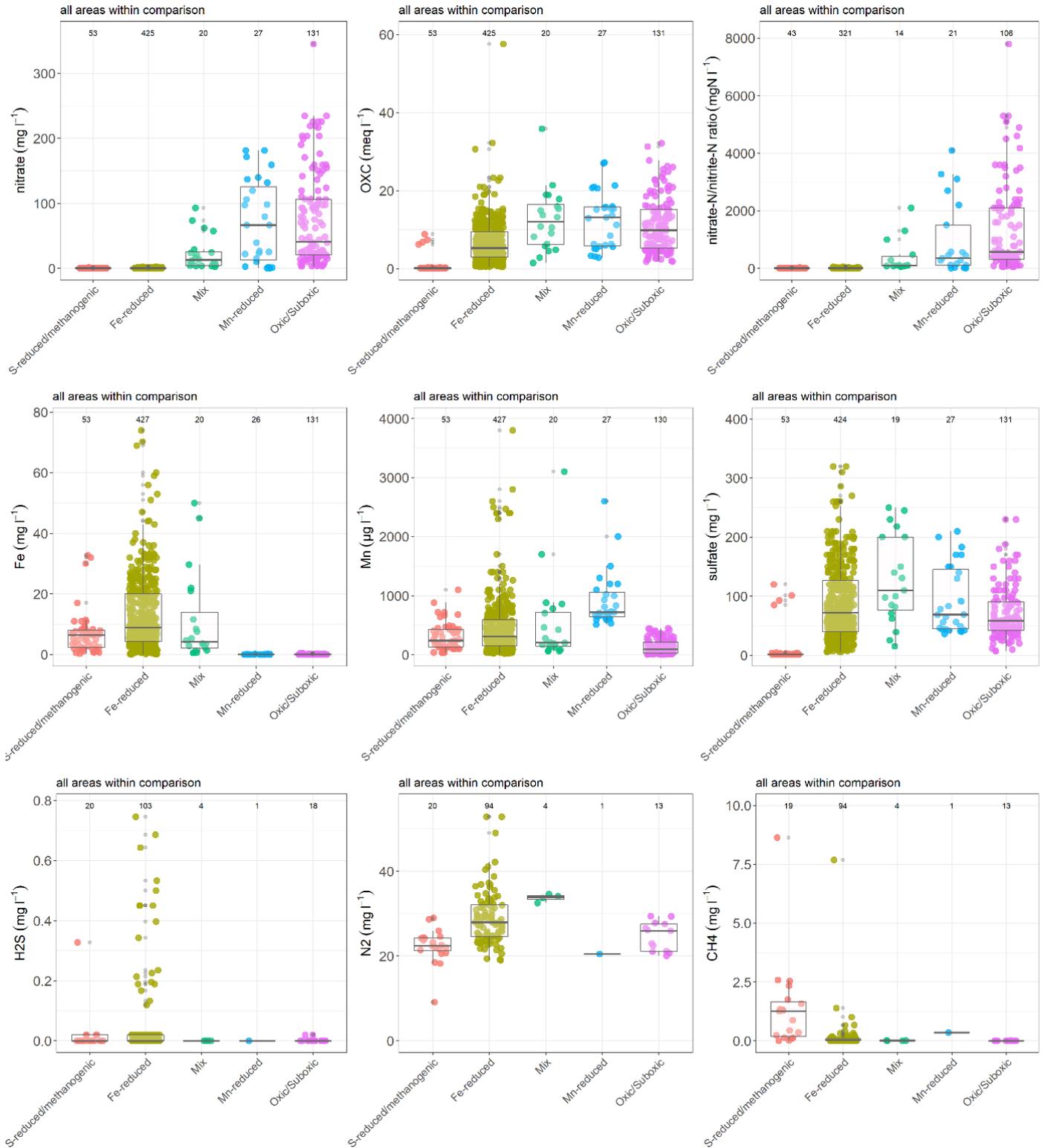
Figure 3.42 Jitters and boxplots of nitrate (mg/l), OXC (meq/l), nitrate-nitrite ratio (mgN/l), iron (mg/l), manganese (μg/l) and sulfate (mg/l), H₂S (mg/l), N₂ (mg/l) and CH₄ (mg/l) per redox class

for all areas within comparison (agriculture, nature, urban areas, areas influenced by Meuse and discharge areas)

For datasets for which a complete gas characterization would be available, we suggest adding two intermediate classes to a more sophisticated redox classification tree:

- A class "Sulfate reducing" in between the classes "Fe-reduced" and "Sulfate reduced", where the new class is characterized by waters that contain both sulfate and H_2S. The class Sulfate-reduced is then solely used for waters that do not contain significant amounts of sulfate, indicating that the process of sulfate reduction is complete.
- Separate the class "Methanogenic" from the class "Sulfate-reduced", to be based on the presence of $CH_4 > 1$ mg/l in the "Methanogenic" and presence of $H_2S > 0.1$ mg/l but no methane in the "Sulfate-reduced".

A detailed study on H_2S concentrations in Brabant groundwater (Broers et al. 2015) revealed that high concentrations of H_2S in our pilot region coincide with waters with high iron and sulfate concentration and low pH (< 5.5). Not measuring H_2S in these waters places those samples in the iron-reducing redox class. Clearly, systematic monitoring of H_2S would improve the redox classification. We tested whether those high Fe, high SO4 and sulfide containing waters have any hits of the pesticides that were investigated in this study. Typically, none of the investigated pesticides showed hits above the detection limits, except for two screens with low concentrations of desphenyl-chloridazon (wells 1807_2 and 1832_2). Relative to the large number of hits in the Fe-reducing redox class (Table 4.1) the newly identified sulfate-reducing waters are very low in pesticide founds.

3.7.2 N_2 and redox classification

As denitrification happens at relatively shallow levels in Brabant groundwater (see section 3.6) the reaction product N_2 is produced at relatively shallow level as well. Previous studies of Visser et al. (2008, 2009b) showed that this may even lead to a N_2 gas phase and degassing under certain conditions and that the Total Dissolved Gas pressure (TDG) is an important indicator for this process. This is illustrated in Figure 3.43 showing the relation between dissolved N_2 and the TDG as measured using an Alpha-TDG meter during sampling. Most samples range between the N_2 concentration at equilibrium with the atmosphere around 20 mg/l and 50 mg/l in samples with 2 atm gas pressure, which is at the limit of the equipment's measuring range. Exceptions are a small number of samples with TDG determined by CH_4 (lower part of the graph, sulfate < 5 mg/l). Clearly, high concentrations of N_2 coincide with high sulfate indicating that pyrite oxidation is an important process in the denitrification (e.g. Zhang et al., 2009, 2013).
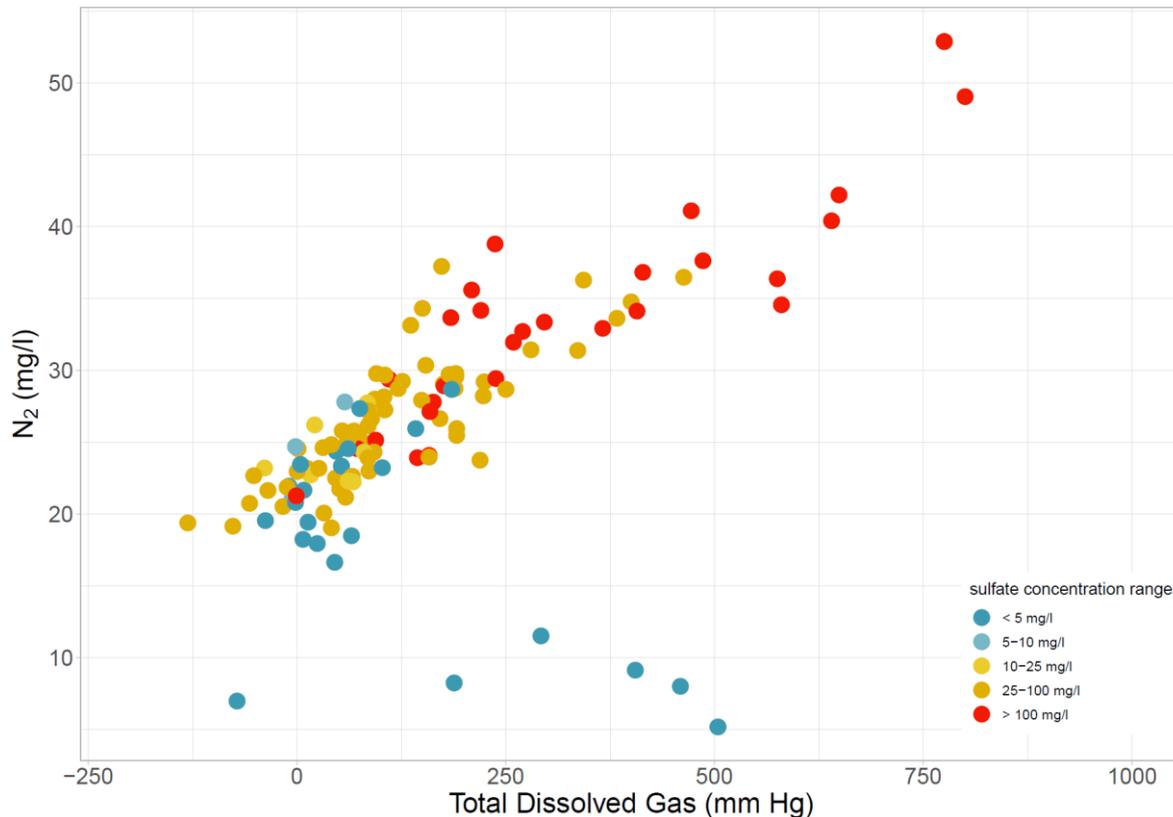
Figure 3.43 Relation between N_2 concentrations of total dissolved gas pressure, classified following sulfate concentrations

We tested how the samples with higher N_2 concentrations are classified in the classification tree of section 3.5.3 (see Figure 3.42, lower panel). Elevated N_2 concentrations above atmospheric equilibrium were mainly found in the redox classes "Mix" and "Fe-reduced", with highest concentrations and largest abundance in the Fe-reduced class. This provides further evidence of subsurface denitrification that elevated the sulfate and N_2 concentrations as reaction products during the process of pyrite oxidation coupled to nitrate reduction (Figure 3.43, Zhang et al. 2009). Following the presence of elevated N2 in the "Oxic/suboxic" class also indicates that denitrification has started or is ongoing in part of the waters that still contain nitrate. Measurement of N2 would specifically help to identify those wells where nitrate reduction is ongoing.

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3.9 CASE STUDY CYPRUS

3.9.1 Description of the study (studies) carried out and outputs

In Cyprus denitrification is found to be active in thick unsaturated zone and where clay layers predominate. Denitrification was studied rather systematically, in 2009 and 2010. During these period, the Geological Survey Department (GSD) collected 135 groundwater samples from 12 Ground Water Bodies (GWBs) of Cyprus and the isotopic composition of nitrate molecules (15N/14N and 18O/16O), was determined. The objective of these studies was to investigate the isotopic composition of nitrates in groundwater samples in order to identify primary and secondary nitrate sources (Hoefs 1997, Clark and Fritz 1997) as well as to evaluate denitrification potential of Cyprus' GWBs (Amberger and Schmidt 1987, Bottcher et al. 1990, Durka et al. 1994).

Cation exchange and neutralization with KOH was used to separate dissolved nitrate molecules in groundwater samples. Sulfate and phosphate were first eliminated with BaCl2 precipitation and samples were then evaporated to dryness. They were heated to 570 °C together with graphite under vacuum and converted to N2 and CO2. Cryogenic separation was used to separate and then determine the isotope ratio of these two gases, via mass spectrometry. A mass spectrometer "MAT-251" with double inlet system was used. The mass spectrometer was calibrated daily with international standards (N-3, SDGS 34, USGS 35). Uncertainty of the isotope results is ⍰0.5 ‰. (Christophi and Constantinou, 2011).

It was concluded that the dominant primary source of nitrates in groundwater samples from rural Cyprus is fertilizers. A secondary nitrate source with an isotopic signature of organic source was found to contribute, in 21% of the samples. This organic source is, for the most part, assumed to be manure. In 16% of the groundwater samples from seven GWBs, manure was identified as the primary nitrate source. Denitrification was sporadically evident in 21% of the samples from seven GWBs. Two GWBs, Germasogia (CY_7) and Central-Western Mesaoria (CY_17) appear to have significant denitrification potential. The former is an alluvial aquifer and the latter a multilayer (alluvial-clastic) aquifer with conditions ranging from unconfined to confined.

