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

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Deliverable 5.2

Evaluating groundwater monitoring data

Version: no. final

This report is part of a project that has received funding by the European Union's Horizon 2020 research and innovation programme under grant agreement number 731166.

Deliverable Data		
Deliverable number	D5.2	
Dissemination level	Pubic	
Deliverable name	Evaluating groundwater monitoring data	
Work package	WP5 Nitrate and pesticides transport from soil to groundwater receptors	
Lead WP/Deliverable beneficiary	TNO	
Deliverable status		
Submitted (Author(s))	23/01/2020	Hans Peter Broers
Verified (WP leader)	24/01/2020	Matthew Ascott
Approved (Coordinator)	25/01/2020	Laurence Gourcy

SUMMARY

This report describes the groundwater monitoring data that is available in the pilot areas of the methodological demonstration project HOVER WP5. For each pilot site, we present a chapter with a description of the monitoring network available, the design of the network, the completion and types of the wells, and complement this with the methods foreseen to process the data of nitrate and pesticides transport that will be used to deliver results for the pilot areas in deliverables D5.3 and D5.4. The methods that are foreseen deal with the overall topic of the *time lags involved in the transport* of nitrate and pesticides and the *attenuating processes during the transport*. As such, methods will address issues such as the determination of flow velocities and vertical age gradients in the groundwater that determine lag times and the indicators about the denitrification potential and/or depth ranges of denitrification in the subsurface.

The report contains a brief synthesis chapter which covers the similarities and disharmonies between the monitoring and interpretation approaches followed in monitoring of nitrate and pesticides, summarizing the information that is currently available on the transport times and time lags and attenuation processes in the pilot areas.

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1 EXECUTIVE SUMMARY

The present document is deliverable D5.2 " Evaluating groundwater monitoring data" 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 pesticides 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. Under Task 5.2, we will make an inventory of existing monitoring networks and corresponding groundwater quality data in order to retrieve processed information of the transport of nitrate and pesticides that will ultimately be presented in the deliverables D5.3 and D5.4.

2 INTRODUCTION

One of the aims of Work Package 5 of HOVER project is to assess nitrate (N) and pesticides (PST) travel times and, where possible, attenuation patterns for a number of relevant European settings for evaluating regulatory timescales for achieving good status and/or trend reversal for nitrate. Under Task 5.2, we will make an inventory of existing monitoring networks and groundwater quality data in order to eventually retrieve processed information of the transport of nitrate and pesticides.

Within the HOVER project, processed data is defined to be " compilations of raw data that are available in national databases into thematic maps or summarizing statistics on the scale of aquifers, countries or federal states, or even pan-European products". HOVER will develop methodologies creating the design for these compilations, delivering templates to participating surveys to harmonize the common data products. HOVER is not planning to collect the raw data from national databases, but merely compiles those data into reports and common data products. These reports and common data products will be made accessible through EGDI. Raw data will still be available within the national databases, to which links may be provided for part of the data and for some case studies, enabling the demonstration of future possible extensions and further developments of EGDI.

Writing this D5.2 deliverable, we work towards the compilation of data that describe the transport of nitrate and pesticides in a harmonized way, integrating data that were collected within the pilot areas within the countries of the participating surveys. In the chapters 3 to 11, we describe the monitoring networks and data sets within the pilot areas, evaluating different approaches and methods that are used to assess travel times and attenuation processes in these pilot areas. This could include the use of tracer age dating, but could also imply a modelling approach, depending on the choices made within the different countries participating. Making an overview of the different approaches followed over Europe for estimation of transfer times and attenation patterns is a crucial first step that achieves mutual understanding, and helps to create an overview of similarities and differences that are inherently present given the varied hydrogeological setup observed over Europe. Chapter 12 gives an overview of this comparison and gives first ideas about harmonisation at the larger European scale. The data will ultimately be presented in D5.3 that cover the modelling of transport and D5.4 that covers attenuating processes in the pilot areas.

The following case studies are presented in the subsequent chapters of this deliverable:

Case Study	**Region**	**Nitrate**	**Pesticides**
Netherlands	Noord-Brabant and Limburg age dated waters and gas compositions	X	X
Slovenia/Croatia	Transboundary Drava aquifer, unsaturated zone 18O/2H/3H recharge estimates and lysimeter data	X	
Slovenia	Lysimeter data	X	
Denmark	National denitrification map, groundwater age dating and pesticide permission monitoring including both the variably-saturated zone and the groundwater zone	X	X
UK	Unsaturated zone profiles, denitrification mapping	X	
France	National scale transfer times nitrate, denitrification mapping		
Ireland	National assessment of unsaturated and saturated zone data	X	
Malta	Nitrate time series at water supply wells	X	
Cyprus	National scale nitrate and denitrification potential	X	
Latvia	National scale nitrate monitoring	X	

3 CASE STUDY BRABANT/LIMBURG (NETHERLANDS)

3.1 Description of Monitoring network

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 which is used for compliance and surveillance monitoring for the EU WFD. The Netherlands is characterized by shallow water tables and unconsolidated deltaic deposits; the altitudes in the pilot area ranges between -5 and 3 above mean sea level. The South part of the Netherlands is one of the largest producers of agricultural products worldwide, and is 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 law, 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).

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 $^{3}H/^{3}He$ 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 $^{3}H/^{3}He$ 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.

Figure 3.1 Monitoring wells available in the Dutch case study

3.2 Information about travel times in the saturated and unsaturated zones

3.2.1 Age dating

Information about travel times in the saturated and unsaturated zones is derived from age dating using $^3H/^3He$ (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. The design of the WFD monitoring network in the Meuse region distinguished specific combinations of land use and hydrological situations, which were called "homogeneous area types" (e.g. Broers 2004, Broers & van der Grift, 2004). These combinations include: "farmlands on dry sandy soils", "farmlands on wet sandy soils", "farmlands on clay soils", "nature reserves", "urban areas" and "discharge areas in the sandy region". The age dating results of a recent study helped to identity areas in which Meuse water recharges groundwater, and the wells that show signals of Meuse water recharge have been distinguished separately since (Kivits et al. 2019). Using the age dating results, age-depth relation was visualized for each of those area types (Figure 3.2).

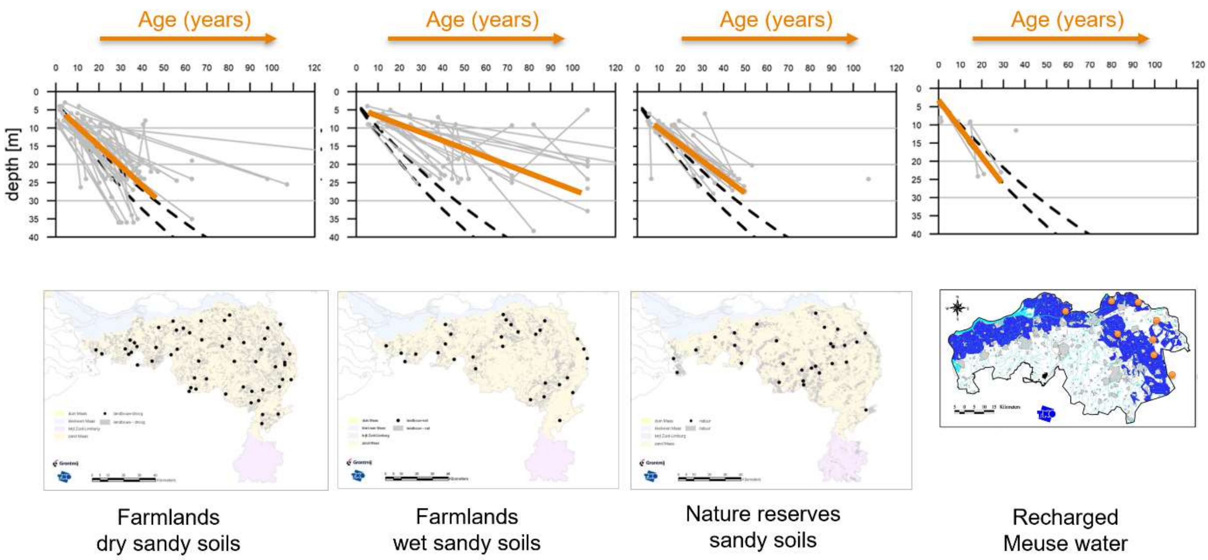

Figure 3.2 Age-depth profiles for different land use types in the pilot area. Grey lines connect shallower and deeper monitoring screens, visualizing the age-dept relation for the individual screens. The orange line suggests the median age-depth relation for the area type as a whole

The age-depth relation for farmlands on dry sandy soils was established first (Visser et al. 2007, 2009). The average age-depth relation corresponds with recharge velocities in the order of 1 m per year in the upper parts of the saturated groundwater. The dashed line indicates estimate of the age-depth relation based on Vogel's model (Vogel 1967, Raats 1981) for a porosity of 0.35 and recharge rates of 250 and 320 mm yr^{-1}, respectively. The new age dating programs of 2017/2018 enable new interpretations for the other area types as well. Clearly, the overall age-depth pattern for farmlands on wet sandy soils is less steep and indicates much smaller overall vertical velocities as a result of shallow drainage of groundwater and associated mixing of water (Broers 2004). Contrary, the measurements under nature reserves show age-depth profiles that are comparable to farmlands at dry sandy soils but indicating a somewhat smaller groundwater recharge rate, presumably induced by extra evapotranspiration of forests. The steepest age-depth gradient was found for the recharging

Meuse water, which is logical because the downward flux of this water is not limited by the precipitation surplus, but dependent on the established surface water level regimes.

For many objectives, the age dating results are aggregated to age groups, which are summarized in Table 3.1. Samples that have a discrete apparent age form $^3H/^3He$ dating are labeled as “discrete age”, whereas samples that suggest mixing of modern and pre-modern waters have been distinguished separately, just as water which such low ^3H concentrations that they can be attributed to recharge before 1950. A special group with very old water was detected based on elevated ^4He concentrations.

Table 3.1: Proportion of the deeper screens (20-25 bsl) of wells that agree with the 5 age groups

Area type	Discrete age	Mix modern - pre-1950	Mix mostly pre-1950	Pre-1950	Mix with old /old
Dry farmlands	59%	23%	6%	4%	2%
Wet farmlands	34%	20%	10%	27%	6%
Nature reserves	83%	13%		4%	
Urban	67%	17%			8%
Discharge	13%	13%	20%	47%	
Meuse river	100%				

The table shows that modern water with a discrete age has arrived at most of the deeper screens under dry farmlands, nature resources, urban areas and in areas where Meuse river water has recharged. Much less deep penetration of modern water is reported for wet farmlands and groundwater discharge areas in the sandy region, which is attributed to upward flow of older water and mixing between younger and older water in areas with converging flows (see Broers 2004). Knowledge of the age structure was of great help in identifying time lags and relating the application history of pesticides and nutrients to the occurrence in the monitoring wells (see section 3.4).

3.3 Information about attenuating processes in the subsurface

Using the setup with dedicated multi-level monitoring wells, the monitoring results yield information of data at a specific depth level, or to derive information about different chemical parameters as a function of depth. In order to obtain information about attenuating processes, we typically relied on a classification tree for redox characterization (section 3.3.1), but we recently complemented the dataset with information about gas composition which we will use to refine our classification (section 3.3.2).

3.3.1 Redox mapping of groundwater

Figure 3.3 shows the redox decision tree used to identify the redox level of groundwater samples. The classification is based on Graf Pannetier 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 dataset. 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 or suboxic. Groundwater in the class ‘Mix’ contains iron and nitrate. Mn-reduced groundwater contains manganese, for which a threshold of 0,5 mg/l is used to distinguish between oxic and 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. 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. 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.

This classification scheme is implemented in the current Dutch database that will be used within GeoERA 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.

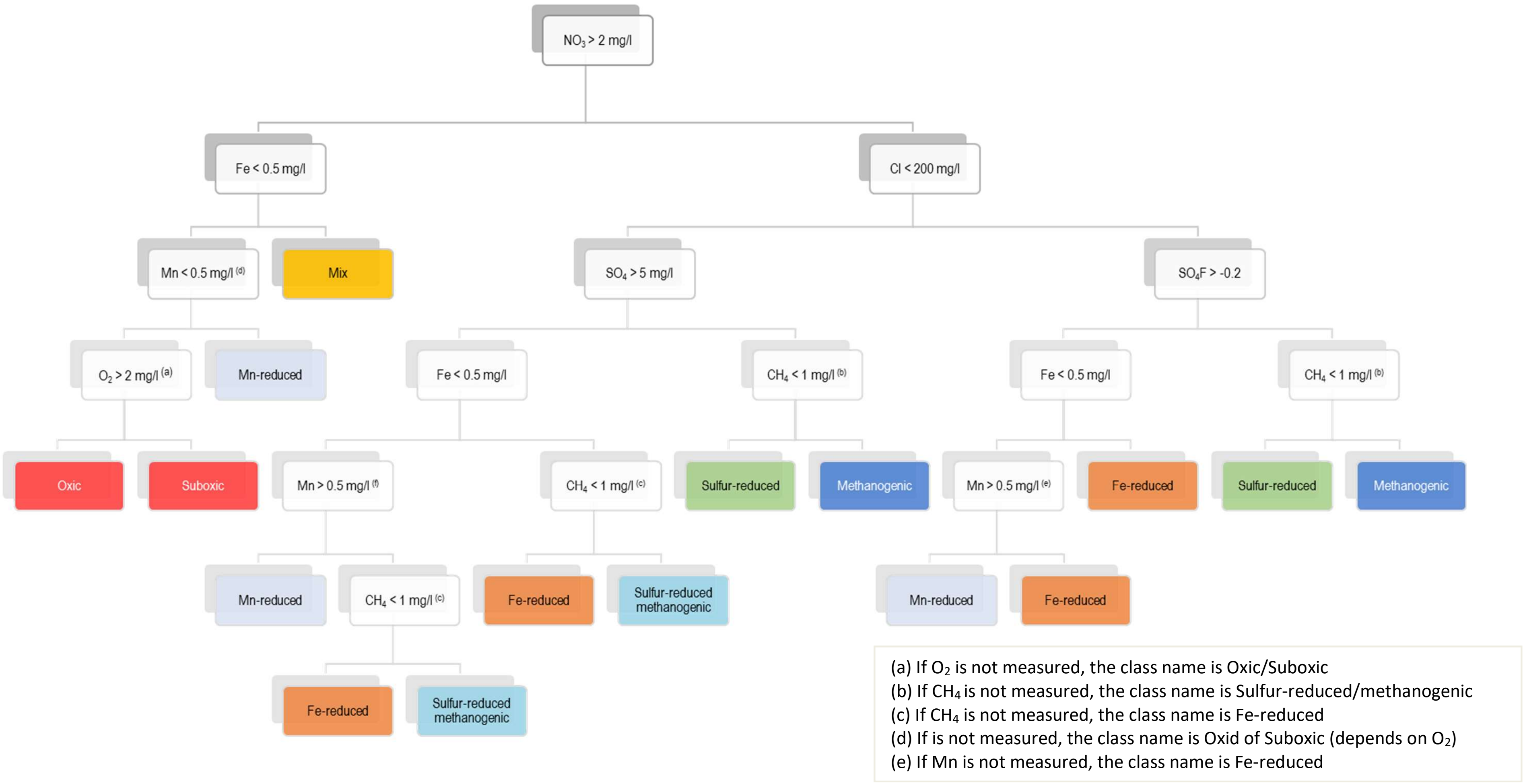

Figure 3.3 Redox classification tree. Diversion to left = "yes", diversion to right = "no".

3.3.2 Gases in groundwater

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 photospectrometer.

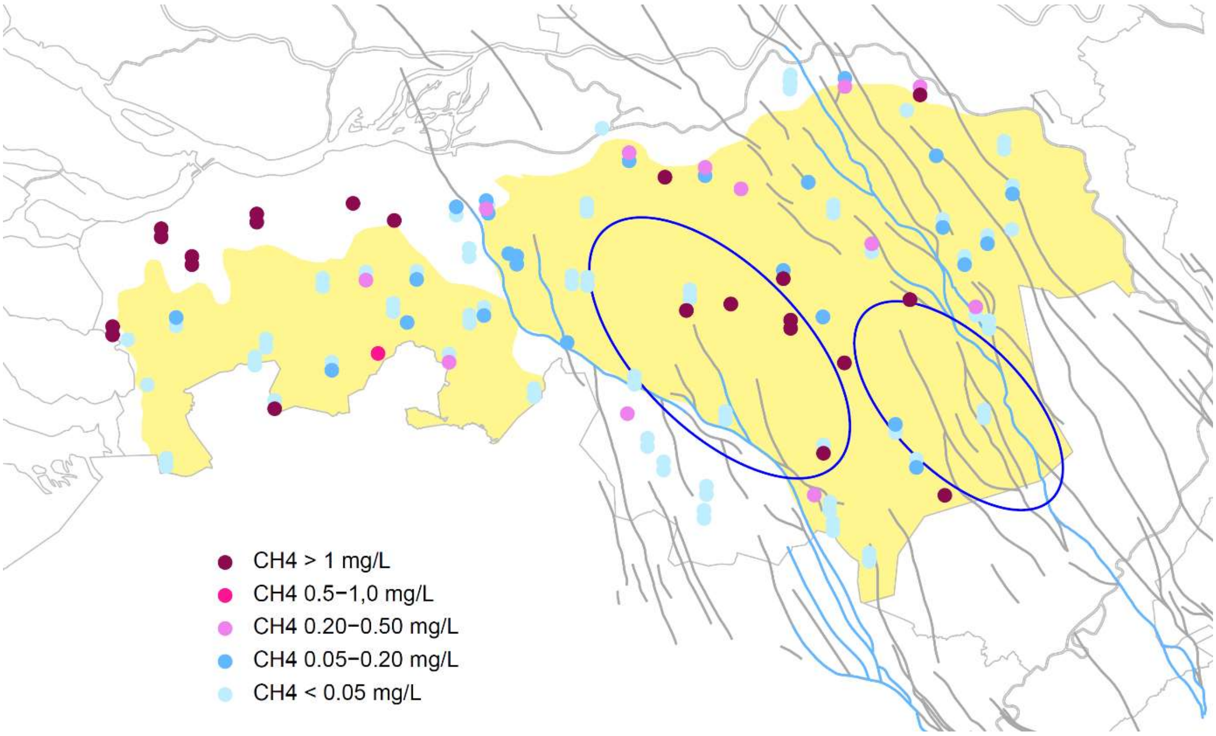

Figure 3.4 Map of CH_4 concentrations in monitoring screens at 10 and 25 m depth

Up to now the collected gas data have not been interpreted for classifying groundwater according to redox status. This interpretation will be reported as part of Deliverable 5.4 of HOVER, as one of the tools for deriving information about attenuating processes, such as denitrification and pesticide degradation.

3.4 Combined analysis of transport and attenuating processes in the pilot area

Groundwater composition at a specific monitoring point is typically determined by three main factors: 1. the history of leaching of solutes and contaminants for the soil zone towards the groundwater, 2. the transport time towards the monitoring screen and 3. reactive processes that alter the chemical composition by processes such as precipitation, dissolution, sorption, radioactive decay and microbial degradation. The effects of the factors are often difficult to unravel, especially when either the leaching history or the travel times are unknown. Therefore, the age dating was a crucial step to clarify at least one of these factors, ultimately also helping to unravel the chemical processes (Visser et al. 2009). Using the monitoring network to be used in HOVER, we aim to further refine our methods to unravel these 3 factors and to study whether we can define approaches that would work in other GeoERA pilots under HOVER. In the following, we introduce four approaches that we will further elaborate under WP3 and WP4 of HOVER.

3.4.1 Concentration-age plots

Knowing the relations between depth and age as described under section 3.2, we can replace the depth axis of concentration-depth plots (Broers & van der Grift, 2004) into concentration-age plots (see Figure 3.5 for one example). Typically, a large ranges of apparent groundwater ages is found at a specific monitoring depth, resembling heterogeneity in flow paths and groundwater recharge rates. Visser et al. (2009) give a conceptual overview of the interpretation options after age dating for this same area type, using the infiltration year approach as is further illustrated and elaborated under section 3.4.2. We tested whether conversing the depth scale into a groundwater age scale is a sound alternative way to unravel the hydrogeochemical processes in Figure 3.5.

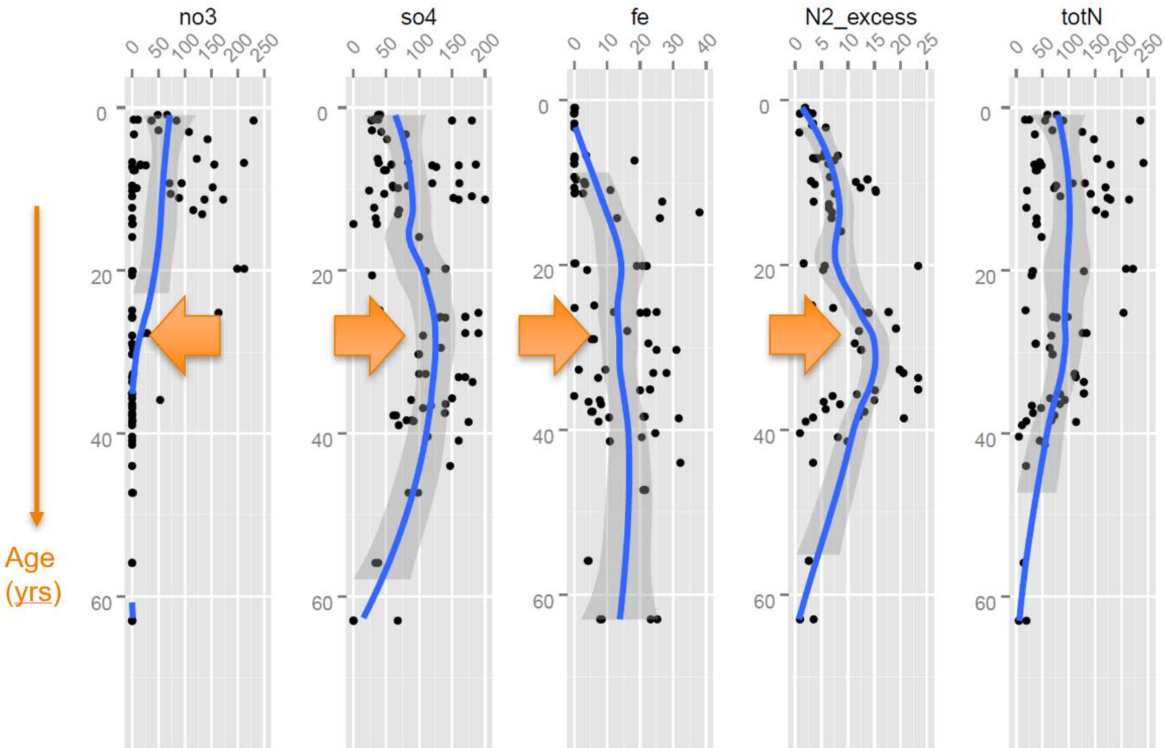

Figure 3.5 Concentration age plots for farmlands under dry agricultural soils

Figure 3.5 is merely representative for groundwater nitrate patterns in the south of the Netherlands. Nitrate is often found in high concentrations in groundwater that is aged less than 15 to 20 years.

However, typically a significant proportion of the wells with water ages in this range does not contain nitrate concentrations above detection limits. In groundwater older than 20 years, nitrate is virtually absent as is also suggested by the blue LOWESS smooth in Figure 3.5. We can infer the attenuating processes for nitrate by also plotting the reaction products that result from denitrification (N_2) and or denitrification coupled with pyrite oxidation (Zhang et al. 2009, 2012: N_2, Fe and SO_4). Here, N_2-excess is defined as N_2 in excess of N_2 in water that is equilibrated with the atmosphere, which we estimate from measured Total Dissolved Gas content or direct measurement of the gas composition. In case all nitrogen remained in solution then the N-total (defined as NO_3 + N_2-excess) gives a good representation of the nitrogen leached to groundwater. The Total-N graph of Figure 3.5 strongly suggests that nitrogen inputs were present in water aged up to 40 years, which means that all nitrate leached 20 to 40 years ago has been lost through denitrification. This is in accordance with increases of the reaction products Fe, SO_4 and N_2 in water aged between 15 and 40 years. Given that these reaction products already show substantial concentrations in water aged between 8 and 15, the process of denitrification starts already in relatively young water. We relate the large differences between the individual monitoring screens to differences in leaching concentrations, but mainly to differences in subsurface reactivity. Especially the depth of encountering reactive organic matter or iron sulfides in the subsurface is a key factor that defines the age at which nitrate in the water will start to denitrify.

With the knowledge obtained from these graphs for all area types in the pilot monitoring network, we hope to contribute to establish a common method to define the depth of complete denitrification and the depth range of ongoing denitrification in the subsequent deliverables for HOVER WP5.

3.4.2 Infiltration year analysis

Age dating of the water of small screen multi-level monitoring wells helps to apply the "Infiltration Year" or "Recharge Year" approach as was proposed by Bohlke 2002, Visser et al. 2007 and Hansen et al. 2010. The infiltration year approach estimates the infiltration year by subtracting the apparent age of the sample form the year of sampling itself. Plotting all measured concentrations against infiltration year is an efficient way to relate the measured concentration to the application history of nutrients and pesticides. The method works very well for solutes that behave conservatively in groundwater but needs attention for solutes that undergo degradation or sorption or precipitation reactions (see Visser et al. 2009 for a conceptual analysis). Figure 3.6 gives examples of the use of the infiltration year approach for area types in the Dutch pilot monitoring network of the Meuse-Sand region. In the Figure, all the data of the individual monitoring screens is left out, and the overall shape is kept which is detected using a LOWESS smooth (Visser et al. 2012, 2013). The left graph of Figure 3.6 shows the patterns that is found for farmlands with dry and wet soils, respectively for the indicator OXIV which summarizes the sum of nitrate and sulfate in meq/l (oxidation capacity, see Postma et al. 1991, Visser et al. 2007). In the Netherlands, OXIV is an efficient indicator for agricultural contamination of groundwater as it includes the reaction product sulfate which is formed by the reaction of denitrification coupled with pyrite oxidation. The shape of the curves nicely reflects the effects of reducing the N applications after the 1985 Manure Law which clearly led to overall decreasing concentrations in water that recharged since 1985. For comparison, Figure 3.6b shows the recharge year plots for farmlands and nature reserves, respectively, which give conclusive evidence that the pattern under farmlands is related to N applications on land, and not to atmospheric deposition alone.