3.9.2 References

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3.10 CASE STUDY DENMARK

3.10.1 Introduction

The Danish groundwater monitoring programs GRUMO and LOOP classify groundwater redox types according to the classification tree shown in Figure 5.1. The classification system are used to understand and assess the fate and migration of nitrate (Postma et al., 1991; Jakobsen et al., 2019) and other redox-sensitive contaminants (Hinsby et al., 2007) in Danish groundwater bodies.
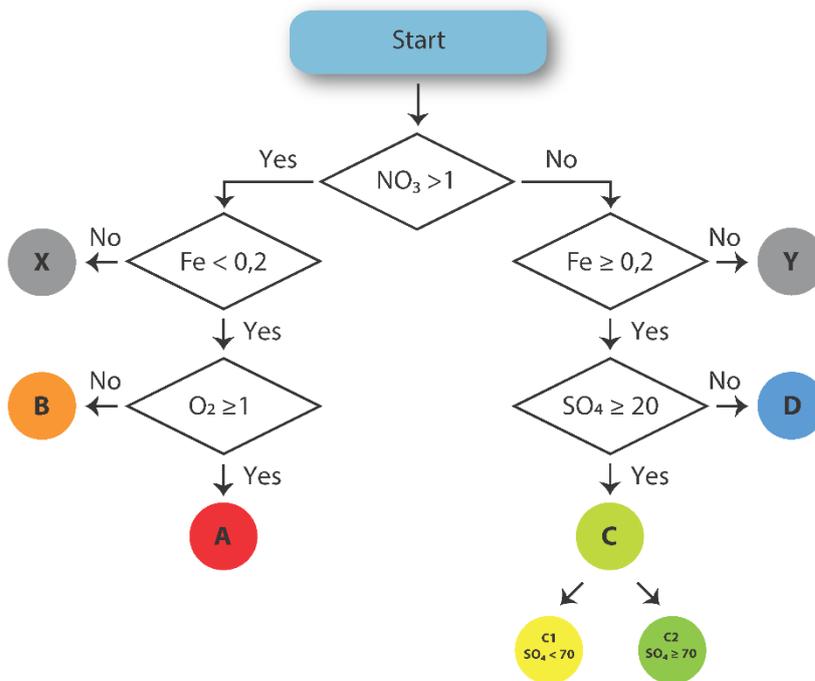
Figure 5.1 Algorithm used for classification of the redox conditions of groundwater in the Danish groundwater monitoring programs (Hansen and Thorling, 2018).

Samples collected in the groundwater monitoring networks GRUMO and LOOP in 2018 were recently classified according to the redox types defined in Figure 5.1 (Table 5.1; Thorling et al. 2019, appendix 2).

Table 5.1 Number of samples within the different redox classes applied in the Danish groundwater monitoring programs GRUMO and LOOP in 2018 (Thorling et al., 2019).

2018		Number of samples	Number of sampling points	Oxic samples (Type A)	Anoxic samples (Type B)	Reduced samples (Type C & D)
GRUMO		1109	884	468	124	292
LOOP		328	83	43	18	32
	LOOP 1 (ler)	41	16	2	6	8
	LOOP 2 (sand)[1]	58	15	7	2	6
	LOOP 3 (ler)	74	19	14	5	0
	LOOP 4 (ler)	50	14	7	2	5
	LOOP 6 (sand)	105	19	13	1	5
ler = clay; sand = sand indicate the main lithology at the LOOP monitoring sites						

The GRUMO groundwater monitoring network consists of sampling points down to a depth of about 100 m distributed at national scale. The LOOP program consists of sampling points installed at plot scale down to approximately five meters depth within saturated and unsaturated zones in five sandy and loamy agricultural areas. The redox interface in phreatic sandy aquifers is typically found at depths of more than 20 meters as e.g. found and described by Postma et al. (1991), while it in clay till areas typically is found at depth of less than five meters (Jakobsen et al., 2019). Further details of groundwater monitoring and modelling in Denmark may be found in other HOVER deliverables (Ascott et al., 2020, Broers et al., 2020) and (Hinsby and Jørgensen, 2009).

Figure 5.2 shows the percentage of nitrate in different concentrations intervals at different depth intervals.The figure illustrates the increasing amount of reduced water types without nitrate with depth (Thorling et al. 2019). Red indicate nitrate concentrations above the drinking water standard of 50 mg/l nitrate.
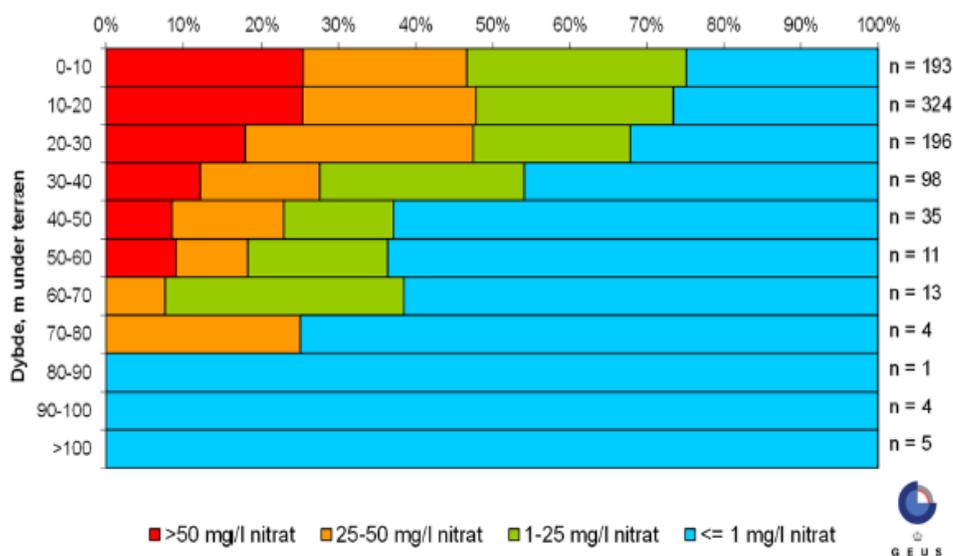

Figure 5.2 Illustration of nitrate concentration intervals at different depths (Thorling et al. 2019).

3.10.2   Denitrification concept considered

We consider denitrification potential and nitrate retention in groundwater and surface water at small catchment and national scale as assessed by the Danish National Nitrogen Model (Højberg at al., 2015) and a national map of the depth to the redox interface controlled by the sediments and rocks of the groundwater bodies (Figure 5.3, Koch et al., 2019). A recent more detailed investigation of the distribution of the redox interface at local scale is described by Kim et al. (2019).
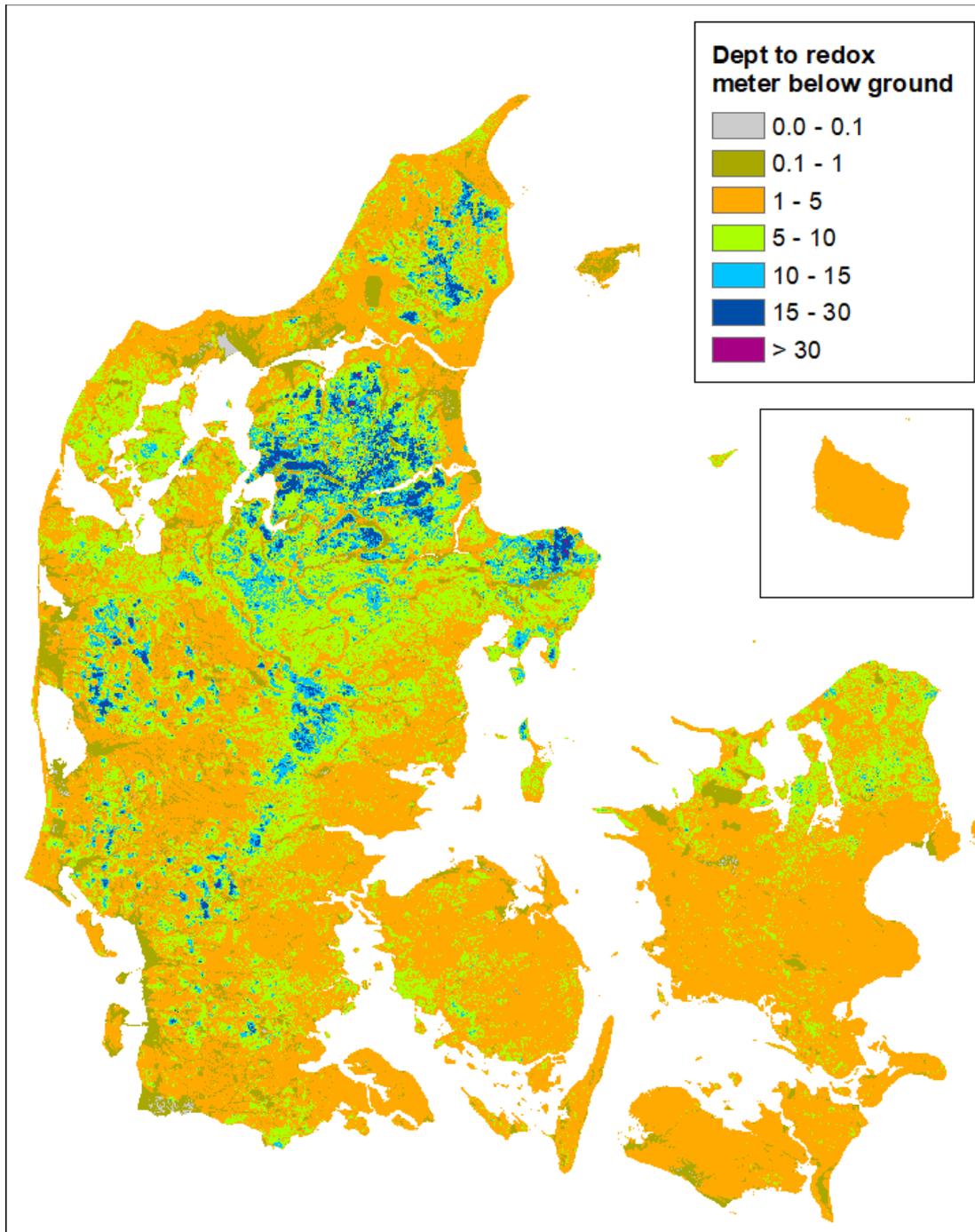
Figure 5.3. Depth to redox interface in Danish groundwater bodies based on geological information from the Danish borehole database at GEUS, expert knowledge and machine learning (Koch et al., 2019).
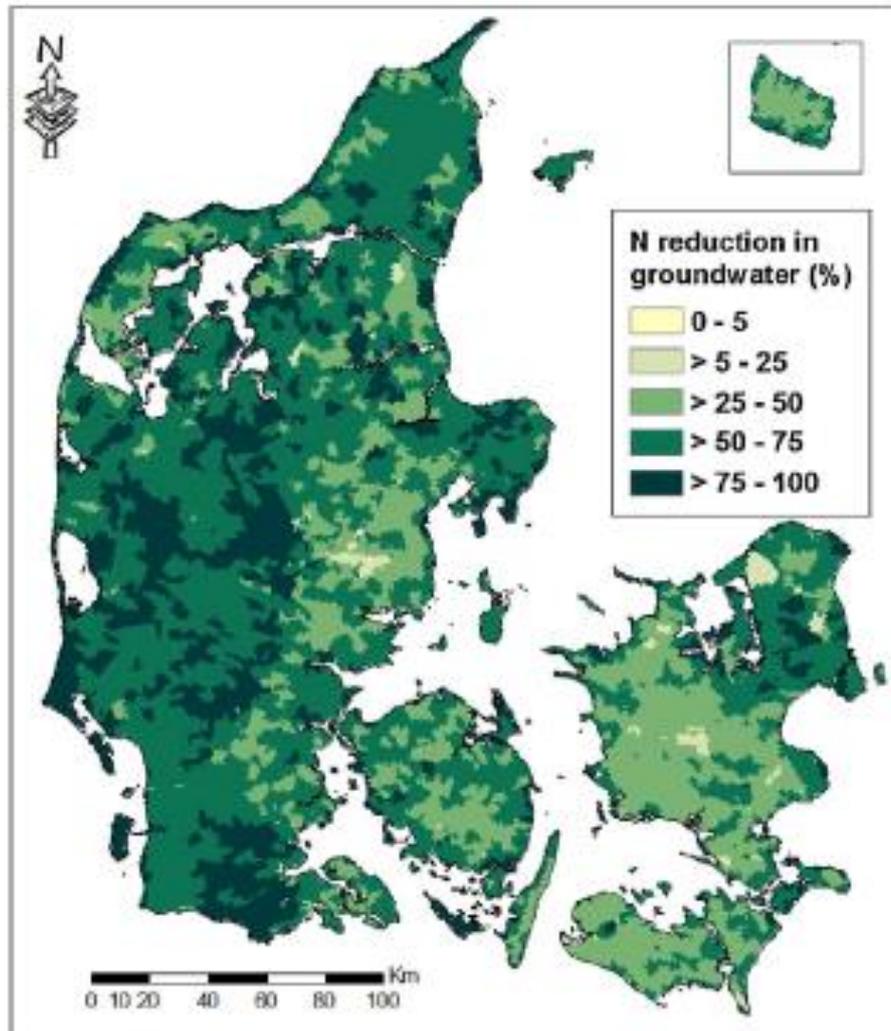
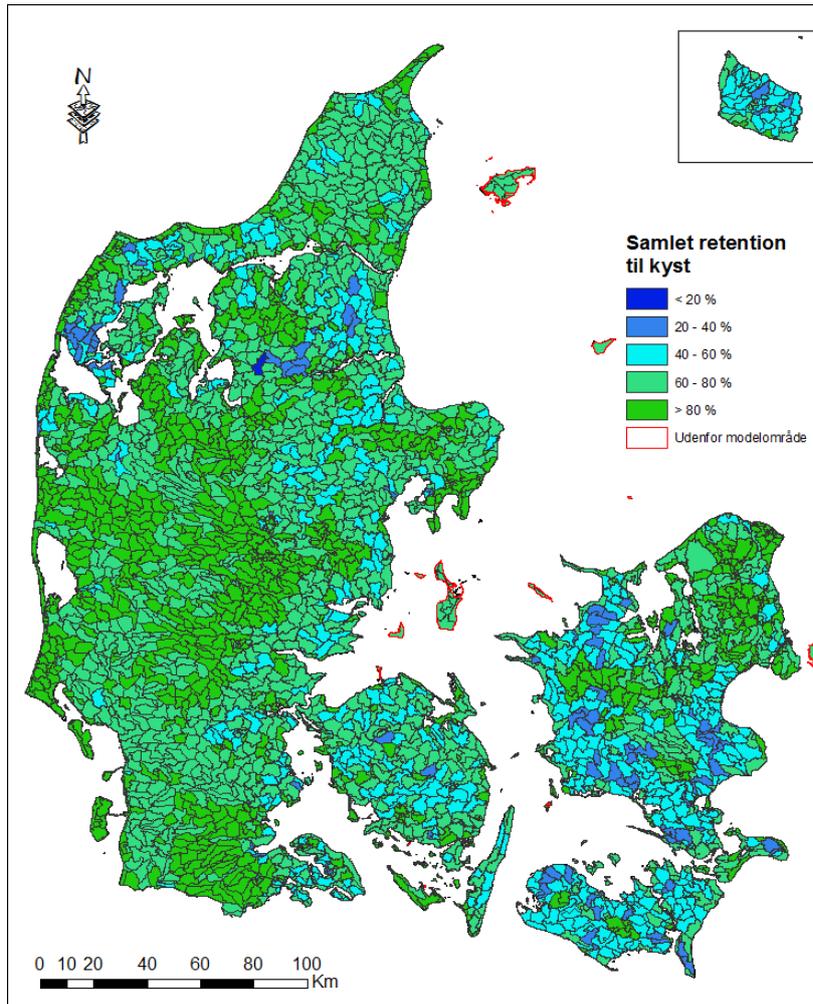Figure 5.4. Nitrate reduction in groundwater in Denmark (Højberg et al., 2017)