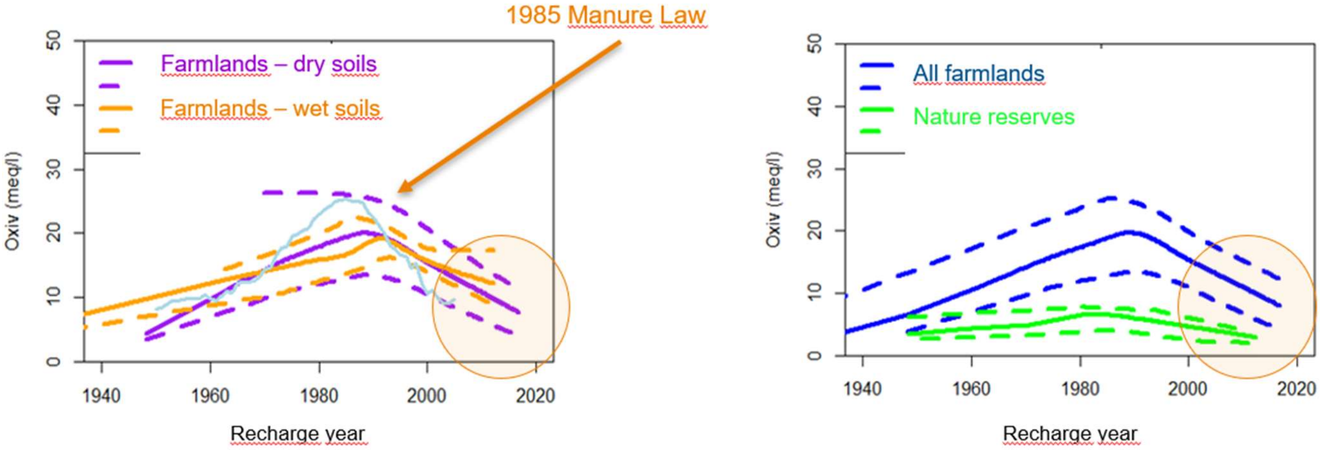

Figure 3.6. Infiltration year plots for OXIV for farmlands on wet and dry soils (left) and farmlands and nature reserves (right). The LOWESS smooth gives the local median of all data in the area type. The area between the dashed bands cover all data between the 25- and 75-percentiles.

Although the infiltration year plots nicely reflect the overall shape of the increase and decrease of the leaching of agricultural solutes in groundwater, it is not well constrained at the right side of the curves. This is because, typically, only a small number of wells have very young water and there is no constraint to the curve for the present or future. Therefore, the current trend in the youngest recharging water is not very well constrained. Within GeoERA HOVER, we therefore developed a method to combine the infiltration year approach with trend analysis for water ages less than 15 years. This is reported in section 3.4.3.

3.4.3 Trend analysis of youngest 15-year groundwater

For trend analysis of water aged less than 15 years, we applied the method that was first described by Broers and van der Grift (2004). This stepwise approach first estimates the trend in an individual monitoring screen, testing it using the Mann-Kendall trend test and deriving the Kendall-Theil robust line and Sen Slope (Helsel & Hirsch 2002). In the second step these individual Sen slopes are aggregated to find the aggregated median trend slope for a set of wells, testing the significance non-parametrically following Helsel and Hirsch (2002). Figure 3.7 illustrates this approach. In this GeoERA case, we defined the set of slopes to be tested to be all the monitoring screens that contain water aged less than 15 years. Figure 3.7, right side, show all the individual trend slopes that are visualized on the left side as a function of groundwater age. Upward slopes plot in red, downward slopes plot in green. For the sulfate example of Figure 3.7, the average trend slope of all water aged less than 15 year is indicated with the blue bullet.

The slope that was defined through this new approach was then visualized in the Infiltration Year plot as an arrow that describes the overall trend for the measured solute. The arrow is much better constrained than the LOWESS smooth slope of the Infiltration Year plot and helps to evaluate effects of recent land use changes or action programs to reduce inputs of solutes to groundwater. As these trends cover the monitoring period 1997-2007 for which the monitoring data was evaluated the arrow was positioned in that time range of the infiltration year plot. For solutes that behave conservatively, as sulfate in Figure 3.8, the arrow confirms the pattern that is visible in the infiltration year plot, giving additional information about the significance of the pattern. For solutes that are known not to behave conservatively (Visser et al. 2009), the arrows help to identify virtual trends that are not significant. An example of this latter is the graph for Potassium in Figure 3.8, where the infiltration year approach may suggest increasing concentrations, which are definitely not occurring as is confirmed by testing the 15-year youngest groundwater. The trend that was suggested for potassium is due to the retarded transport of potassium; the transport speed of potassium is clearly decoupled from the transport speed of water as it was characterized by the groundwater age.

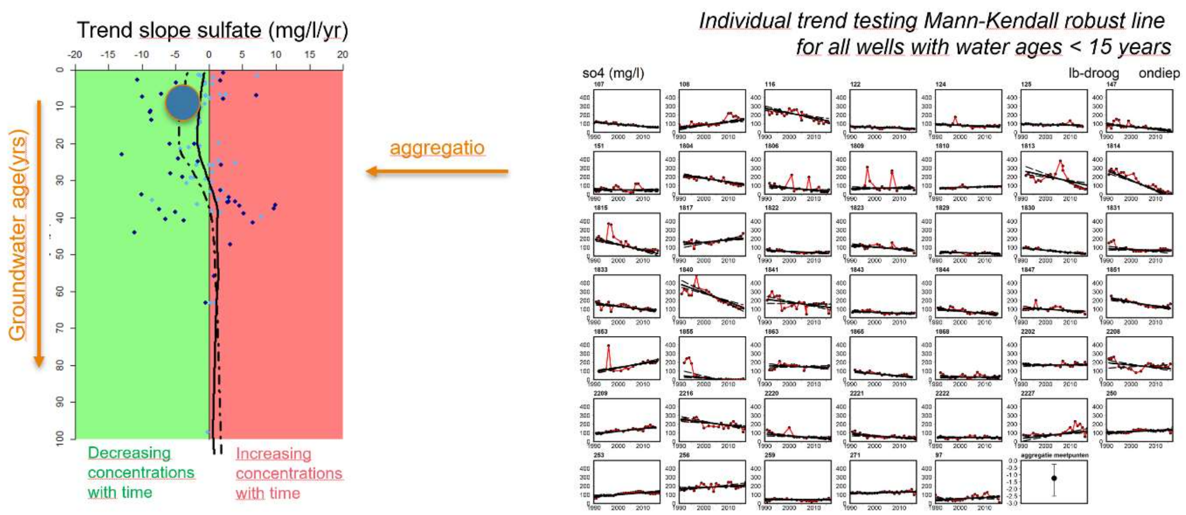

Figure 3.7 Aggregating trends using information about saturated zone travel times

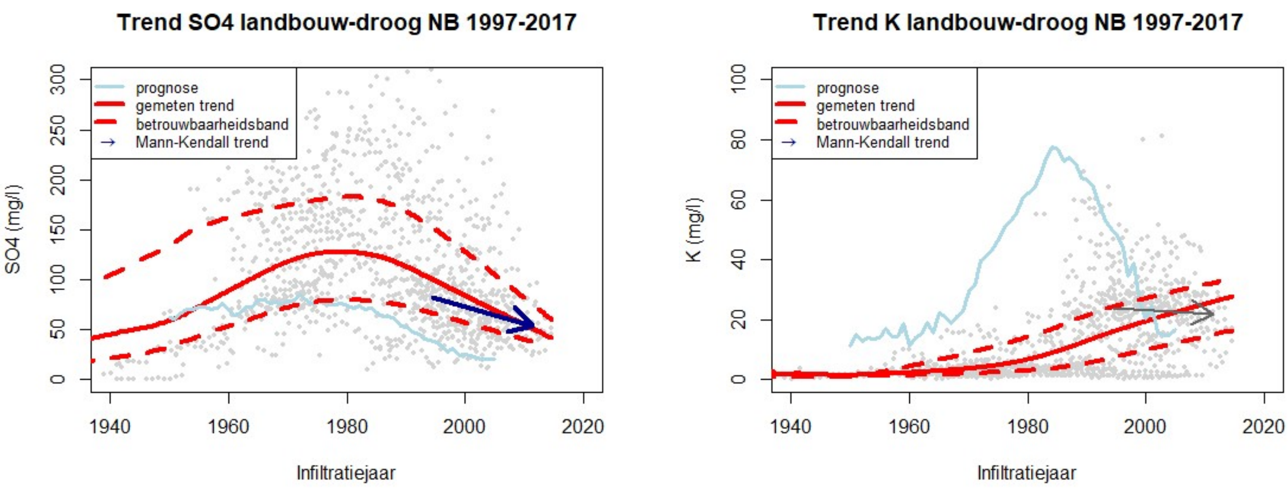

Figure 3.8 Example trend arrow graphs for sulphate (a) and potassium (b) for farmlands at dry sandy soils

3.4.4 Pesticide forensics based on groundwater age

Most of the work we performed in the Netherlands using the age dating results and transit time approaches were focused on nutrients and macro-chemistry of the water. For GeoERA HOVER, we intend to extend this work to pesticides, using the measured groundwater ages as a forensic tool, evaluating pesticides patterns with age and relating it to the period when the specific pesticides were permitted. Therefore, we again calculated the $^3H/^3He$ recharge year ('infiltration year') by subtracting the $^3H/^3He$ apparent age from the sample date and then group by infiltration year classes.

Organic contaminants typically occur in much lower concentration ranges and datasets of these substances are typically characterized by a large number of non-detects. This makes the general Infiltration Year approach and LOWESS smoothing less useful for signaling patterns of pesticides concentrations with age. For GeoERA HOVER we tested whether an approach using jitter plots may work better, relating pesticide concentrations to classes of infiltration years, and applying a log scale for the concentrations. The advantage of jitter plots is that non-detects can be plotted at the concentration level of the detection limit itself, but pesticides "hits" can still be recognized. We applied a boxplot as a background, which gives an immediate overview of the frequency distribution, indicating which concentrations should be regarded as outliers in the distribution.

Figure 3.9 shows on x-axis the infiltration year classes and on the y-axis the concentration of nitrate, oxidation capacity, bentazon and carbamazepine. Nitrate and OXC were used as a reference, to show how the method would compare with the Infiltration Year approach that we have been applying routinely. The oxidation capacity (OXC) is defined as the weighted sum of molar concentrations of NO3 and SO4 as is our best performing indicator for overall agricultural contamination of groundwater. OXC behaves conservatively during the process of nitrate reduction by pyrite oxidation assuming that no denitrification by organic matter occurs below the groundwater table (Visser et al, 2007).

For nitrate and OXC the jitter plots resemble the Infiltration Year plots, showing that the OXC concentration are elevated since the 1960's and highest median concentrations between 1980 and 1990. This is in line with the known application history of N in Dutch farming (see section 3.4.2). Nitrate is only present in the infiltration year classes 1990-2000, 2000-2010 and 2010-2020. The absence of nitrate in water older than 1990 is completely determined by the process of denitrification (see section 3.4.1).

We used the "broad screening" dataset of the province of Noord-Brabant to evaluate the concentration of a number of pesticides for HOVER WP5. The part of the dataset that is age dated was used for our analysis, which corresponds with the monitoring network described under section 3.1.

Bentazon is a pesticide (herbicide) and has been permitted under Dutch regulations since the end of the 80's. The bentazon jitter plot (see Figure 3.9, bottom left) shows concentrations below detection limit for infiltration year classes older than 1980. Note that different sampling campaigns in 2012, 2016 and 2019 yielded different detection limits, which is directly imminent form this type of Figure which helps the interpretation of the data. Detections for bentazon occur only in water that has recharged after 1980. All concentrations of bentazon in water aged before 1980 are below detection limits as should be expected from the application history. The median concentration of bentazon correspond to detection limits, which makes the jitter plot approach better suitable for this type of contaminants, The graph suggests that most bentazon was leached between 2000 and 2010 (highest outliers) or 1990-2000 (highest median) but we cannot rule out that part of the bentazon that has recharged before 1990 or 2000 has been degraded in the subsurface. Overall, the pattern of bentazon is compatible with that of nitrate, and bentazon is clearly quite mobile in the Brabant subsurface.