Figure 5.5. Nitrate retention in groundwater and surface water between soils and the coast in Danish agricultural subcatchments (ID15, Højberg et al., 2015).
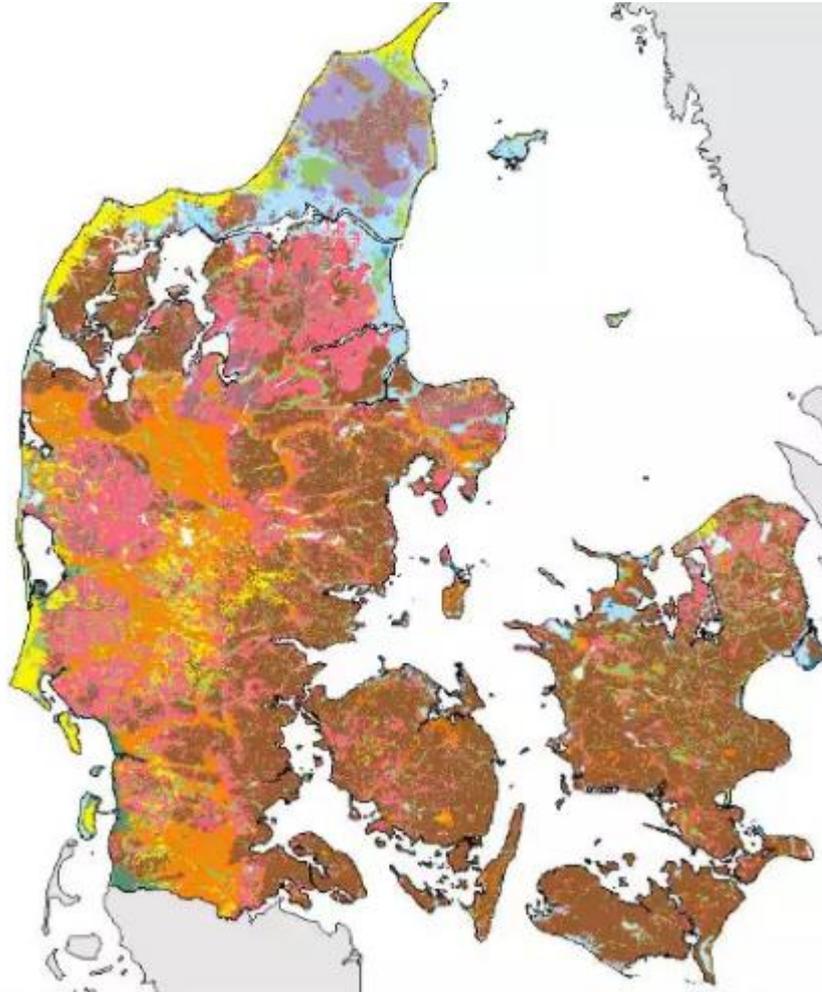
Figure 5.6. Geological map of Denmark showing Quaternary mainly Pleistocene sediments of the Danish subsurface. Brown colours indicate clayey tills deposited during the Weichselian glaciation, which is typically intensively drained. Orange and pink colours are glacial outwash sand and gravel (GEUS, 2020).

Areas illustrated by brown colours in Figure 5.6 will generally have shallow redox interfaces at less than five meters depth (Jakobsen et al., 2019), while the redox interface is found at depths of typically more than 20 meters in orange and pink areas due to smaller contents of reducing minerals and reactive organic carbon (Postma et al., 1991).

Hence, nitrate concentrations and removal are highest in groundwater bodies in the orange and pink areas. Typically, nitrate concentrations are already reduced before reaching deeper parts (> 5m) of groundwater bodies below brown areas (Jakobsen et al., 2019), but the brown areas have high nitrate loadings via drainage systems directly to streams and coastal waters (Hinsby et al. 2012).

3.10.3   References

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4 METHOD PROPOSED FOR HOVER

4.1 Type of product to be prepared

Within HOVER project we propose a simple method to be applied in different case studies in order to propose a Pan European map of Redox conditions in groundwater, map that could be extended by time with new case studies or national scale application of the proposed method.
The method should use data available in many countries and be applicable at groundwater body scale. Due to the great variability of methods used for monitoring and aquifer types the method proposed does not pretend to give precise and accurate information on redox processes in aquifer but should permit to distinguish oxid to anoxid environment and mix conditions.

4.2 Description of the method

From the case studies presented it appears than the methods that can be applied at large scale using existing data are based on the use of redox sensible parameters and indicators, O2, Eh, NO3, NO2, NH4, SO4, DOC, Fe and Mn. The use of N isotope ($\delta^{15}N/\delta^{18}O\_NO3$) is quite powerful however cannot be proposed for large scale studies.

In the USA (USGS), Netherlands/Flanders (N/F), France, UK quite similar approaches were used in order to define the oxic/anoxic groundwater. The data used in the different methods are logically the elements informative of redox status and usually included in the GW monitoring programs, dissolved O_2, Mn, NO_3, Fe and SO_4 and the potential Redox indicator (Eh). The threshold concentrations of cited elements in groundwater are used to define the redox categories. The threshold values (in mg/L) collected in various case studies collected among GEOERA partners, the USGS study (factsheet 2009) and Hinckle & Tesorerio 2014 can be found in *Limit of Quantification usually found in GW database* Figure 44.

Parameter	France	H&T 2014	UK	NL/Flander	DK	USGS	LoQ*
Eh							
O_2	2	1.9	1	2	1	0.5	0.5
N			1	*0.45*		0.5	
NO_3+NO_2			1				
NO_3				2	1	*2.21*	0.5
NO_2							0.01
NH_4			0.3				0.01
Fe^{2+}	0.72	0.72	0.1	0.5	0.2	0.1	0.002
Mn^{2+}	0.14	0.14	0.1	0.5	0.1	0.05	0.001
SO_4			0.5	5		0.5	0.5
DOC			3				0.5
CH_4				1			

Limit of Quantification usually found in GW database
Figure 44: Threshold values used in some countries/studies for denitrification and redox classification (in mg/L)

4.3 Data available

From the questionnaire sent at the beginning of HOVER project it appears that most of the elements cited in the chapter 5.2 are available in the different EU countries participating in WP5 however:
- N_2 excess is not measured (except in UK)
- O_2 and Eh are quite often missing or not measured
- O_2 is not a reliable parameter
- NO_2 is measured sometime together with NO_3 (sum of NO_3+NO_2)

A method than could be applied to many EU countries within HOVER projects may then rely mainly on NO_3, NH_4, NO_3, Fe and Mn. Other parameters such as SO_4 or DOC may be useful to determine the degree of reduction (S reduction, methanisation,…), information not requested in this study.

4.4 Decision trees/classification table

The decision tree obliged prioritizing the entry element, the tree can then allow a redirection of samples (ie French case study) in case of bad quality of data. A choice of a defined number of categories based on the concentration of samples in all the key elements is another possible approach.

In order to propose a first classification table/trees, a test was realised for a well-known study area in France, the Bassee alluvial plain (FRHG006). We know that the alluvial aquifer at the right bank of the Seine River is mainly under anoxic condition leading to clear denitrification comparing to the left bank influenced by a deepest aquifer recharge (Gourcy et al., 2000).

For the oxic water (confirmed by Eh, NO3>25 mg/L, complete geological and hydrogeological study):
- the Fe and Mn concentrations are below LoQ (0.001 mg/L).
- O2 (mg/L) varies from 2.7 to 7.2 mg/L
- NH4 is below LoQ (0.05 mg/L)
- SO4 highly variable
- NO2 only very low % with some concentration closed to the LoQ and <0.03 mg/L
- COD 0.56 to 0.9 mg/L

For the anoxic water (NO3 <2 and complete geological and hydrogeological study)
- the Fe concentrations are >1.8 mg/L
- The Mn concentrations are >0.19 mg/L.
- O2 (mg/L) varies from 2.7 to 7.2 mg/L
- NH4 is >0.16 mg/L up to 32 mg/L
- SO4 variable
- NO2 is >0.03 mg/L
- COD 0.56 to 0.9 mg/L

In the French database, O_2 seems to be not very reliable, Eh and DOC not always measured so should not be mandatory for the decision tree/table. Eh is sometimes not corrected to NHE so not reliable neither. Sulphate is more linked to pressure/lithology than redox condition. NO_2 can be present in oxic condition (highly vulnerable wells, badly constructed) and very few values higher than LoQ. So, from the dataset used for testing the method, the 4 more reliable parameters of the French dataset are NH_4, NO_3, Fe and Mn.

After a short discussion with countries proposing case studies (UK, NL/Flanders, DK, FR) it was proposed to use a decision tree in order to give more flexibility in case of use of a great number of data from monitoring networks of different quality.

The more reliable parameters to be used are NO_3 (or N but concentration recalculated in NO_3) and Fe. NH_4 and O_2 could be additional parameters of interest but cannot be key parameters of the decision tree. So it is proposed 2 mandatory steps and 2 additional steps to be selected depending on data available (use of NH_4 or O_2).

Oxic and anoxic conditions are clearly defined while the mix category could integrate various specific cases :

- water supply wells with long screens – mixing of deep water (anoxic) with more superficial water due to pumping
- no pressure environment – no nitrate in oxic environment possible
- semi-reductive aquifer – Redox conditions variable in space and time, depend on pumping/water level conditions
- mixing of water from two different aquifers (or layers or surface water) one oxic and the other anoxic

Caution: the Fe and Mn concentrations may be very different if water sample is filtered or not. Great care should be taken to raw data for these two elements. Filtered samples are more reliable.

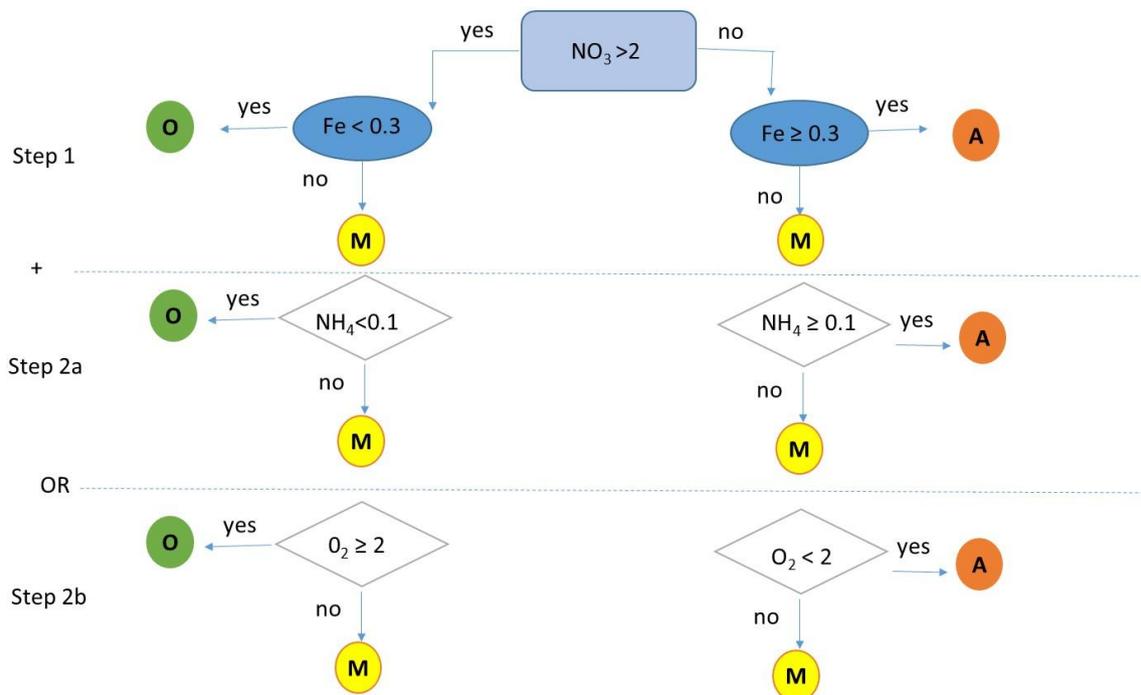Using these 4 parameters we can propose a first classification table ().

Figure 45: Proposed classification tree

The minimum requirements is to carry on step 1 of the method. If NH_4 or O_2 reliable data in the GW database it is possible to add one step to the decision tree. Step 2a and 2b are not meant to be executed one after the other, only one should be selected.

Data to be used could come from a major sampling campaign or the mean or median of various sampling campaigns in the same monitoring wells.

The decision tree can be apply for each sampling point of an aquifer or one the mean/median values of all sampling points of the aquifers.

Netherland/Flanders made a first test using the proposed decision tree and the results are as following:

Count of nwtree	Column Labels ▼			
Row Labels ▼	anoxisch	mix	oxisch	Grand Total
Fe-reduced	474	3	1	478
Mix		15	5	20
Mn-reduced	5		23	28
Oxic/Suboxic		1	129	130
Sulfur-reduced/methanogenic	95			95
Grand Total	574	19	158	751

474 out of 478 Fe-reduced are judged to be anoxic: 99% of results fine
15 out of 20 Mix are judged to be mix : 75% of results fine
129 of 130 oxic/suboxic are judged oxic: 99% of results fine
All sulfur-reduced were anoxic: 100% of results fine
Mn-reduced was split into 5 anoxic and 23 oxic what is quite fine for the goal

The test succeeded with a set of samples for which all nitrate, iron, ammonium and oxygen concentrations were registered. This is for short screened observation wells screened up to 30 m depth. So no physical mixing through pumping. In total, 76% of our pilot area samples are anoxic, 21% oxic, and 3% mix.

France carried out tests at for two groundwater bodies where denitrification is well known and for granite (Leon, FRGG001) and Chalk of the Canche valley (FRAG005).

For Leon, carrying out the test using average values at point sites and individual calculation:
25 monitoring points – <LoQ were transformed by LoQmin/2.

Result of Step 1 average values:
3 monitoring point anoxic – also Mn>0.15, O_2 <4.85, NH4 from 0.02 to 0.04
22 monitoring point oxic – Mn<0.15, O_2 from 4.5 to 9.11

Result of Step 1 individual set of analyses with at least NO_3, Fe and Mn measured (n=298, p=25):
19 samples anoxic – Mn>0.11 (up to 10), O_2 from 2.3 to 6.3
3 samples mix – NO_3<2 but Fe <0.3 (0.005 to 0.038) – Mn 0.13 to 0.8
275 samples oxic – Mn from <LoQ to 0.15, O_2 from 1.5 to 10

Using Step2a for the 3 mix samples, NH_4 <0.1 then samples remains in mix
Using Step2b for the 3 mix samples, O_2 is >2 then samples remains in mix

NH$_4$ and O$_2$ cannot be used for this dataset, ammonium because of the LoQ and low values and O2 because of high uncertainty. The proposed method gives results corresponding to the known redox status in this aquifer.

For the chalk aquifer in the Canche valley; 45 sampling points
Result of Step 1 – All 45 point oxic

For the individual set of analyses with at least NO$_3$, Fe and Mn measured (all points, 1802 concentrations, 43 set of data):
4 samples mix – NO$_3$ <2; Fe <0.3, O$_2$ from 6.4 to 8.8 and NH$_4$ below LoQ and Mn<LoQ
4 samples mix - NO$_3$ >2; Fe >0.3, O$_2$ from 6.6 to 9 and NH$_4$ below LoQ and Mn<LoQ to 0.08 (concern only 1 sampling point, 4 different samples)
1798 samples oxic - NO$_3$ >2; Fe <0.3, O$_2$ from 0.4 to 10 and NH$_4$ from LoQ to 0.62 and Mn<LoQ to 0.08

Step2 for the 4 sample "mix" with NO$_3$>2, NH$_4$ is below LoQ and O$_2$ higher than 2 indicating oxic water. Step 2 for the 4 samples "mix" with NO$_3$<2, one has NH$_4$ of 0.64 and O$_2$ of 1.2 so can be anoxic while the three others remained in mix.
As a synthesis, 1 anoxic, 5 mix and 1799 oxic

4.5   Mapping

For each monitoring point the proposed method will allow us to have three water categories, oxic, anoxic, mix. In the case studies and literature explored in this deliverable there are various proposed representation of data distribution:
-    Point information and aquifer potential denitrification
-    Point information and 2D depth of complete denitrification/redox estimation
-    Point information and spatial display by modeling of denitrification/depth to the redox interface
-    Point information extended to aquifers using frequency of denitrification potential
-    Pie chart indicating the % of well that were oxic, anoxic and mix

4.6   Perspectives

It is proposed, to carry on some tests using subdataset in order to validate the proposal and compare the results to the results obtained already and to present the data in pie chart at EU scale (or other depending on the number and extend of case studies). The maps will be published within D5.5.

Supplementary material from Netherland case study

Appendix A: Validation of the provincial data

Validation of the provincial data

As mentioned in paragraph 3.4.2, both measurements from the provincial and the national monitoring network are combined in the monitoring network for the WFD in the Sand-Meuse region. The national groundwater monitoring network is managed by the RIVM, the National Institute for Public Health and the Environment (or 'Rijksinstituut voor Volksgezondheid en Milieu'). The national monitoring network of the RIVM contains a number of wells which are also measured by the provinces. The sampling and laboratory analysis of these two monitoring networks are done independently from each other since 2010. As both the RIVM and the provinces sample and analyse the wells quite often, there are many cases where the same well is measured twice a year. This allows for the direct comparison of these measurements, which can help to validate the groundwater quality data that is used in this deliverable. Below, several figures are given for NO_3, SO_4 and Fe, which make the comparison between the provincial data and the data of the RIVM. The figures are given for all years together (2010-2018) and for the years in which the sampling for the pesticides as mentioned in paragraph 1.4.1 was done (2012, 2016 and 2018).

Two comparisons between the data from the province and the RIVM are given below for each parameter. The comparisons are made between measurements which have been carried out in the same filter of a monitoring well within the same year. First, the difference of the provincial data in relation to the RIVM measurements is given expressed as a percentage, calculated as follows:

$$\frac{abs(Measurement_{RIVM} - Measurement_{province})}{Measurement_{RIVM}} * 100$$

Or in words: the absolute difference between the RIVM and provincial measurement divided by the measurement from the RIVM. The measurements are divided in four groups: less than 10% difference, between 10% and 20%, between 20% and 30%, and more than 30% difference.

The second comparison is made on basis of sampling data: a distinction is made between measurements that were sampled within one month of each other and samples with a longer time between them. Different icons are also used in the figures to distinguish between shallow (<10 m below surface) and deep (>10 m) filters. In the bar charts the measurements are divided in the same groups as the previous images, but here with a distinction between the deep and shallow filters as a percentage of the total amount of filters in those categories.

NO_3

Erreur ! Source du renvoi introuvable. shows the provincial measurements in relation to the data from the RIVM. In general, most of the measurements fall within the <10% group, indicating that there is not much difference between these datasets. For NO_3 there is a large group of samples near or at detection limit. For these figures, those values are equalled to each other so that a difference in detection limit between two laboratories is not seen as a difference in the actual concentration. There are about 45 measurements where there is >30% difference between the provincial and RIVM sample, in the higher concentration ranges these differences can be quite big (e.g. the province measures 10 mg/l where the RIVM measures 110 mg/l), although in general the concentrations are comparable. The extremes also go both ways, it's not the case that either the province or the RIVM is consistently measuring higher or lower concentrations than the other group. For the sample years of

the "Brede screening" of 2012, 2016 and 2018 the image is nearly equal to the figure for all years. So, in general, there is a small difference between the two data sets although there are some points with a large difference.
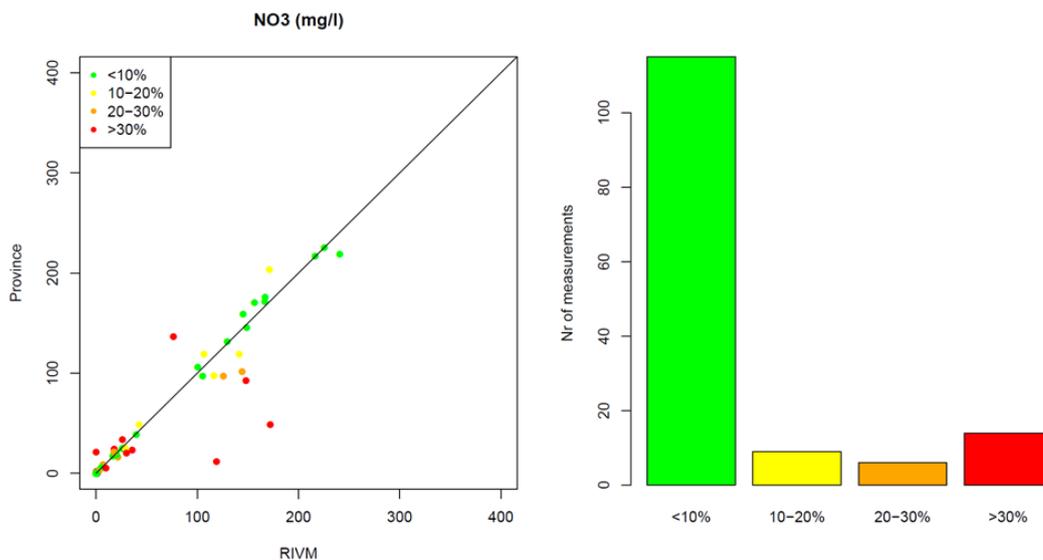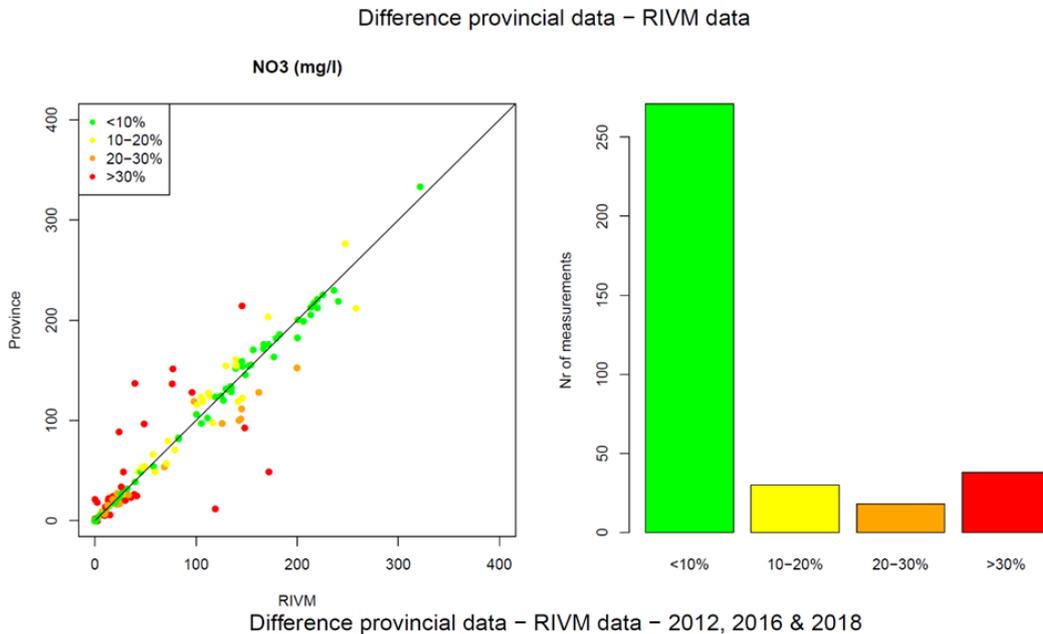

Figure 4.3 Difference between the NO_3 measurements in mg/l of the province in relation to the measurements of the RIVM taken in the same year. The top figure is for all years from 2010-2018, the bottom figure is for the years of the "brede screening". The line in the scatterplot indicates the 1:1 line.