Carbamazepine (figure 3.9, bottom right)) is an anticonvulsant medication and only detected in the youngest infiltration year class '2010-2020'. For carbamazepine there are only a few detects in groundwater, all are in the infiltration year class 2010-2020. This could mean that carbamazepine was only used recently, which is not probable, or would degrade in the subsurface. A first screening clarified that all hits of carbamazepine occur in water that is recharged from Meuse water (see section 3.2.1), which suggest it is not common in water leaching from farmlands.

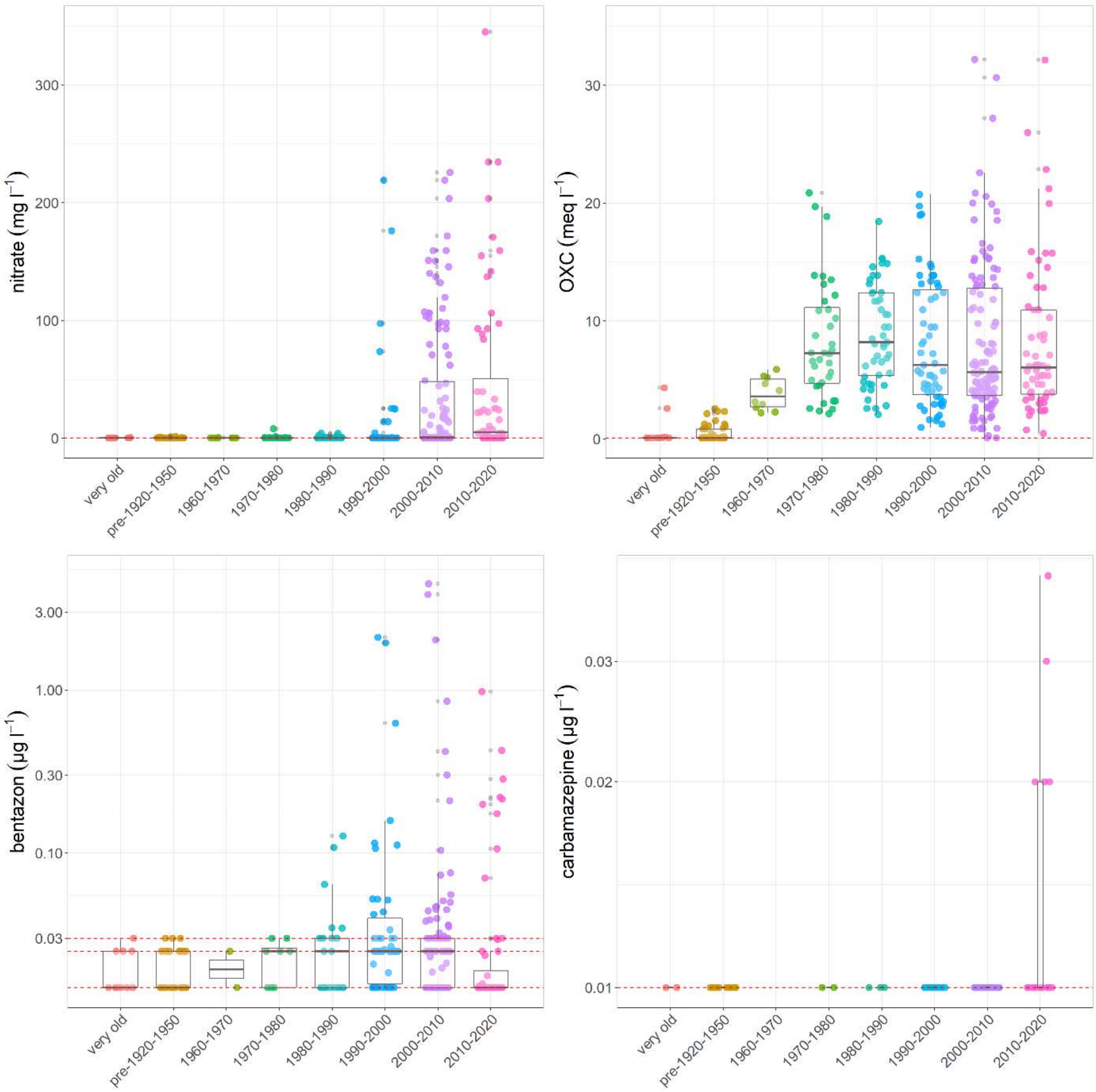

Figure 3.9 Jitter and boxplots of nitrate (mg/l), oxidation capacity (OXC, meq/l), bentazon (ug/l, log scale) and carbamazepine concentrations (ug/l, log scale) per infiltration year class. Red dashed lines are detection limits. Note that different detection limits for bentazon apply to different sampling campaigns.

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4 CASE STUDY DRAVA AQUIFER (SLOVENIA/CROATIA)

4.1 Description of Monitoring network

Slovenia

In Slovenia, groundwater quantitative and chemical monitoring is performed by the National Environmental Agency (ARSO). There are 176 observation points included in the groundwater monitoring network, 123 at alluvial aquifers and 53 at karst aquifers.

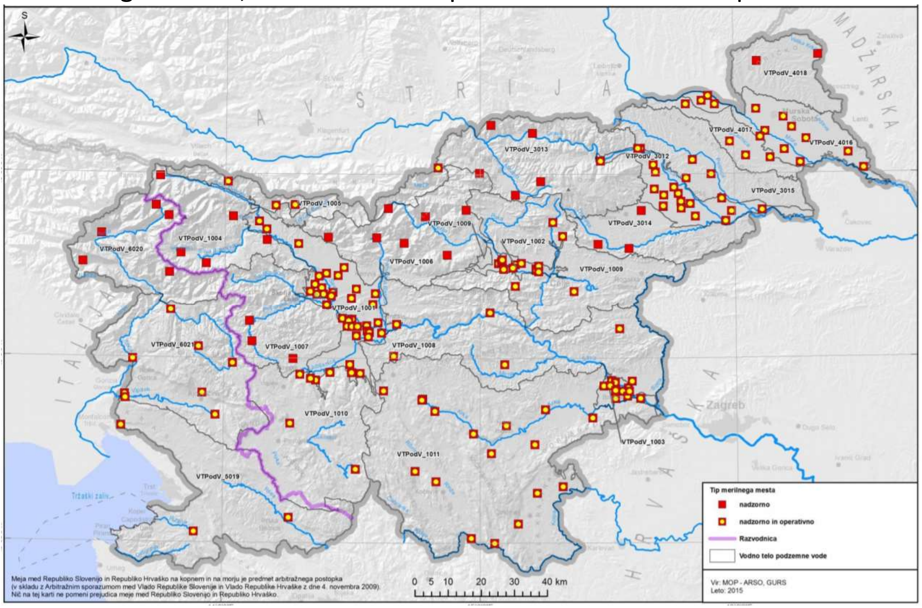

Figure 4.1: Slovenian national groundwater monitoring network

At the Slovenian part of the Drava aquifer case study, there are 13 national groundwater monitoring points (Fig. 4.2.)

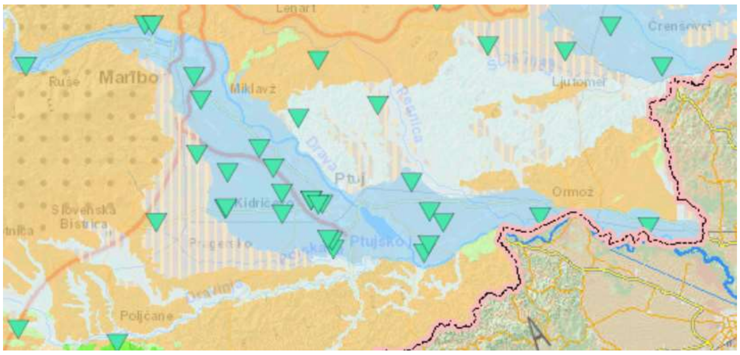

Figure 4.2: National groundwater monitoring points at the Slovenian part of the Drava aquifer case study

Croatia

The national surveillance monitoring network that forms the basis for this research is developed for groundwater quality compliance monitoring in accordance with EU WFD requirements. The monitoring is performed, and all data is stored in databases managed by Croatian Waters, which is a legal entity for water management in Croatia.

The pilot area at Croatian side covers four groundwater bodies: “Varaždinsko područje”, “Međimurje”, “Novo Virje” and “Legrad-Slatina” (Fig 4.3). The are 26 observation wells in total within the monitoring network and all are completed in saturated zone, i.e. there is no date on travel times nor attenuation processes in unsaturated zone. There is one well at each location with one or several screens.
The age dating is not performed in the scope of the monitoring. However, there is data on groundwater mean residence time (MRT) acquired within several research projects carried out in Croatian geological survey.

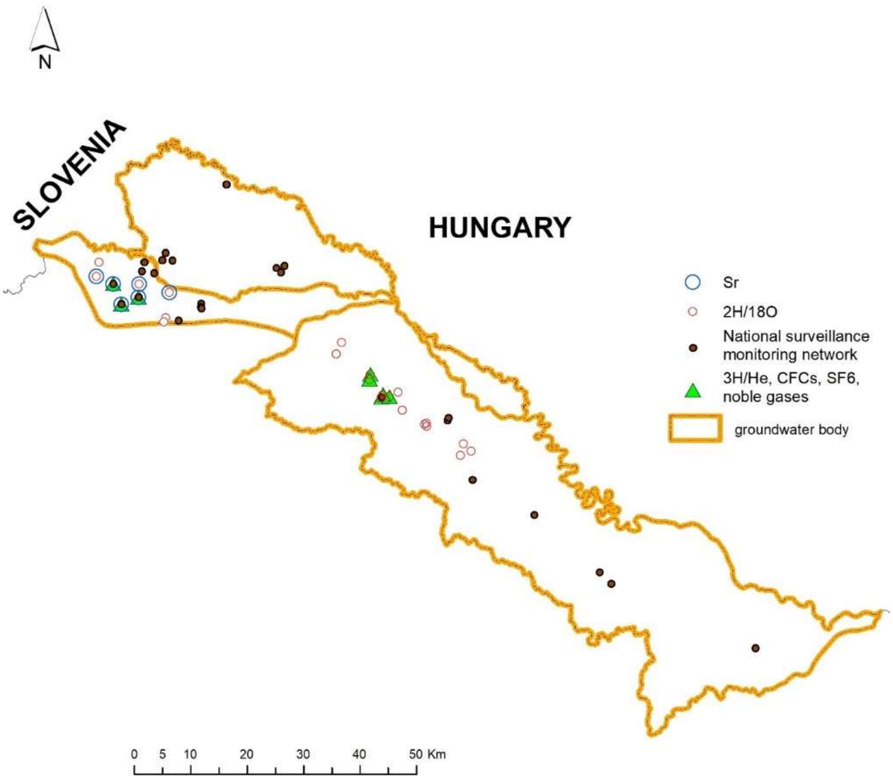

Figure 4.3: Location map

4.2 Information about travel times in the saturated and unsaturated zones

Slovenia

Vertical flow velocity in the aquifer’s unsaturated zone was studied in a field laboratory – lysimeter in Selniška dobrava. Based on the tracer test, the fastest and dominant flow velocities were calculated. On the basis of the tracing experiment results, estimations of the mean flow velocity and vertical dispersion were made by the analytical best-fit method (Fig. 4.4). One dimensional convection-dispersion-model with standardising values for single porosity was used.

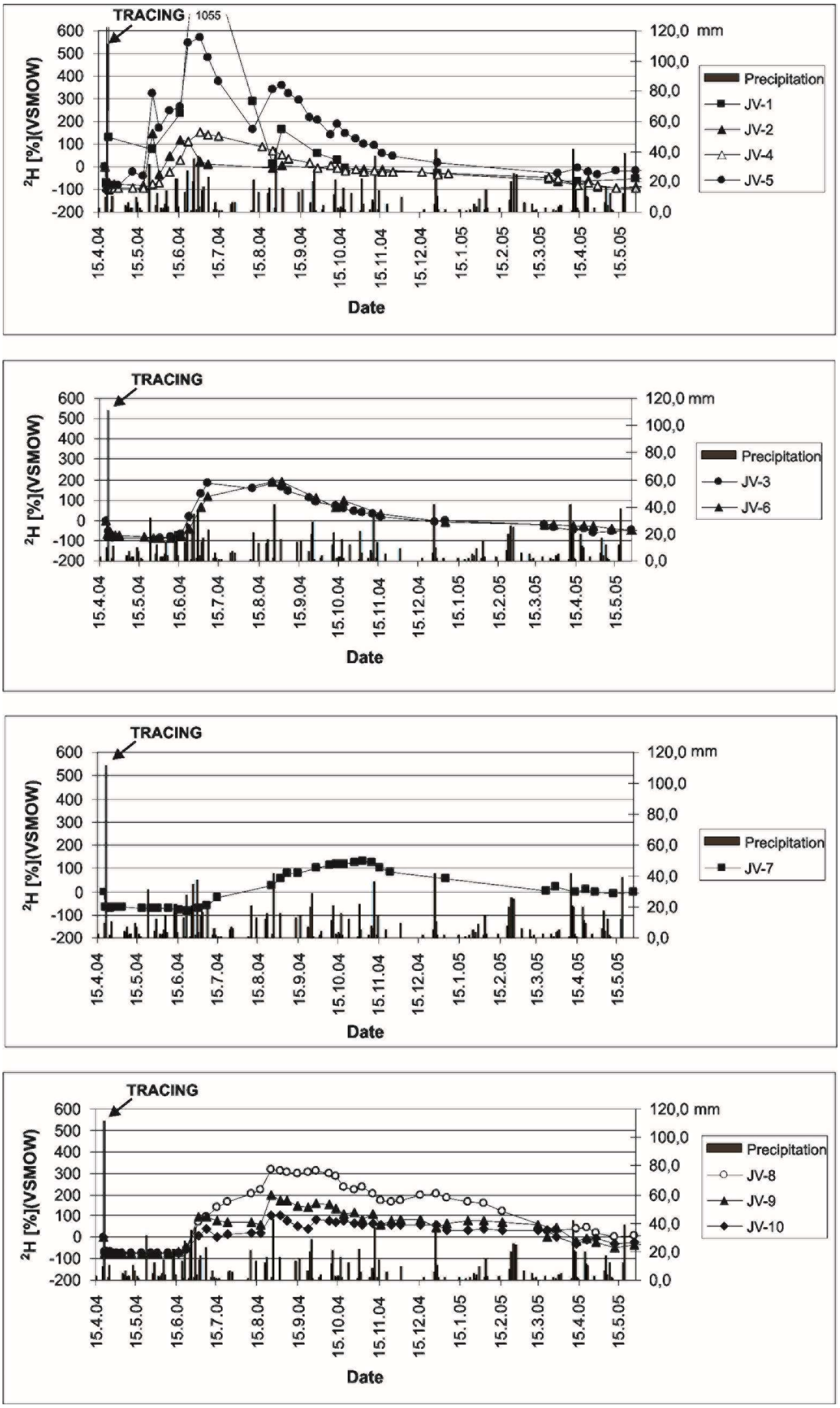

Figure 4.4: Results of the tracing experiment in aquifer's unsaturated zone

Based on the results of the tracing experiment some properties of the coarse gravel unsaturated zone at the location of the lysimeter were described. Results generally show that the water discharge in the drain system as well as the dispersion coefficient for deuterium increase with depth. The estimation of the mean flow velocity of the matrix flow is between 0.014-0.017 m/d. If it is assumed that the ground water level is 27 m deep, it could be concluded that the mean residence time through the unsaturated zone in Selniška Dobrava coarse gravel aquifer is 4.4-5.4 years. For groundwater protection and for measures performed for the purpose of this protection, the first arrival of the tracer through the unsaturated zone is important. If it is accepted that the pollutant behaves like a conservative tracer, and with the estimation of the fastest flow velocity in lysimeter in the range of 0.1-0.07 m/d, a pollutant can reach groundwater in 9-12 months. Based on the dominant flow velocity of 0.03 m/d the percolation time is 2.5 years.

Even if the aquifer of Selniška Dobrava is treated as homogeneous, there are some differences in the results between single observation points which show distinctions in the local unsaturated zone structure. The heterogeneous matrix in micro scale causes the differences in water flow. Results (profiles δ^2H values, breakthrough curves of both tracers, calculations of different flow velocity parameters and recovery curves of deuterium) show that more preferential flows occur on the north side of the lysimeter observation wall. It can be concluded, that in the unsaturated zone, especially in the high permeable coarse gravel aquifer, the local structure of the unsaturated zone has great influence on the water flow properties.

In the saturated zone of the Slovenian part of the Drava aquifer, groundwater age was estimated using tritium isotopes. There is no regular monitoring of groundwater tritium activities, thus only occasional tritium data is available. For the alluvial aquifer the tritium activities were quite comparable with recent tritium activities in precipitation, therefore it is assumed that groundwater is relatively young, less than five years.

Croatia

The groundwater age dated observation wells are shown in Fig 4.3. The data acquisition has not been performed on regular basis, but within the scope of several research projects carried out from 2004 until present days.

Since there is one observation well at each location, screened over one or several intervals along the aquifer depth, it is only possible to infer the MRT of groundwater within the tapped aquifer without the insight into vertical differentiation of groundwater age.

The radioactive isotopes used for groundwater age dating in saturated zone of aquifer at the pilot site include 3H/He, Sr, noble gases - He, Ne, Ar, Kr and Xe and industrial gases CFCs, SF_6. In addition, there is also dataset containing information on stable isotope composition $^2H/^{18}O$ in groundwater (Fig 4.3).

4.3 Information about attenuating processes in the subsurface

Slovenia

The groundwater dataset for the Drava aquifer in Slovenia contains information about redox processes in the saturated zone of the aquifer. Data is available for T, pH, EC, OXI, TOC, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, SiO_2, Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe, Mn, HCO_3^-. Results point to only one water type, i.e. the carbonate water type (Koroša, 2019). Based on the values of redox indicators, it can be concluded that oxic conditions prevail at the pilot area. Denitrification in unconfined saturated aquifers is mostly insignificant.

In the Drava aquifer, research about crop rotations and their impact on groundwater was also carried out (Glavan et al., 2015). They used extensive monitoring and the Soil and Water Assessment Tool (SWAT) to investigate the influence of different combinations of soil types and crop management on environmental processes (nitrogen (N) leaching and plant growth) at three study sites (Ptuj, Maribor and Dobrovce) in Slovenia.

In the scope of the project "Farming opportunities in water protection areas" the research of nitrate contents and their ^{15}N isotopic signature was conducted. Results can be found in Urbanc et al. (2014).

Croatia

Groundwater quality datasets contain the following information on redox processes in the saturated zone of aquifer: concentration of Fe, Mn, SO_4, NH_4 and gases such as dissolved oxygen and H_2S.
Based on the values of redox indictors, it was concluded that oxic conditions prevail at the pilot area, which further leads to the conclusion that denitrification in unconfined saturated aquifers is mostly insignificant. Only small parts of the aquifer are characterized by anoxic or mixed oxic/anoxic conditions, which usually coincides with fine grained layers rich in organic matter. In such circumstance's groundwater contains relatively high concentrations of Fe, Mn, NH_4 and low amount of dissolved oxygen.

4.4 Combined analysis of transport and attenuating processes in the pilot area

Slovenia

Study of water and nitrate pollution transport in the unsaturated zone was carried out in a field laboratory – lysimeter in Selniška dobrava (Fig. 4.5). Water and nitrate transport were estimated by a combined tracing experiment with deuterated water and $Ca(NO_3)_2$. Deuterium was used as a conservative tracer of water movement, and $Ca(NO_3)_2$ was used as a nitrate tracer in a high-permeable coarse gravel unsaturated zone. One of the aims of this research (Koroša & Mali, 2015) was to specify parameters of nitrate transport in a coarse gravel unsaturated zone which will be used to model nitrate transport in other aquifers with similar hydrogeological characteristics, such as for example the Drava aquifer, which was declared as a water body at risk due to the presence of nitrate.

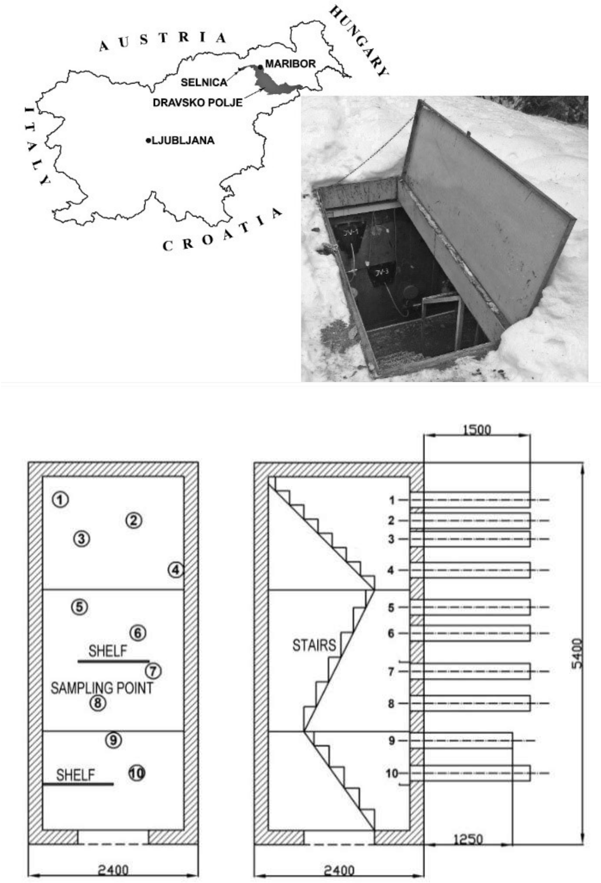

Figure 4.5: Area of lysimeter location and lysimeter cross-section

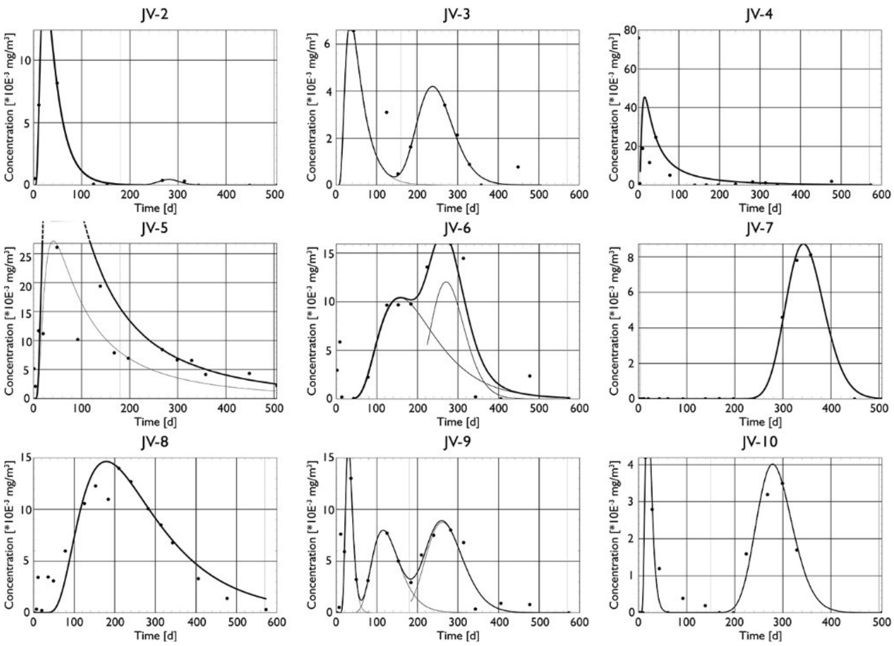

Figure 4.6: Best fit curves for nitrate concentrations (10^{-3} mg/m^3)

The mean flow velocities based on nitrate concentration breakthrough curves were estimated by the analytical best-fit method (Fig. 4.6). For JV-2, JV-3, JV-5, JV-6, JV-9, and JV-10 the Multi-Peak-Modus model was used. Up to the depth of 1.08 m (JV-2, JV-3) the mean flow velocities are estimated at 0.003-0.019 m/d, on average 0.011 m/d. In JV-4 the mean flow velocity is 0.016 m/s. From sampling points JV-5 to JV-8 the mean flow velocities range between 0.008-0.12 m/d, on average 0.010 m/d. The highest mean flow velocities were calculated in the lower part of the lysimeter at JV-9 and JV-10. Concentrations range between 0.014-0.197 m/d. Not considering the highest estimated mean flow velocities at JV-9 and JV-10, the average mean flow velocity is estimated at 0.013 m/d. We anticipate that these unrealistically high concentrations of first peak occurred due to high background concentrations (Table 4.1).

Table 4.1: Fastest, dominant (dom.) and mean flow velocities (m/s) of nitrate

		JV-2	*JV-3*	*JV-4*	*JV-5*	*JV-6*	*JV-7*	*JV-8*	*JV-9*	*JV-10*
Distance	m	0.82	1.08	1.58	2.04	2.41	2.95	3.4	3.93	4.39
Fastest f.	m/d	-	-	0.19	0.255	0.301	0.369	0.425	0.491	0.549
Dom. f.	m/d	0.02	0.026	0.036	0.032	0.009	0.009	0.015	0.028	0.023
Mean f.-1	m/d	0.019	0.019	0.016	0.01	0.011	0.008	0.012	0.117	0.197
Mean f.-2	m/d	0.003	0.004	-	0.01	0.009	-	-	0.03	0.015
Mean f.-3	m/d	-	-	-	-	-	-	-	0.014	
Dispersion-1	m2/s	0.003	0.003	0.024	0.016	0.003	0,000	0.006	0.019	0.051
Dispersion-2	m2/s	0.000	0.000	-	0.016	0.000	-	-	0.005	0.001
Dispersion-3	m2/s	-	-	-	-	-	-	-	0.001	-

The thickness of the unsaturated zone at the lysimeter location reaches 27.5 m. If it is assumed that the ground water level is 27.5 and the average first speed of nitrate is 0.369 m/d, then the first contamination can reach the water in 74 days. Based on the average dominant flow velocity (0.022 m/d) the percolation time is 3.42 years. When the estimated mean flow velocity is 0.013 m/d, the time of pollution arrival is estimated at 5.80 years.