Erreur ! Source du renvoi introuvable. shows the relation between the two data sets with a distinction between the difference in sample date and depth of the filter. This figure indicates that samples taken within one month of each other are generally more alike than samples with a longer time period between sampling. For the years of the "brede screening" it seems that this is less of an issue, here the two groups are very similar. The relation to the depth of the filter is not very clear, although it seems that there are more points with a large difference for the shallow filters. However, this is not a fair

comparison, since in many deep filters nitrate is reduced and therefore both measurements will be at or near detection limit.
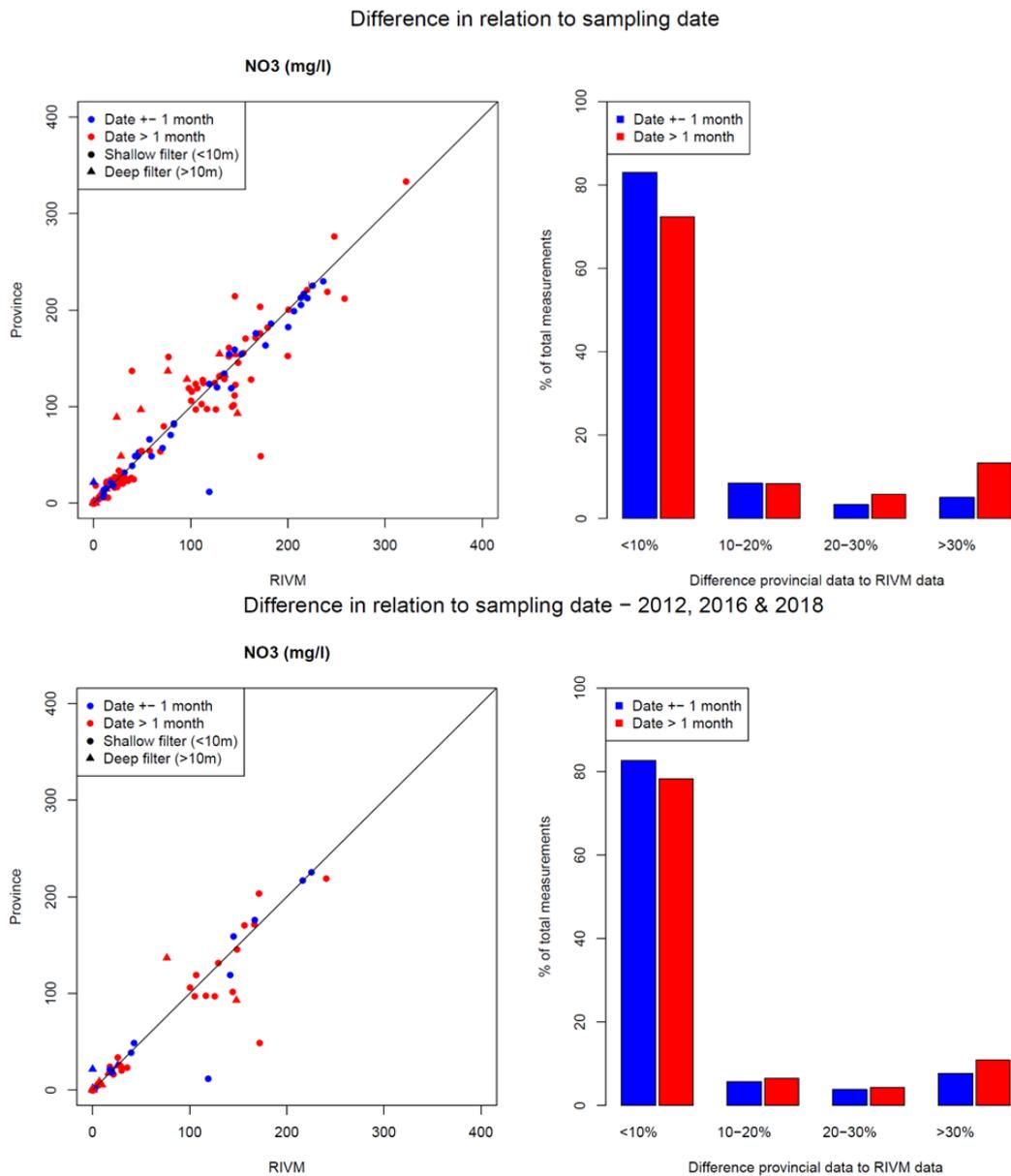

Figure 4.4 Difference between the NO_3 measurements in mg/l of the province to the measurements of the RIVM with a relation to the sampling date: in blue the samples that were taken within one month of each other and in red the samples with a longer time interval. In the scatterplot the depth of the filter is indicated with an icon, a dot for shallow filters (<10m) and a triangle for deep filters (>10m).

SO₄

For sulfate, the majority of samples yields a fine 1:1 comparison with less than 10% deviation between the province and RIVM. In general, most of the values have less than 10% difference between the provincial and RIVM data. However, compared with nitrate, the sulphate concentrations show a larger proportion of deviations over 10%, 20% and 30%. (**Erreur ! Source du renvoi introuvable.**). This could

due to the fact that there are less samples below detection limit for sulfate, thus decreasing the <10% group.

There are again some extremes, for example a measurement of the province of ~15 mg/l where the RIVM measures 160 mg/l. The sampling years of the "brede screening" again seem to perform equally to all the other years, although some of the larger extremes belong to these three years.
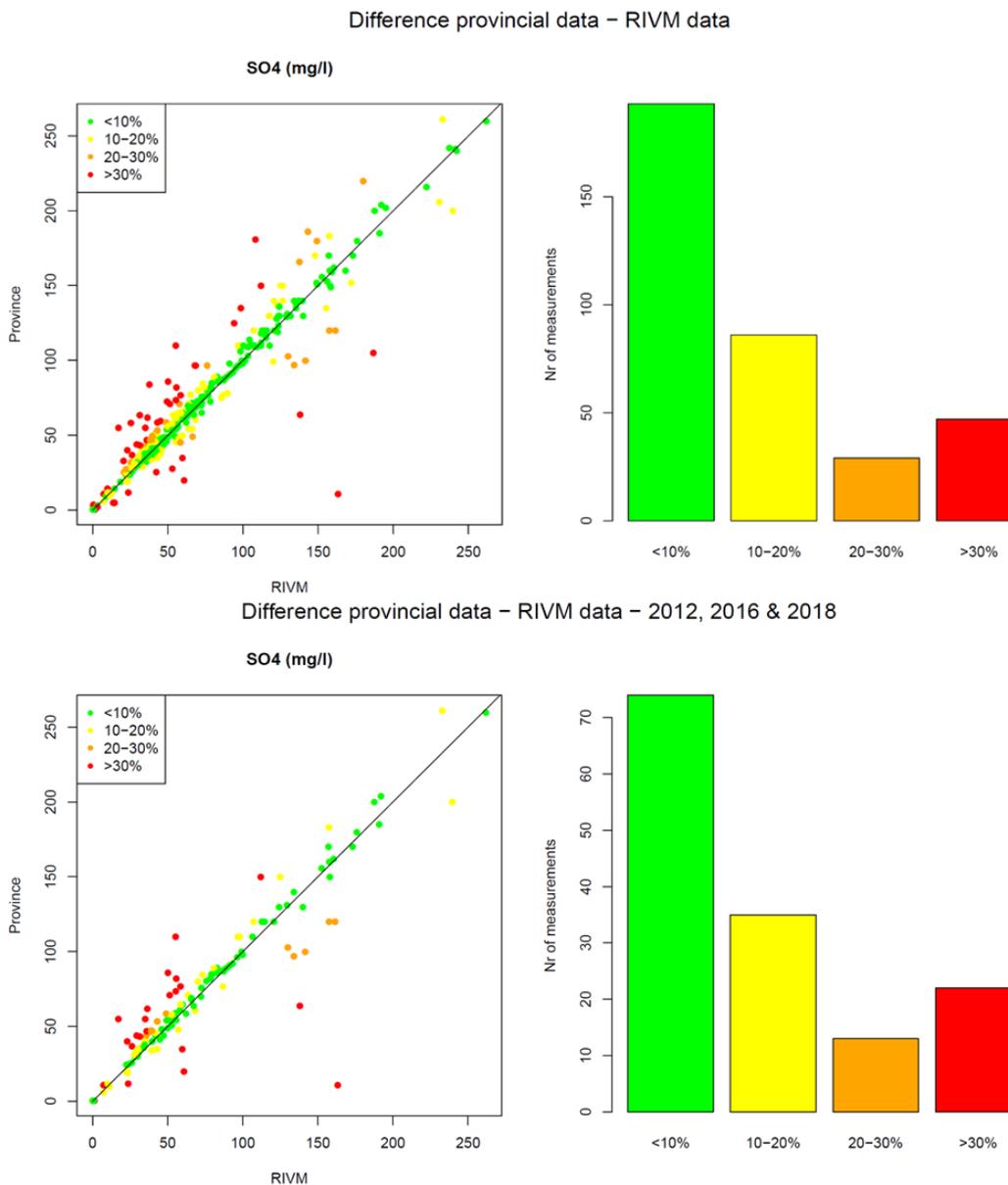
Difference provincial data − RIVM data

SO4 (mg/l)

Difference provincial data − RIVM data − 2012, 2016 & 2018

SO4 (mg/l)

Figure 4.5 Difference between the so_4 measurements in mg/l of the province in relation to the measurements of the RIVM taken in the same year. The top figure is for all years from 2010-2018, the bottom figure is for the years of the "brede screening". The line in the scatterplot indicates the 1:1 line.

Erreur ! Source du renvoi introuvable. again shows the same image but now with the relation to sampling data. Here, it is quite clear that samples taken within one month of each other are much more comparable than the other samples. This effect seems to be larger for sulfate than for nitrate,

possibly also relating to the larger amount of measurements below detection limit for nitrate. The relation with depth of the filter again shows a mixed image, with not a clear group performing better or worse than the other. The same can be said for the years 2012, 2016 and 2018, which are equal to the other years.
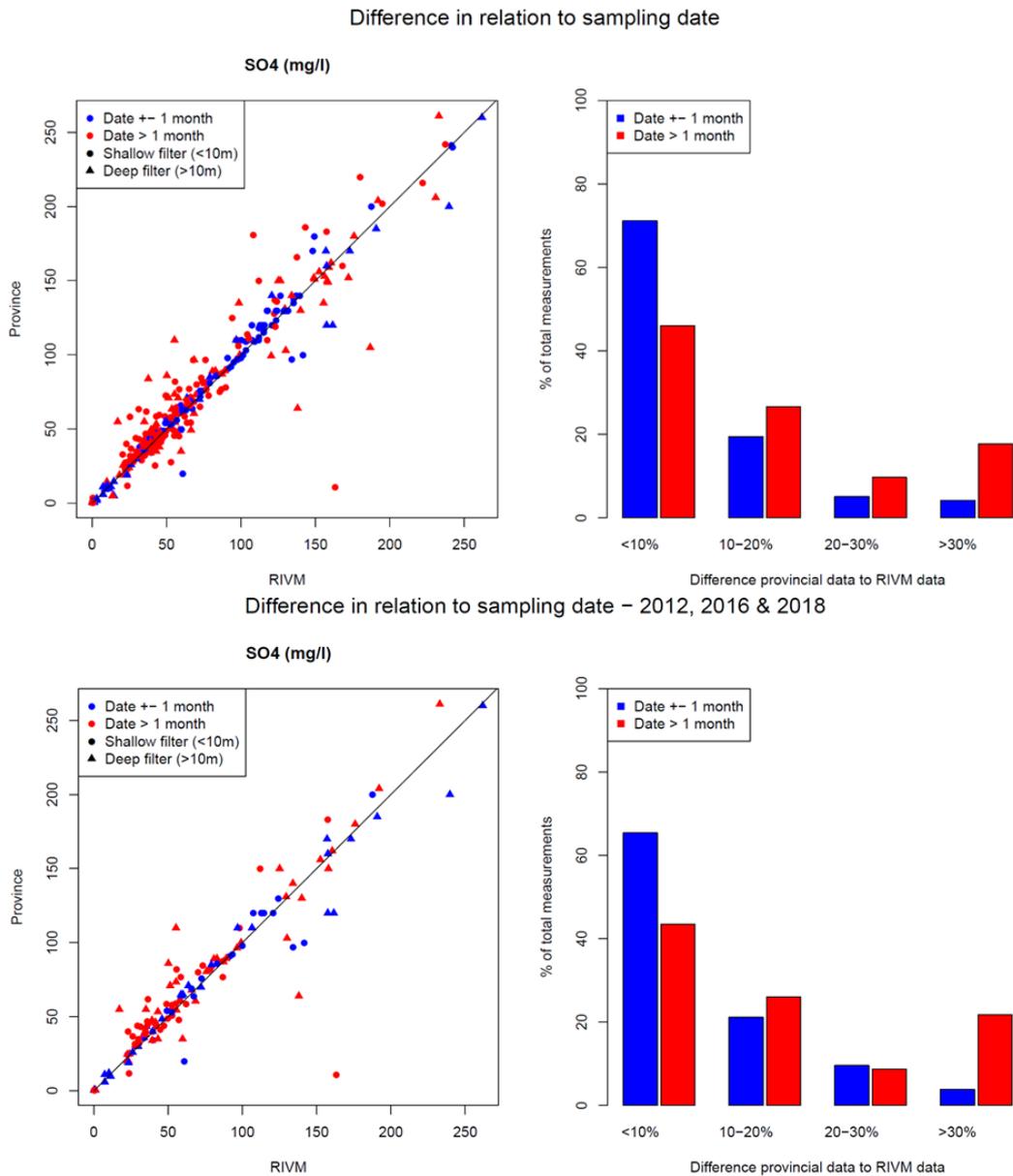

Figure 4.6 Difference between the SO_4 measurements in mg/l of the province to the measurements of the RIVM with a relation to the sampling date: in blue the samples that were taken within one month of each other and in red the samples with a longer time interval. In the scatterplot the depth of the filter is indicated with an icon, a dot for shallow filters (<10m) and a triangle for deep filters (>10m).