Croatia

In the Croatian part of the pilot area there is no information on transport and attenuation processes in unsaturated zone of the aquifer. This information will be obtained from the research performed in the Slovenian part of the pilot, which includes analysis of data from lysimeter installed in the similar hydrogeological setting.

4.5 Testing approaches to harmonized, processed data for supraregional evaluations

The approach that will be applied in the pilot site includes development of groundwater flow model for saturated zone of the aquifer in order to assess the time lags and effects of attenuation processes (primarily dilution and hydrodynamic dispersion) along the path to receptors such as groundwater sources, watercourses, groundwater dependent ecosystems, etc. The model will be calibrated by historic groundwater level data and results from age indicators described in 4.2. The idea is to make use of national datasets on fertilizers and results obtained from lysimeter in Slovenia in order to define NO_3 input function for 3D numerical model of solute transport.

4.6 References

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5 CASE STUDY DENMARK

5.1 Description of Monitoring network

In Denmark, practically all the drinking water originates directly from the groundwater. Since Denmark is an agricultural country where fertilizers and pesticides have been extensively used in agriculture since the 1950s, it is essential to build up knowledge that can be used to assess whether nutrients, pesticides and their degradation products leach to the groundwater in unacceptable concentrations and to what extend they migrate to water abstraction wells, dependent terrestrial or associated aquatic ecosystems. The national groundwater monitoring GRUMO (https://www.geus.dk/vandressourcer/overvaagningsprogrammer/grundvandsovervaagning/) along with other related monitoring programs as The agricultural catchment monitoring program LOOP (https://www.geus.dk/vandressourcer/overvaagningsprogrammer/landovervaagning-loop/) included in NOVANA (https://mst.dk/natur-vand/overvaagning-af-vand-og-natur/) was initiated in 1988 to monitor the quality of the groundwater in the catchments of waterworks. With an increasing number of findings of pesticide and / or their degradation products in the groundwater and a lack of knowledge as to whether this was due to agriculture's use of approved pesticides, the Danish Pesticide Leaching Assessment Program (PLAP; http://pesticidvarsling.dk/om_os_uk/uk-forside.html) was granted funding in 1998 by the Danish Parliament, which has provided funding until 2021. In 1999, PLAP was established by GEUS and Aarhus University linking to the Danish EPA.

The monitoring design of the two NOVANA networks (GRUMO and LOOP) and PLAP are described in the following:

The National Water and Nature Monitoring Program, NOVANA
The nationwide groundwater monitoring system, GRUMO, is part of the National Monitoring Program for Aquatic Environment and Nature (NOVANA). The Agricultural catchment Monitoring (LOOP) has also a groundwater component, as groundwater in the upper 5 m in monitored. NOVANA encompasses monitoring of all parts of the aquatic environment as well as nature and air (Dansih Environmental Protection Agency, NERI & GEUS, 2017).

The groundwater monitoring program, GRUMO
The current purpose of groundwater monitoring is described in the program description for NOVANA in the period 2017-21, (Danish Environmental Protection Agency, DCE and GEUS, 2017):

- To Provide data describing the general chemical state and trends, including long-term changes in groundwater (Surveillance monitoring)
- To provide data describing the status and trends of the presence of environmentally hazardous pollutants in groundwater (Surveillance monitoring)
- To provide data describing the chemical status of groundwater bodies considered to be 'at risk', including whether there is a long-term man-made tendency to increase the concentration of any of the pollutants (operational monitoring).
- To provide data documenting the effectiveness of national aquatic environment plans, river basin management plans, nitrate action programs and other management actions (operational monitoring).
- To contribute with data that can support the annual update of the requirements for the quality control of the water works well,(the national act on control of abstraction wells) as to illustrate whether there is reason to believe that in the groundwater and thus the drinking water there are substances that have not been investigated so far and which may pose a potential health hazard.

- To provide data describing the state and trends of changes in groundwater levels (quantitative monitoring)
- To provide data that describe how water abstraction and surface water flows affect groundwater levels for groundwater bodies, that are at risk of failure to meet the Water Framework Directive's goals of good quantitative status, (quantitative monitoring)
- To contribute to the data basis for the development of models for use in, inter alia, the watershed plans.

The National Water and Nature Monitoring Program, NOVANA, of which the groundwater monitoring program, GRUMO, is part, was originally a national aquatic environment monitoring program and was launched as part of the first Aquatic Environment Plan in 1987. The implementation of which took place from 1988. The first program had two main purposes: firstly, to monitor the effectiveness of the aquatic environment plan and the general agricultural regulations in relation to the nutrient load (the phosphorus and nitrate load) of the aquatic environment, and secondly to ensure the supply of good quality drinking water to the population (Danish Environmental Protection Agency, 1988). Note this was before the WFD and Nitrates Directive.

The Groundwater monitoring network was originally designed to provide a picture of the groundwater's condition and development in a number of selected catchments, the GRUMO areas. It was estimated that these areas would be representative for the groundwater of the country. The GRUMO program has since been updated - and adapted continuously - on the basis of greater knowledge and due to the varying administrative needs, including the fulfillment of the reporting obligations under EU directives particularly the WFD and the Nitrates Directive.

Table 5.1 provides an overview of the different program periods since the start of the monitoring and provides references to the program descriptions over time.

Table 5.1 History of the National Monitoring Program of Water and Nature, NOVANA. EPA is short for The Danish environmental Protection Agency, NERI for The National Environmental Research Institute. (Thorling et al., 2019)

Period	Program name (Danish)	No of years	Remarks	Reference
1988-1992	Vandmiljøplanens overvågningsprogram	5	Establishment of GRUMO areas	EPA, 1988 og 1989
1993-1997	Vandmiljøplanens overvågningsprogram	5		EPA, 1993
1998-2003	NOVA-2003	6		EPA, 2000
2004-2009	NOVANA	6	Administrative reform of DK &	NERI, 2004
(2007-2009)		(3)	Mid-term review	NERI, 2007 a,b
2010	NOVANA	1	Extension 1 year	NERI 2010
2011-2015	NOVANA 2011-2015	5		EPA, NERI & GEUS, 2011
2016	NOVANA	1	Extension 1 year	EPA & NERI, 2016
2017-2021	NOVANA 2017-2021	5		EPA, NERI & GEUS, 2017

Figure 5.1 shows the total network of monitoring wells used for groundwater monitoring during the period 1989-2017. The wells are divided into the original GRUMO wells (located in the old groundwater monitoring areas), wells in the distributed network (established in the period 2007-2017 for reasons of the Water Framework Directive and the Groundwater Directive) and wells in the six agricultural catchments (LOOP, Fig. 5.4), which are monitored for the Danish derogation from the Nitrate Directive.

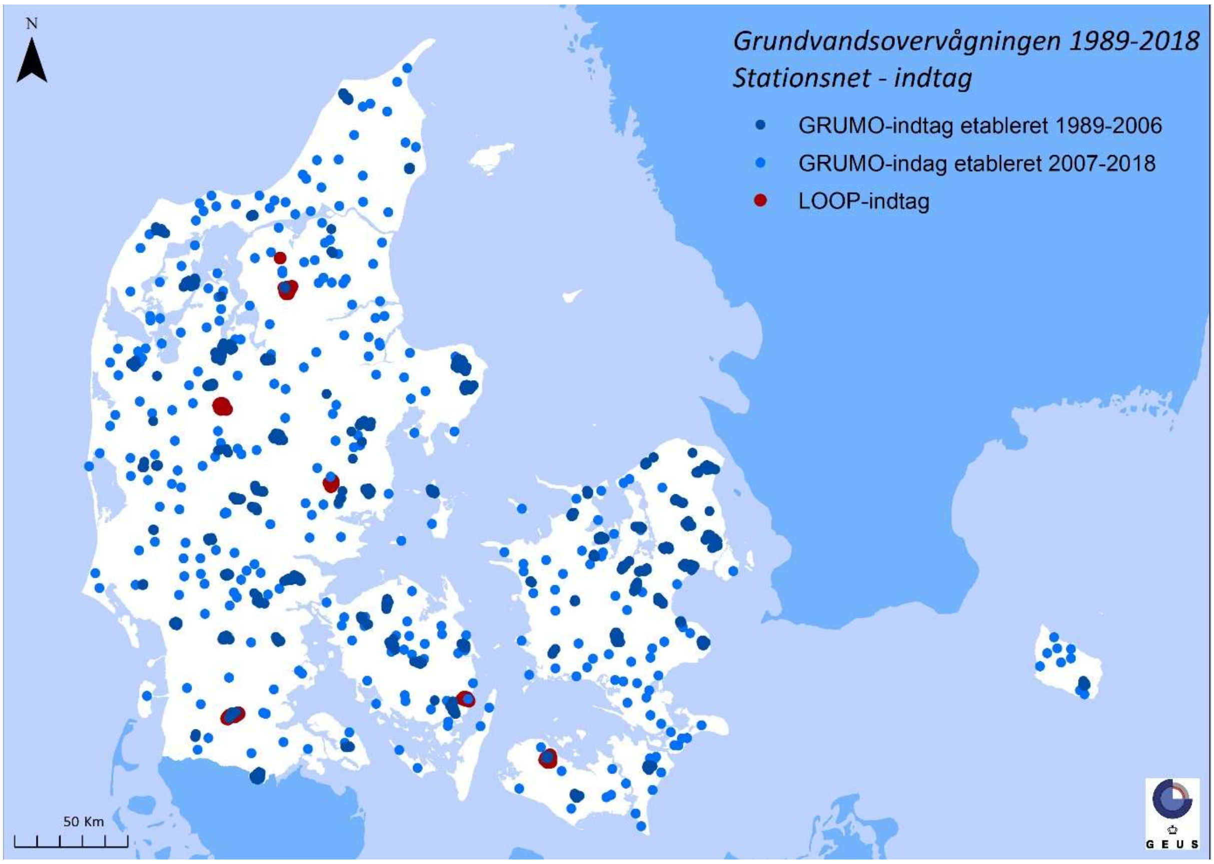

Figure 5.1 GRUMO. The total network for groundwater monitoring in Denmark for the period 1989-2018. The map shows monitoring points in the original 73 groundwater monitoring areas ('GRUMO-indtag' 1989-2006) and monitoring points in monitoring wells in the distributed station network '(GRUMO-indtag' 2007-2018). Included is also the LOOP monitoring of the six agricultural catchments, one of which was later closed in Central Jutland. (Thorling et al., 2019)

Figure 5.2 shows the geographical distribution of the depth to the top of the screens in GRUMO monitoring network, which were still included in the program in 2017. Data are sorted with decreasing depths drawn last. Monitoring points established down to approx. 40 meters are more or less evenly distributed over Denmark, while the deeper monitoring points show significant regional differences. Thus, on Bornholm, the vast majority of monitoring points are within the upper 20 meters, while the vast majority of deep boreholes (80-372 m b.s.) are found in Jutland with the largest occurrence in southern Jutland.