Fe

Erreur ! Source du renvoi introuvable. shows the difference between the provincial and RIVM data for iron. The difference here seems to be very small; most measurements fall withing the <10% difference

group. Like nitrate, this is mostly due to the large amount of measurements below detection limits, which occur in mostly shallow nitrate-containing filters. However, the scatter shows that, especially in the higher concentration ranges, most of the data falls neatly on the 1:1 line. There are some larger extremes at lower concentration ranges. In contrast with nitrate and sulfate it seems that the extremes are one-sided, meaning that the provinces tend to measure higher iron concentrations in some wells than the RIVM. However, because of the small number of samples involved it is likely that this is a coincidence rather than a consistent error.
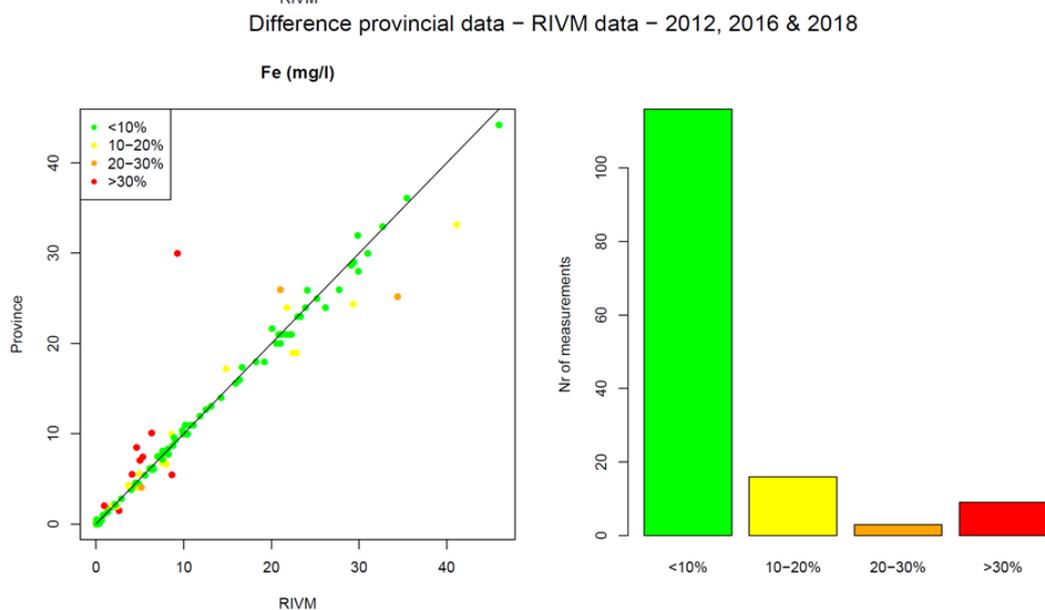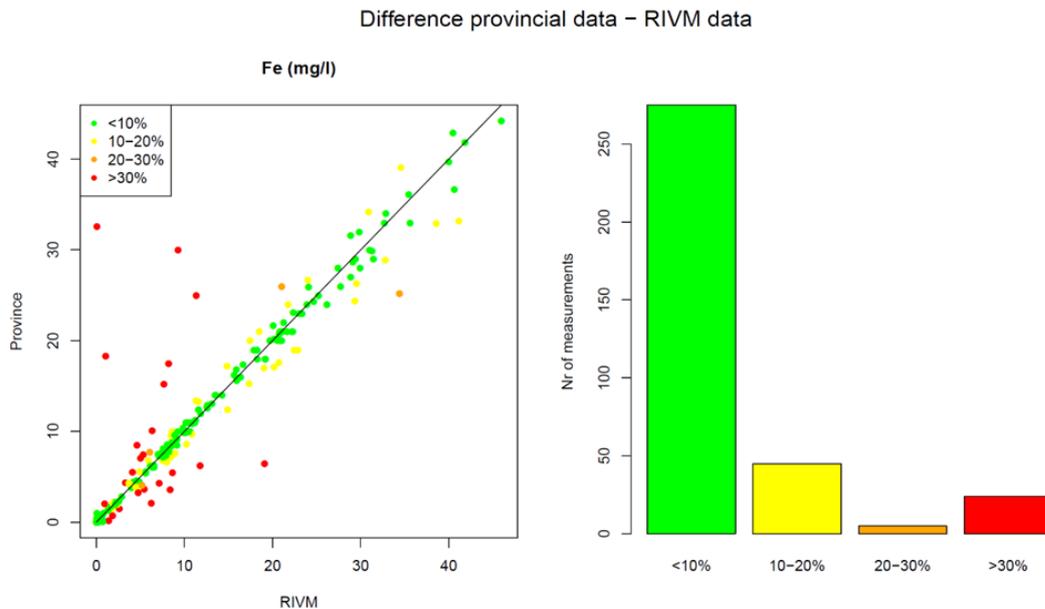

Figure 4.7 Difference between the Fe measurements in mg/l of the province in relation to the measurements of the RIVM taken in the same year. The top figure is for all years from 2010-2018, the bottom figure is for the years of the "brede screening". The line in the scatterplot indicates the 1:1 line.
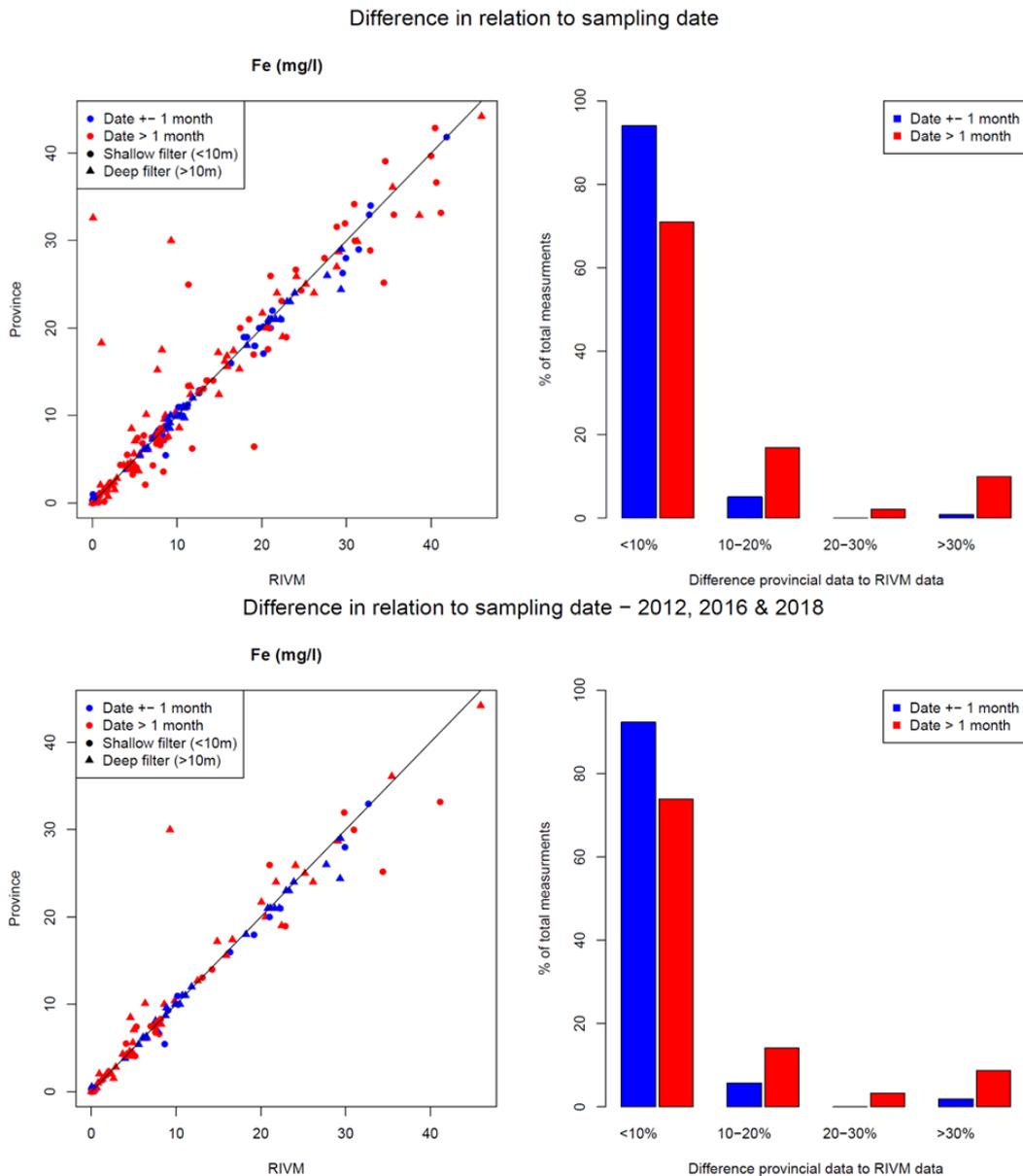
Figure 4.8 Difference between the Fe measurements in mg/l of the province to the measurements of the RIVM with a relation to the sampling date: in blue the samples that were taken within one month of each other and in red the samples with a longer time interval. In the scatterplot the depth of the filter is indicated with an icon, a dot for shallow filters (<10m) and a triangle for deep filters (>10m).

The relation to the sampling date in Figure 4.8 shows that samples taken within one-month difference are more comparable than the other measurement. For iron, most of the larger extremes also seem to occur in the deep filters. There is again not a difference for the years 2012, 2016 and 2018, these perform comparable to the other years.

Conclusion

From looking at the comparisons between the provincial measurements and the data from the RIVM, it can be concluded that there are not any significant differences between the two data sets. We

therefore conclude that the measurements that we used to define our redox classes in the deliverable are now validated; the classification would not change by introducing the RIVM dataset instead of the provincial dataset. The two data sets compare quite well with most of the values showing a smaller than 10% difference in NO_3, SO_4 and Fe concentrations from samples taken in the same year. These parameters also perform equally well for the years that the sampling for the pesticides described in this report were carried out, validating the use of these data.

One observation that seems to be consistent is that samples taken within one month of each other show a smaller difference than those measurements which have a larger time between them. This is the case for all three parameters, although for nitrate it is less pronounced than for sulfate and iron. This relation with sampling date suggests that there is some temporal fluctuation in the concentrations of these substances. For filters with strong upward or downward trends in concentrations the difference between the sampling dates can be easily imagined, as those closer to each other will have more similar concentrations than those were the sampling dates are far apart. Trends have been observed for nitrate, sulfate and iron.

Given those observations, we may conclude that spreading the sampling activities within a monitoring year would increase the amount of "noise" in the dataset somewhat. This would imply that the most consistent time series would be acquired by sampling the wells in the same month or season. One may also consider harmonizing the sampling months between the provinces and RIVM as this would help to increase the comparability for results even further. In general however, both datasets already fulfil their objectives; the work gives a clear message that the data are comparable and can be applied for the interpretations of nitrate, sulfate and iron concentration, derived redox classes and interpretations about subsurface denitrification processes and other redox sensitive transformation processes in the subsurface.

Appendix B: Redox transitions for 3 additional geological Formations

This appendix lists the concentration-depth profiles for 4 additional geological Formations. A description of the methodology can be found under section 3.6.1.
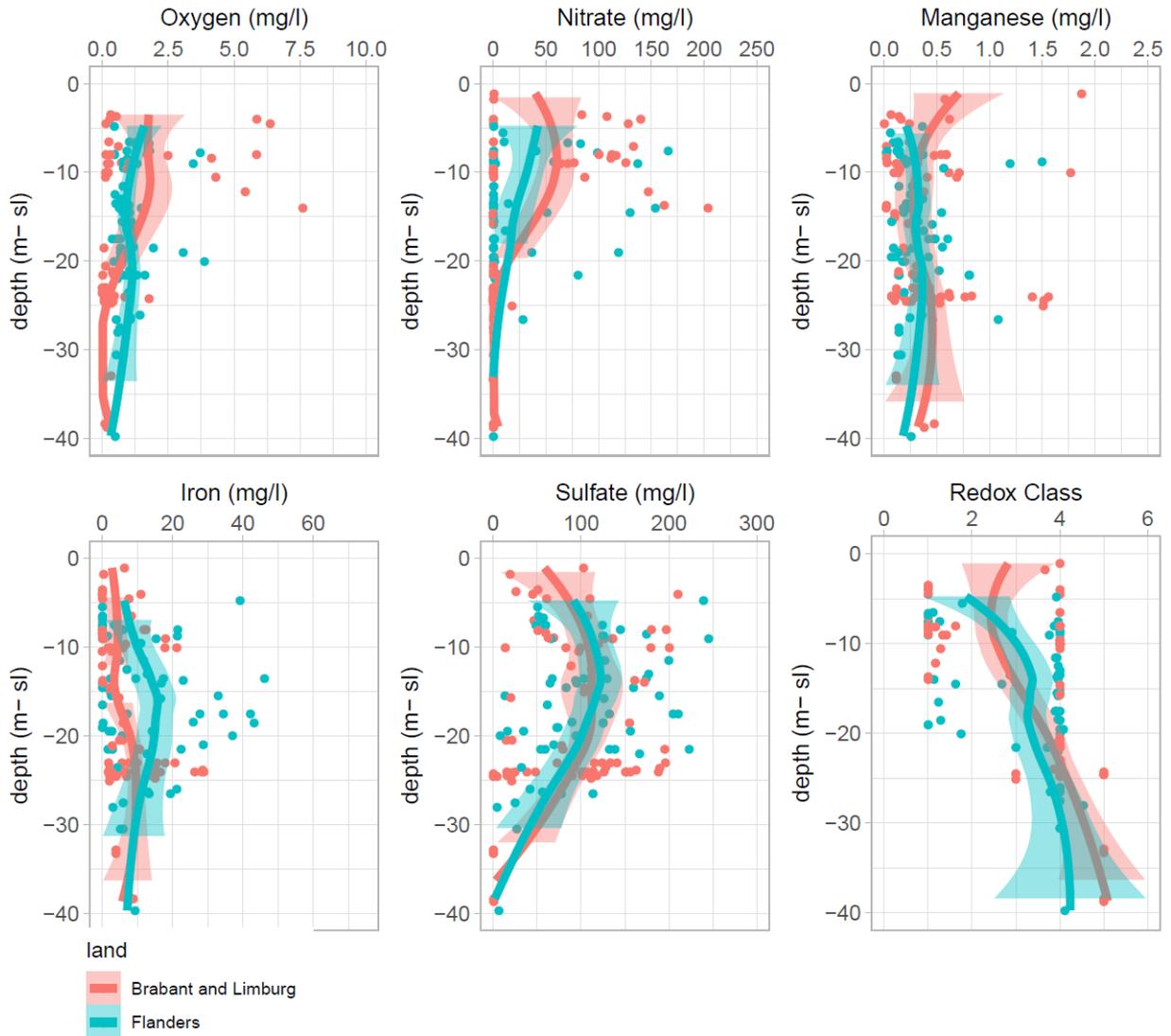

Figure 4.52 Concentration-depth profiles for agricultural areas in the Sterksel Formation (st). Concentrations are averages per monitoring screen over the period 2005-2020
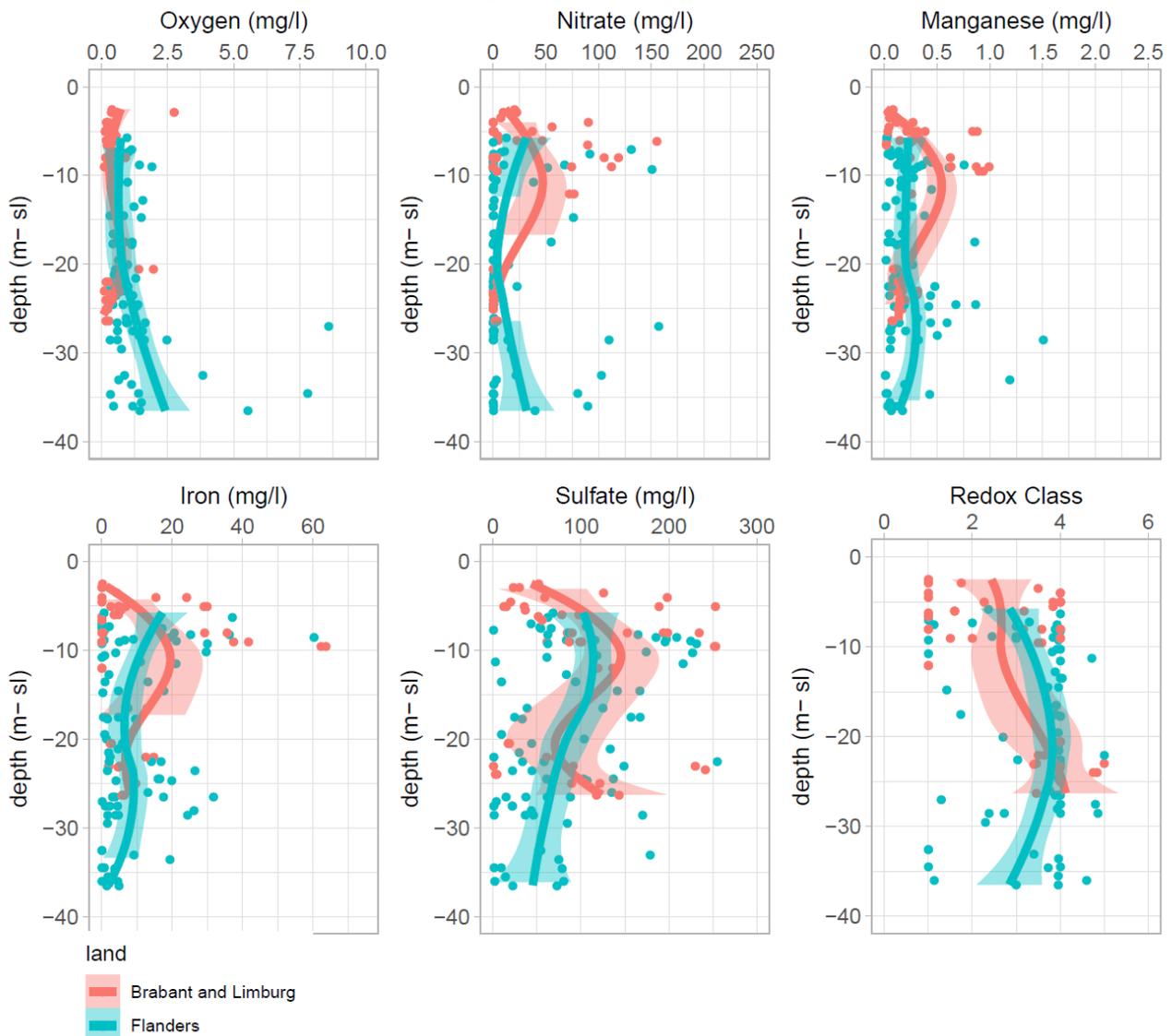
Figure 4.53 Concentration-depth profiles for agricultural areas in the Stramproy Formation (sy). Concentrations are averages per monitoring screen over the period 2005-2020
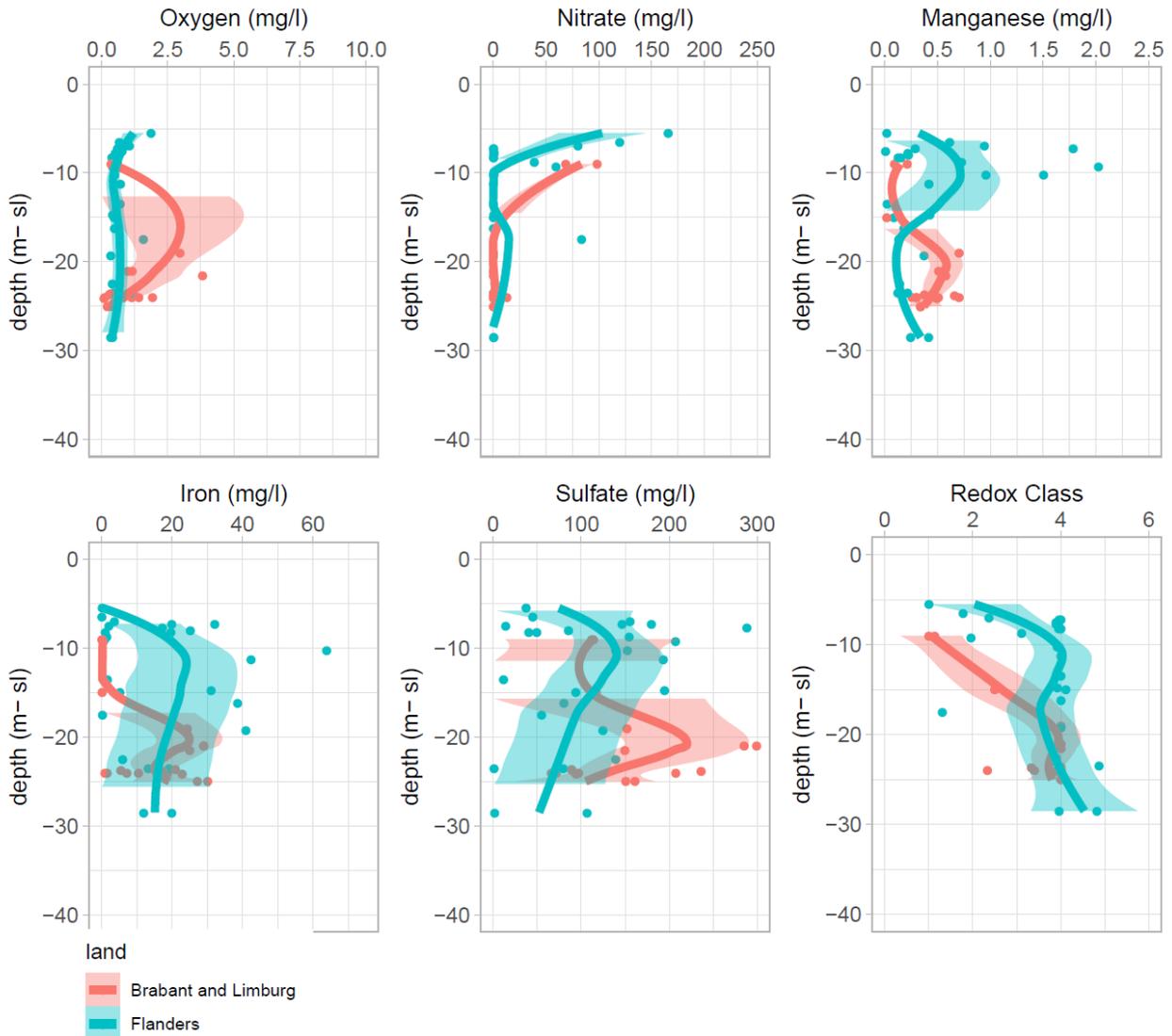
Figure 4.11   Concentration-depth profiles for agricultural areas in the Kieselooilite Formation (ki). Concentrations are averages per monitoring screen over the period 2005-2020

Assessing attenuation patterns of selected pesticides

Pesticide redox jitters

As an application of the redox classification procedure that was introduced in the previous chapters, we analysed the monitoring data of the "Brede Screening" and "Smalle screening" database of the Noord-Brabant and Limburg provinces. The "brede screening" consists data of the years 2012, 2016, 2018 and the "smalle screening" only from 2019. See Deliverable 5.3 for more information about this

data set. In Deliverable 5.3 we assessed the concentration of 19 pesticides and metabolites in relation to the age of the groundwater, using the infiltration year approach. Here, we evaluate the relation between redox status and pesticide concentrations under a number of land uses.

BAM

Figure 4.55 shows the concentrations of BAM in relation to the redox classes that were defined in Section 3.5. BAM appears to be present in substantial concentrations exceeding 1 µg/l in all redox classes except Mn-reduced. As expected, BAM is mainly found under farmlands (panel B), and shows a large number of hits above 1 µg/l in both Oxic/Suboxic water and Fe-reduced water. This effectively means that BAM is mobile under aerobic conditions, under nitrate -reducing conditions, which means that it remains mobile when passing the NO_3/Fe redox cline. A significant number of hits is also found in urban areas which suggest application and leaching of dichlobenyl and further degradation into BAM under urban areas. A number of hits in S-reduced/methanogenic urban waters suggest it may stay mobile even under strongly reducing conditions.
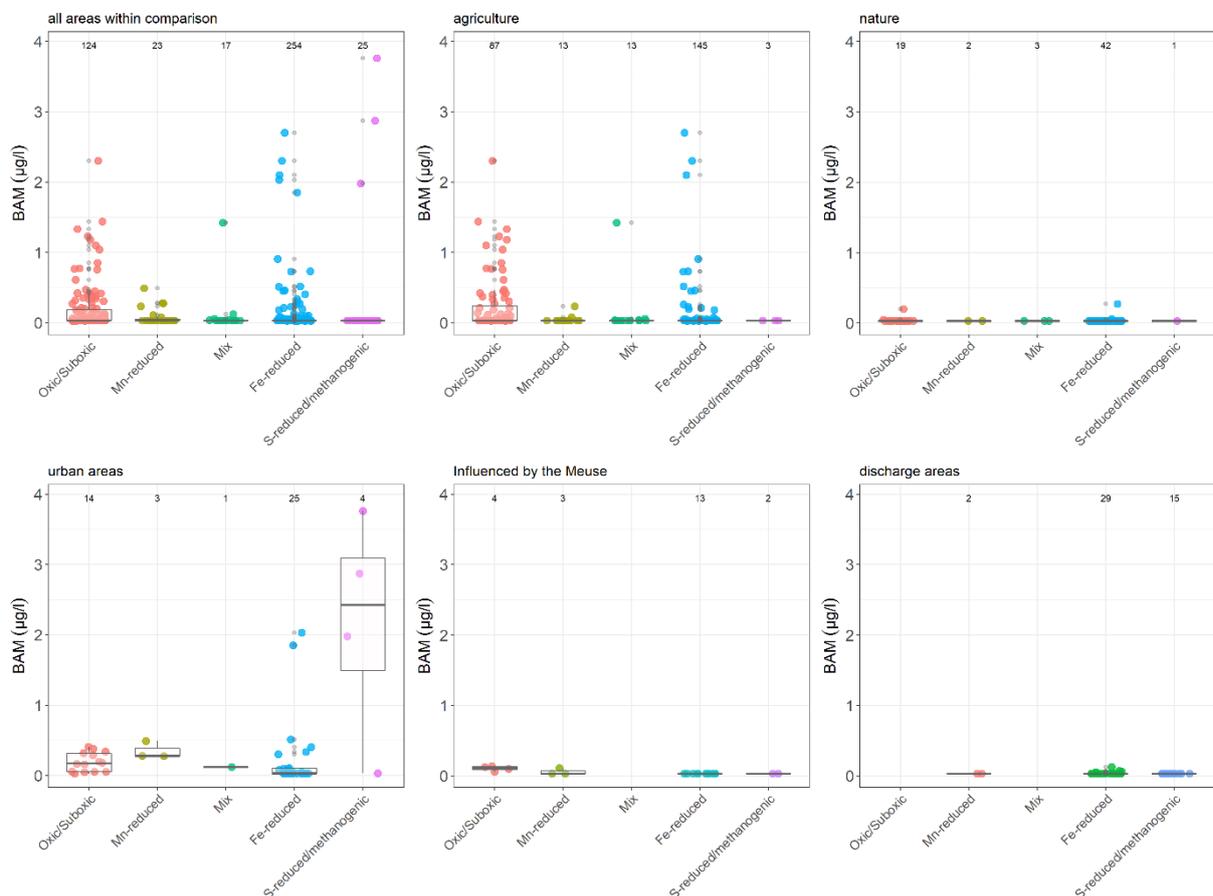

Figure 4.55 Jitters and boxplots of BAM (µq/l) per redox class for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas