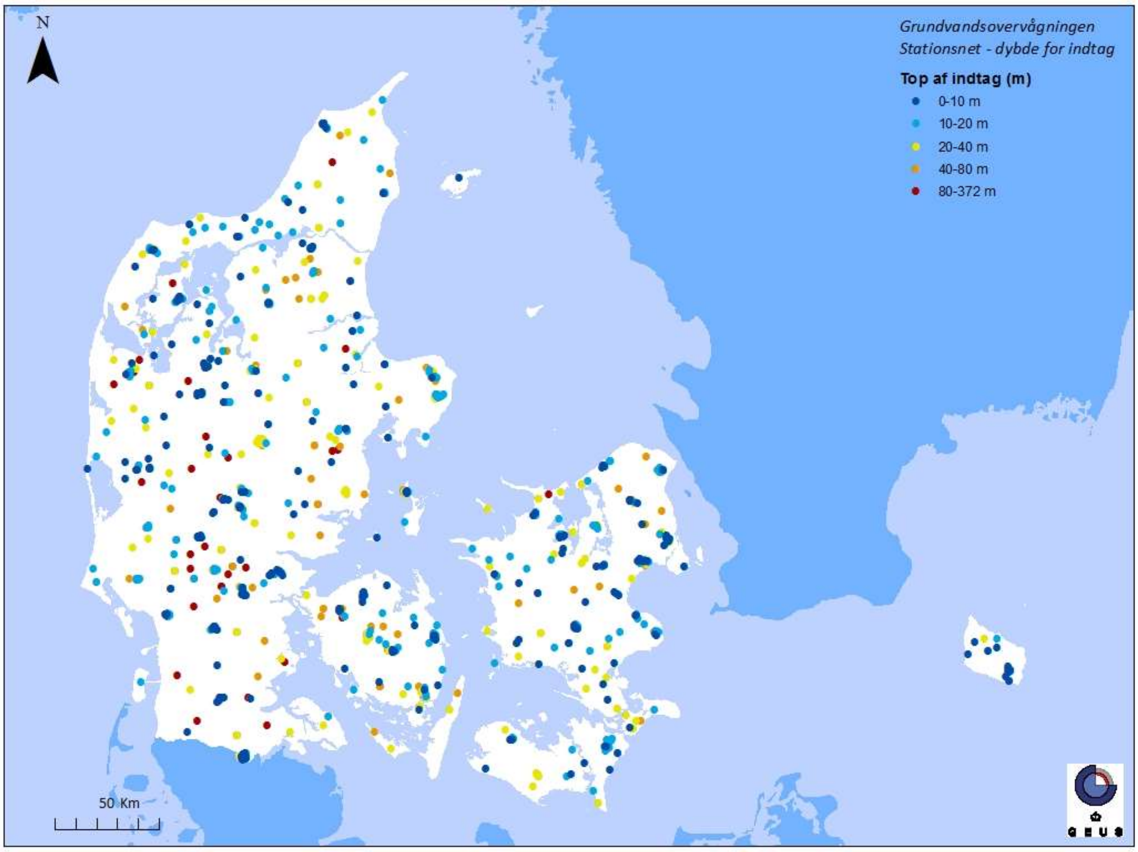

Figure 5.2 GRUMO. Depth to top (m b.s.) of 1,411 monitoring points with known depth in the Monitoring network of the Danish groundwater monitoring 2018-2021. (Thorling et al., 2019)

Figure 5.3 shows the depth distribution to the top of the screens for all GRUMO monitoring points and waterworks wells in 2018. Figure 5.3 shows that 50-60% of GRUMO monitoring points are established within the upper 20 m while just 10% are established deeper than 50 m b.s. In the waterworks wells, the screens are placed somewhat deeper. Here, 50% of the waterworks boreholes have the top of the screen located at a depth greater than 40 m b.s. and 10% at depths greater than 80 m b.s.

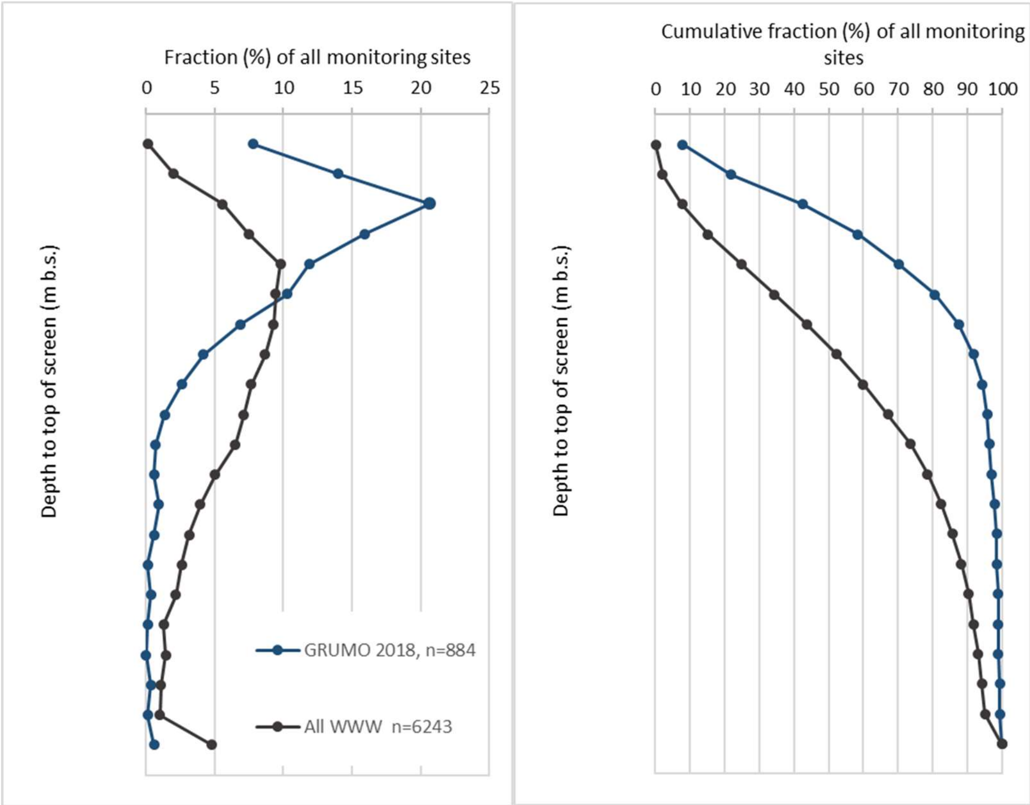

Figure 5.3 The figure on the left shows the fraction for depth to top of screen (m b.s.) calculated at 5 m intervals (%) for active waterworks wells (VV, grey) and GRUMO monitoring points (blueish). The figure on the right shows the accumulated distribution. (Thorling et al., 2019)

The agricultural catchment monitoring program, LOOP

The LOOP monitoring program monitors the quality of water collected from the unsaturated zone, tile drains and shallow groundwater (approx. 3-5 meters depth) in six agricultural catchments in sandy and clayey areas across Denmark primarily focusing on the leaching of nutrients (N and P) to groundwater (Fig. 5.4). The LOOP program plays an important role in the monitoring for the Danish derogation from the Nitrate Directive (Grant et. al 2011).

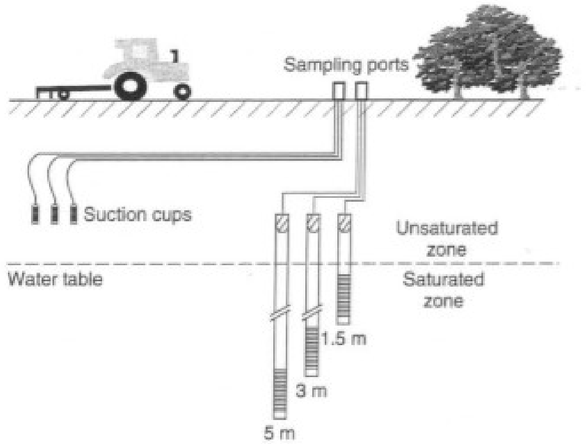

Figure 5.4 Schematic illustration of subsurface monitoring points in the Danish "LOOP" monitoring program. Besides the illustrated monitoring points, tile drains exist at about 1 m depth in clayey subsoils for areal monitoring (Hinsby and Jørgensen, 2009).

The Pesticide Leaching Assessment Program, PLAP

With an increasing number of findings of pesticide and / or their degradation products in the groundwater and a lack of knowledge as to whether this was due to agriculture's use of approved pesticides, the Danish Pesticide Leaching Assessment Program (PLAP; http://pesticidvarsling.dk/om_os_uk/uk-forside.html) was granted funding in 1998 by the Danish Parliament, which has provided funding until 2021. In 1999, PLAP was established by GEUS and Aarhus University linking to the Danish EPA.

PLAP is an early-warning monitoring program that, includes five to six fields (Fig. 5.5) used for arable farming, has the following purposes:

- To evaluate whether regular use of approved pesticides in maximum permitted dosages, under real Danish soil conditions, can result in leaching of the pesticides and/or their degradation products to the groundwater at concentrations above the limit value of 0.1 µg L^{-1}. The test period for a substance is typically 2 years after application. An assessment of the direct relationship between the specific pesticide applied to the experimental field and detections in groundwater is obtained by analyzing water samples from 1 meter depth (obtained via tile drains and suction cells) as well as from horizontal well screens directly beneath the field and vertical well screens installed both downstream and upstream of the experimental field. The survey results are reported annually PLAP report in English and in a special edition with accompanying independent Danish summaries. The annual PLAP reports focus on the last two years of monitoring results; but also includes results published in previous years' PLAP reports.
- Be able to improve and disseminate the scientific basis for optimization of the pesticides approval and regulation procedures of pesticides based on data on crops, cultivation practices, climate, drainage, soil water balance estimated applying the dual permeability model MACRO-model (a FOCUS-model applied in regulation of pesticides) and on high quality monitoring results on concentrations of pesticides and / or their degradation products plus inorganic compounds like nitrate-N in water collected from well screens, tile drain systems and suction cups. A basis that can contribute to optimization of the analysis program for the

nationwide groundwater monitoring (GRUMO and the Waterworks Well Control) and of the European regulation of pesticides as well as the development and commissioning of new analytical methods.

The six agricultural fields (Fig. 5.5) have been selected to represent Danish conditions in geology and climate. The presence of a pesticide in groundwater can thus be linked to a specific use of pesticides in an area in Denmark - a link that is used directly in the regulation of pesticides in agriculture in Denmark and at European level. The number of test fields has varied between five and six fields over the years. For the period 2019-2021, the experimental fields are made up of five active experimental fields (currently Jyndevad, Silstrup, Estrup, Faardrup and Lund) and one experimental field on standby (currently Tylstrup). The characteristics of the individual fields are given in Table 5.2 for:

- the five fields established in 1999 - two sandy (Tylstrup and Jyndevad) and three consisting of clay till/loam (Silstrup, Estrup and Faardrup) - as described in Lindhardt et al. (2001)
- a clay till/loam field established in Lund in 2016-2017 - as described in a yet to be published report (Haarder et al., 2019)

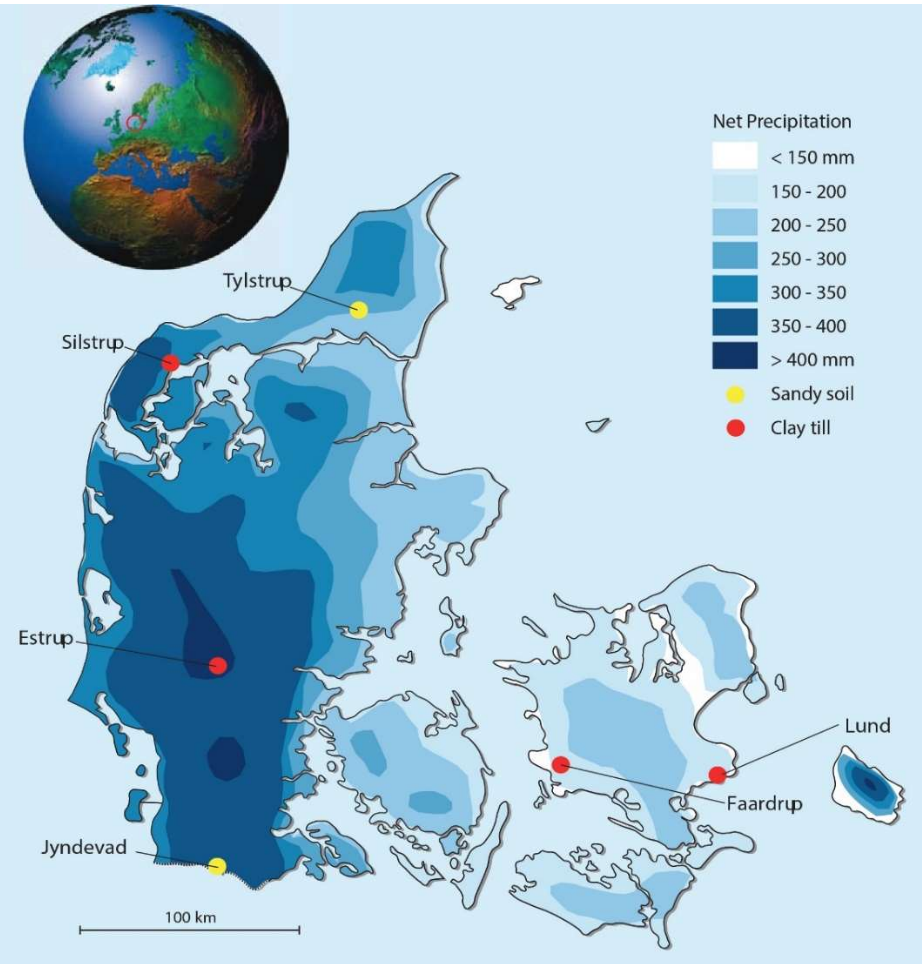

Figure 5.5 Annual net precipitation across Denmark and the geographical location of the six PLAP fields: Tylstrup (sandy), Jyndevad (sandy), Silstrup (clay till), Estrup (clay till) and Faardrup (clay till) included in the monitoring programme since 1999 and the new PLAP field Lund (clay till) included in PLAP from July 2017. It can be seen that the span in net precipitation observed in Denmark is well represented by the PLAP fields.

Table 5.2 Characteristics of the six PLAP fields included in the PLAP-monitoring for the period 1999-2018 (modified from Lindhardt et al., 2001).