Desphenyl-chloridazon

Desphenyl chloridazon is one of the most detected metabolites in Dutch groundwater. Similar to BAM it is mainly found under farmlands, and both under Oxic/Suboxic conditions and Fe-reduced conditions. Desphenyl-chloridazon is thus able to pass the NO_3/Fe redox cline an to move into layers that are below the depth of complete denitrification as mapped in Section 3.6.
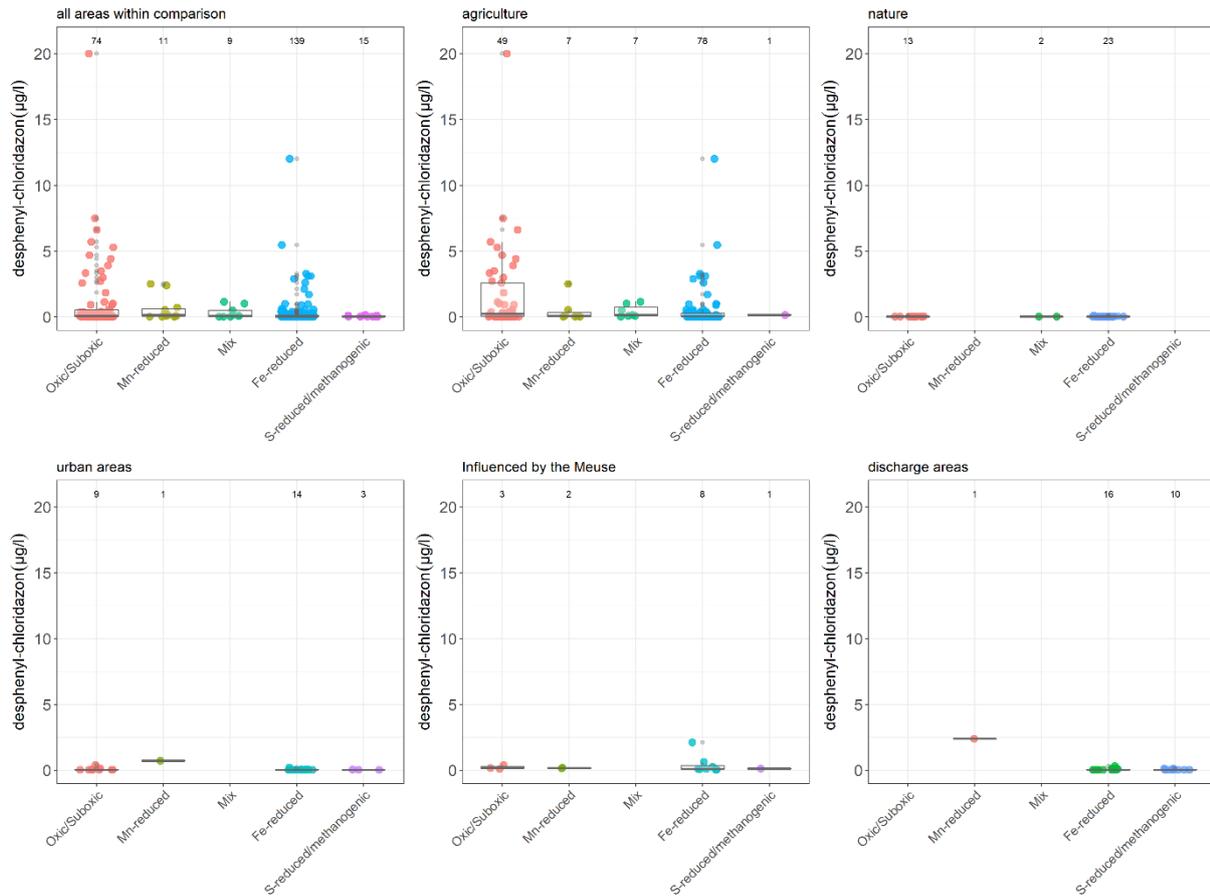
Figure 4.56 Jitters and boxplots of desphenyl-chloridazon (µq/l) per redox class for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas

Bentazon

The story of desphenyl chloridazon and BAM also holds for bentazon, another one the most detected pesticides in Dutch groundwater. Similar to BAM and desphenyl-chloridazon it is mainly found under farmlands, and both under Oxic/Suboxic conditions and Fe-reduced conditions. Bentazon is thus able to pass the NO_3/Fe redox cline an to move into layers that are below the depth of complete denitrification as mapped in Section 3.6.
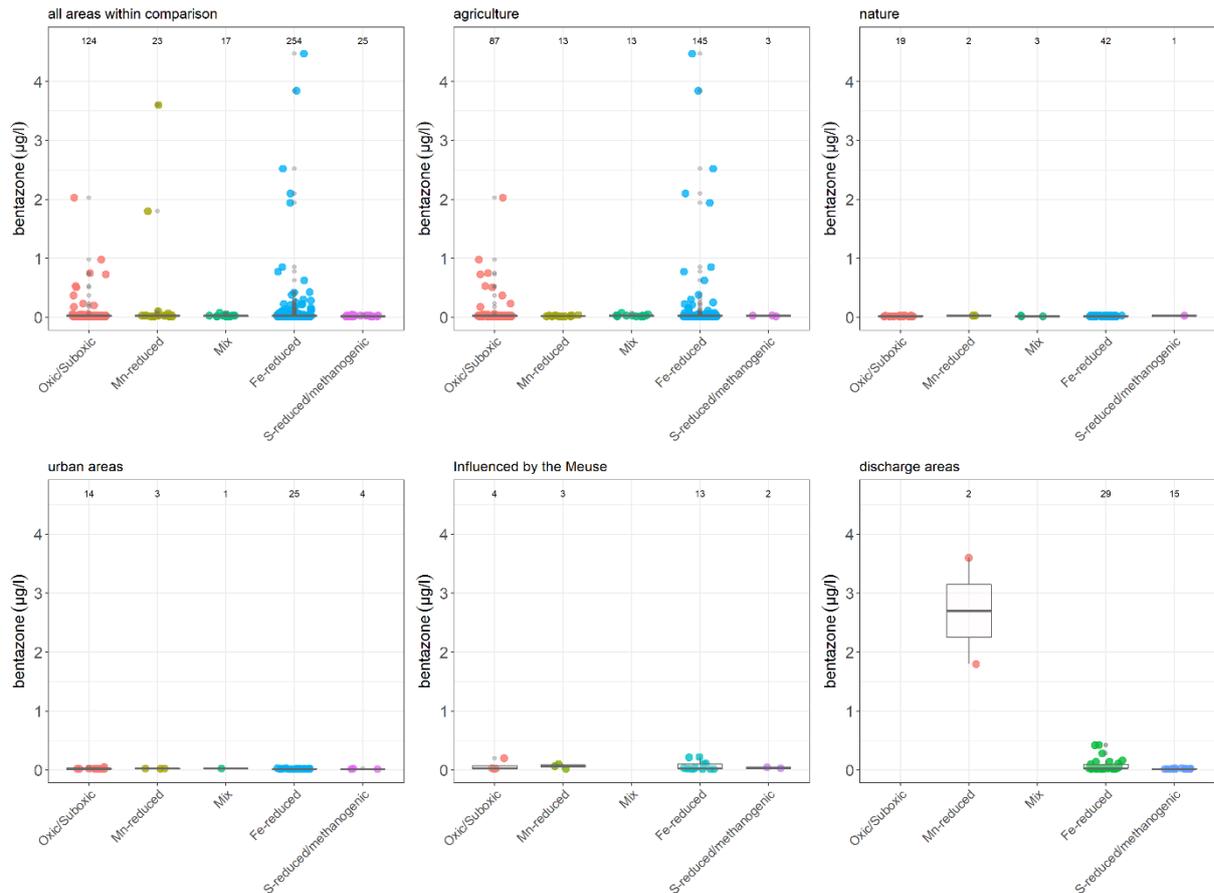
Figure 4.57 Jitters and boxplots of bentazon (µq/l) per redox class for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas

Metalaxyl

Metalaxyl shows a different pattern: the few hits of metalaxyl are all in Oxic/suboxic water, suggesting mobility only under these redox conditions and possibly degradation and denitrifying and Fe-reduced conditions (Figure 4.58). Concentrations above the highest detection limit of 0.03 µg/l only appear under farmlands.
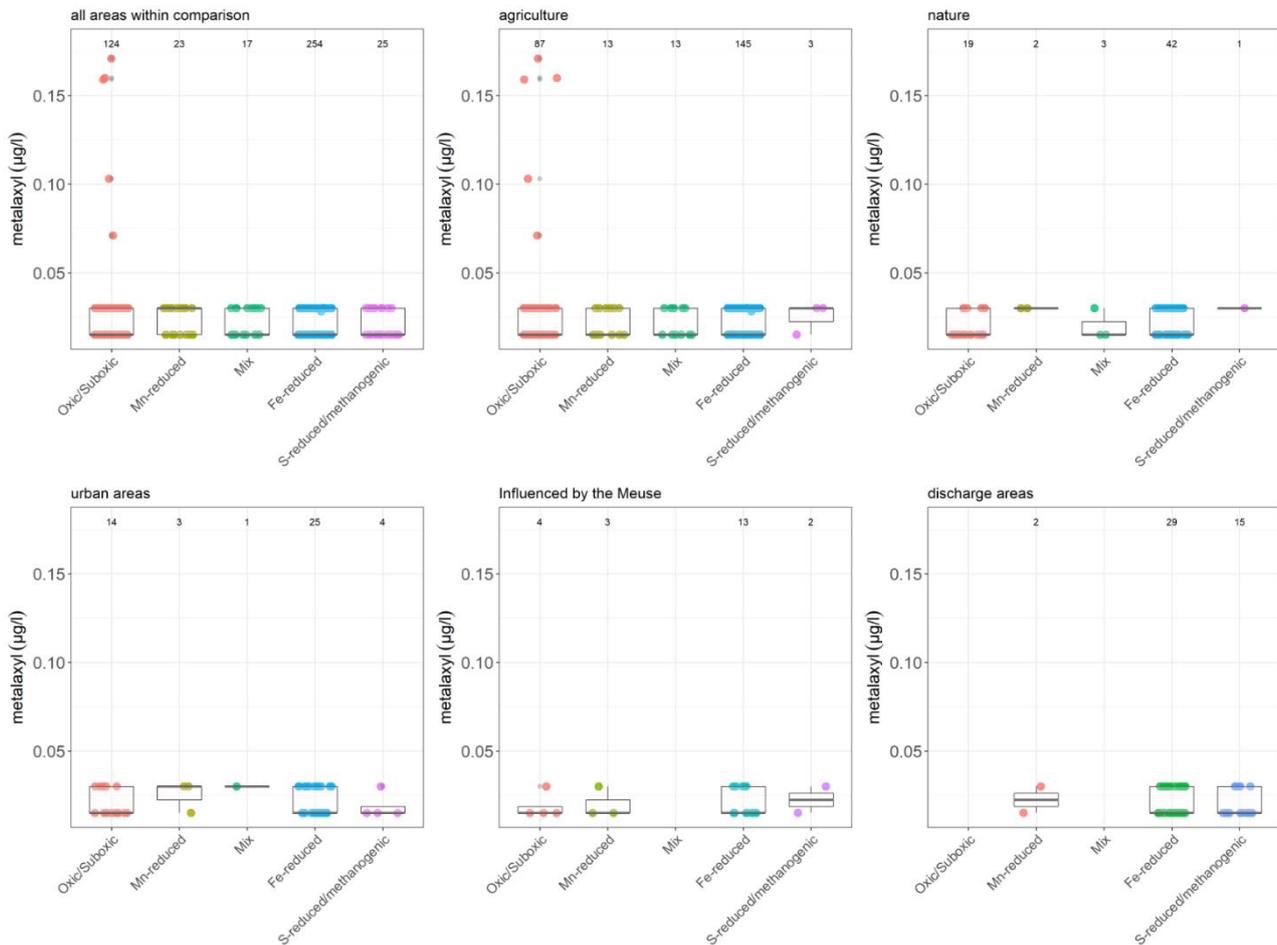
Figure 4.58 Jitters and boxplots of metalaxyl (µq/l) per redox class for several land types: all areas within comparison, agriculture, nature, urban areas, areas influenced by the Meuse and discharge areas

Overall assessment of pesticide patterns related to advective time lags and redox status

Table 4.1 summarizes the occurrence of the 19 pesticides in relation to redox class and land use. Quite a large number of pesticides and metabolites appear mobile under both oxic/suboxic conditions and Fe-reduced conditions: the list includes BAM, desphenyl-chloridazon, 2-hydroxy-atrazine, methyl-despehenyl-chloridazon, bentazon, 2-methyl-thiobenzothiazole and mecoprop. It might also be true for diuron, ethofumesate and glyphosate, but the number of hits is considerably lower, suggesting that these are less mobile and persistent in Dutch groundwater.

Two pesticides clearly are more mobile under Fe-reduced conditions: N,N-diethyl-toluamide and metaldehyde. These do not show up in oxic/suboxic water at all.

AMPA and glyphosate-ammonium seem to be more mobile under reduced conditions as well, but the number of hits are not sufficient to draw any sound conclusions.

Table 4.1   Relations between the 19 measured pesticides and the redox classes

	oxic/suboxic	Mn-reduced	Mix	Fe-reduced	S-reduced/meth		Agriculture	Nature	Urban	Meuse	Discharge
BAM	50	8	3	34	3		49	3	26	5	3
desphenyl-chloridazon	42	10	6	46	4		68	1	5	12	5
methyl-desphenyl-chloridazon	25	2	3	17			37		5		
bentazone	11	3	2	20	1		43		1	10	9
2-hydroxy-atrazine	6			5			2			3	
metalaxyl	5						6				
2-methylthiobenzothiazole	4	1		7			5	4		1	1
mecoprop (MCPP)	4			22	3		18			3	
diuron	1			1						2	
ethofumesate	1			3						1	2
glyphosate	1				1		1				1
carbendazim	1						1				
Dinoterb			1	1			2				
AMPA		1		2	1		2				1
N,N-diethyl-toluamide			1	4			4	1			
metaldehyde				7			4			3	
glyphosate-ammonium					1					1	
chloridazon					1		1				
metalochlor											
	151	25	16	169	15		243	9	32	46	22

In Deliverable 5.5, we aim to combine the knowledge about pesticide behaviour for the Dutch case study, combining the knowledge obtained from the groundwater age and the redox status work.