PLAP-field	**Tylstrup**	**Jyndevad**	**Silstrup**	**Estrup**	**Faardrup**	**Lund**
Location	Brønderslev	Tinglev	Thisted	Askov	Slagelse	Lund
Precipitation[1)] (mm y^{-1})	668	858	866	862	558	
Pot. evapotransp.[1)] (mm y^{-1})	552	555	564	543	585	
Width (m) x Length (m)	70 x 166	135 x 180	91 x 185	105 x 120	150 x 160	100 x 300
Area (ha)	1.2	2.4	1.7	1.3	2.3	2.8
Tile drain	No	No	Yes	Yes	Yes	Yes
Depths to tile drain (m)			1.1	1.1	1.2	1.1
Monitoring initiated	May 1999	Sep 1999	Apr 2000	Apr 2000	Sep 1999	July 2017
Geological characteristics						
– Deposited by	Saltwater	Meltwater	Glacier	Glacier /meltwater	Glacier	Glacier
– Sediment type	Fine sand	Coarse sand	Clayey Till	Clayey till	Clayey till	Clayey till
– DGU symbol	YS	TS	ML	ML	ML	ML
– Depth to the calcareous matrix (m)	6	5–9	1.3	1–4[2)]	1.5	1.5
– Depth to the reduced matrix (m)	>12	10–12	5	>5[2)]	4.2	3.8
– Max. fracture depth[3)] (m)	–	–	4	>6.5	8	>6
– Fracture intensity 3–4 m depth (fractures m^{-1})	–	–	<1	11	4	<1
– Ks in C horizon (m s^{-1})	$2.0{\cdot}10^{-5}$	$1.3{\cdot}10^{-4}$	$3.4{\cdot}10^{-6}$	$8.0{\cdot}10^{-8}$	$7.2{\cdot}10^{-6}$	$5.8{\cdot}10^{-6}$
Topsoil characteristics						
– DK classification	JB2	JB1	JB7	JB5/6	JB5/6	JB5/6
– Classification	Loamy sand	Sand	Sandy clay loam / loam	Sandy sandyloam	Sandy loam	Sandy loam
– Clay content (%)	6	5	18–26	10–20	14–15	10-25
– Silt content (%)	13	4	27	20–27	25	30-35
– Sand content (%)	78	88	8	50–65	57	30-50
– pH	4–4.5	5.6–6.2	6.7–7	6.5–7.8	6.4–6.6	7.4-9.1
– TOC (%)	2.0	1.8	2.2	1.7–7.3	1.4	0-1.3

[1)] Yearly normal based on a time series for the period 1961–90. The data refer to precipitation measured 1.5 m above ground surface.
[2)] Large variation within the field.
[3)] Maximum fracture depth refers to the maximum fracture depth found in excavations and wells.

Each field consists of a cultivated area (1.2 - 2.8 ha) surrounded by a grass buffer zone from which all installations are established. The installations (Fig. 5.6) can be divided into two groups - those for sampling and those for monitoring/estimating the water balance of the field.

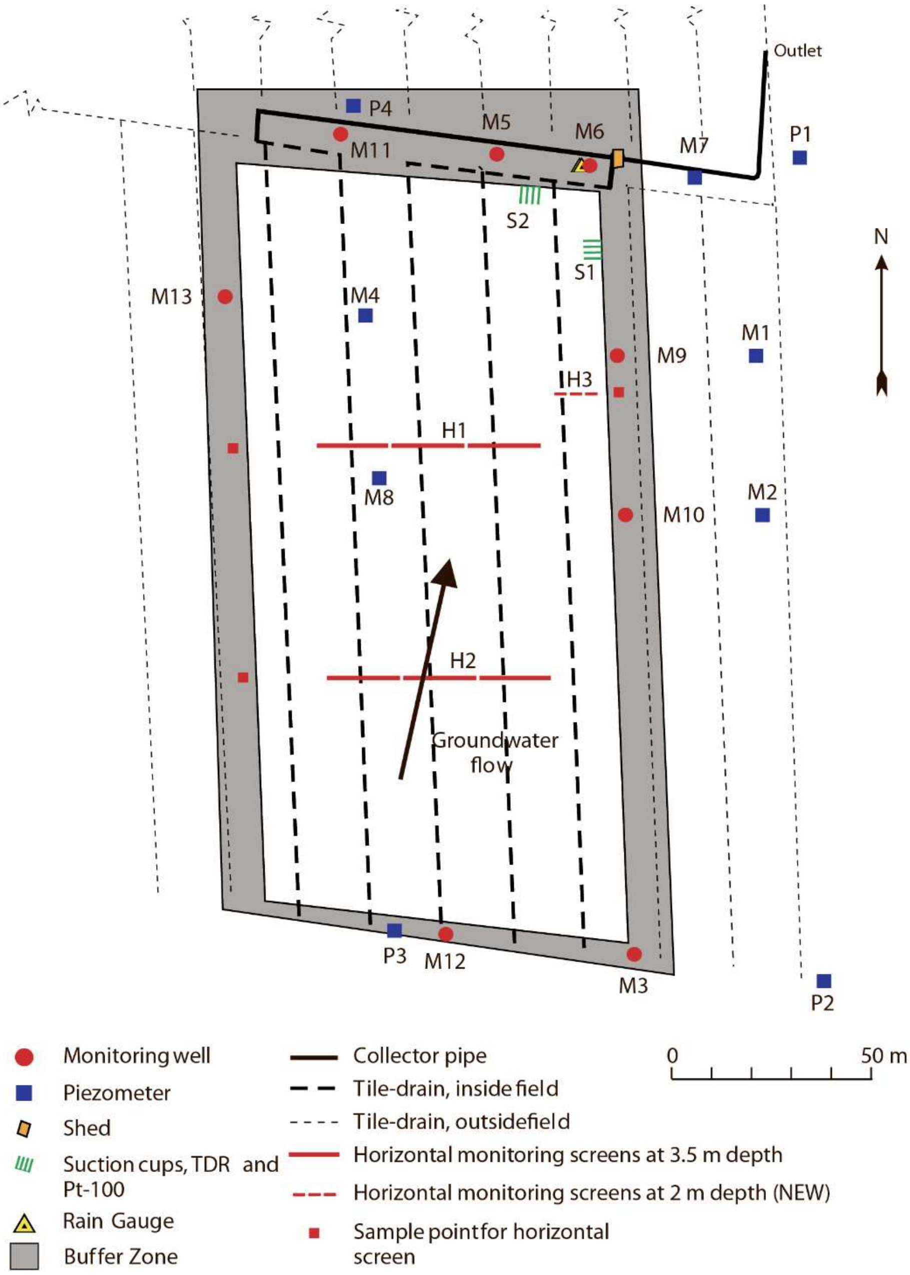

Figure 5.6 Overview of the PLAP-field-design. The innermost white area indicates the cultivated land, while the grey area indicates the surrounding buffer zone. The positions of the various installations are indicated, as is the direction of groundwater flow (by an arrow). Pesticide monitoring is conducted weekly from the drainage at the clay till/loamy fields (during periods of continuous drainage), monthly from the suction cups at the sandy fields, and monthly and half-yearly from selected vertical and horizontal monitoring screens.

Sampling installations include:

- The clay till/loamy fields (Silstrup, Estrup, Faardrup and Lund)
  - 4 suction cells installed at depths of 1 and 2 m at S1 and S2 (total of 16) downstream and below the cultivated area. The water samples are not used for pesticide-related analysis, as the suction used to collect the sample may change the pH of the sample and thus the nature of the sample.

- a tile drain system from 1930-1950, located only below the cultivated area at a depth of 1.1-1.2 m. The drainage system "culminates" in a drainage well in which a V-overflow is established to measure the drainage flow. With this knowledge, flow proportional drainage samples are collected weekly if there is water flowing in the tile drain system.
- Vertical monitoring wells filtered at four depths from which groundwater samples are collected monthly or half yearly from the top two groundwater filled screens. In the fields, an upstream well and 7-8 downstream well have been established - all in the buffer zone, whereby it is possible to take into account any potential. groundwater contribution from upstream fields in relation to detections.
- Horizontal monitoring wells located at 2 m (3 filter sections) and 3.5 m (3 filter sections) depth below the cultivated area from which samples are collected monthly. For the well installed at a depth of 2 m, samples are not collected if the groundwater level measured in the nearest vertical well is installed deeper than 1.7 m. The samples collected from the well sections are normally polled due to VAP's financial framework; but the possibility of analyzing on water from the individual sections exists.

- The sandy fields (Tylstrup and Jyndevad)
    - 4 suction cells located at depths of 1 and 2 m at S1 and S2 (total of 16) downstream and below the cultivated area. The water samples from 2 m depth in Jyndevad are not used, as the groundwater level may be located at this depth.
    - Vertical / vertical monitoring wells filtered at four depths from which groundwater samples are collected monthly or half yearly from the top two groundwater filled sections.
    - Horizontal monitoring wells installed at 2 m (3 filter sections) and 3.5 m (5 filter sections) depth from which samples are collected monthly. For the well located at a depth of 2 m, samples are not collected if the groundwater level measured in the nearest vertical well is located deeper than 1.7 m. The samples collected from the well sections are normally polled due to VAP's financial framework; but the possibility of analyzing on water from the individual sections exists.

Installations for monitoring / estimating the water balance of the field include:
- Precipitation in the field / climate station within 3-4 km (precipitation, evaporation and air temperature)
- TDR for measuring the soil water content at different depths in the upper 2 m
- Temperature sensors for measuring the earth's temperature at various depths in the upper 2 m
- Sensors and V-assault in drainage wells for measuring drainage from the clay till/loamy fields.

Additional:
- crops are registered (BBCH stages, agricultural practices, including registration of all sprays, also need sprays that are not included in the VAP monitoring, and from 2015 which seed dressing are added in the fields.
- the depth of the groundwater level below the field is recorded.
- MACRO modeling (version 5.2; Larsbo et al., 2005) is performed by the five fields established in 1999 to check the water balance data obtained. Such a model is not currently set up for the new VAP mark Lund.
- Concentrations of selected inorganic compounds like nitrate-N are monitored for all samples collected.

5.2 Information about travel times in the saturated and unsaturated zones

5.2.1 The national nitrogen model

Travel times for groundwater, nitrogen, pesticides and other pollutants to water abstraction wells and streams can be estimated by the national Danish nitrogen model and/or the national Danish water resources model / the DK-model (Troldborg et al., 2008, Højberg et al., 2015, Vervloet et al. 2018). In addition, the Danish nitrogen model and the DK-model may be used for estimation of nutrient loadings to groundwater associated aquatic ecosystems, eutrophication risks and derivation of groundwater threshold values (Hinsby et al., 2012, Kronvang et al., 2018, Nilsson et al. 2019).

5.2.2 GRUMO

Interpreting the causes of changes in the quality of the groundwater requires knowledge of the travel time (“age”) of the individual monitoring point. Knowledge of the travel time of the water makes it possible to assess whether the development of the quality of the groundwater shows temporal coincidences with changes in land use or action programs, including aquatic environment plans (Hansen et al., 2012).

Information on travel times to monitoring points of the GRUMO program can be obtained from national Danish nitrogen model similar to the other receptors mentioned above. However, to get more reliable results, the simulated travel times (or alternatively calibrate the flow models) should be corroborated by tracer estimated groundwater age distributions (Jakobsen et al., 2019).

Dating the groundwater in the individual monitoring points is among other things a prerequisite for being able to document an effect on the groundwater nitrate content of altered agricultural practices and nitrate leaching (Hansen et al., 2012). At the same time, dating of the groundwater can be used to demonstrate how the expansion of the monitoring with new boreholes and multiple monitoring points affects the age distribution of the monitored water. The assessment of the effectiveness of pesticide action plans is a more difficult task, since pesticides interact with the sediments through degradation and sorption in a much more complex pattern than nitrate.

5.2.2.1 Groundwater age/ residence time

In Denmark the use of tracers to inform on travel times have been part of the monitoring program since 1990, where the coarse method of ^{3}H dating was applied for all monitoring points with sufficient yields. This made it possible to subdivide the monitoring points into those who had modern water after approx. 1950 and those with ‘prebomb’ age. From 1992 CFC dating was introduced, but that was abandoned after 2005, when the content CFCs in the atmosphere had dropped due to the Montreal protocol, and research had documented degradation of all CFC tracers in anoxic groundwater. Thus, new methods had to be introduced, and $^{3}H/^{3}He$ was considered as the best choice and has been used since 2010. $^{3}H/^{3}He$ is both more expensive and challenging when it comes to sampling than CFC. Therefore, it has not yet been applied to all monitoring points.

The use of multiple tracers is generally recommended in order to identify the mixing of different water types and possible estimation of groundwater age distributions, but these are only applied in a few research projects.

Figure 5.7 shows the groundwater residence time as a function of depth for 932 dated monitoring points, corresponding to > 75% of the monitoring network. Ages are derived from both CFC (in the oxic zone) and $^{3}H/^{3}He$. It can be seen from the figure that in the upper 40 m groundwater has very different residence time, and that in the upper 20 m there is no simple connection between depth and age. However, it should be noted that the average age and median age increase with increasing depth as the proportion of young water decreases with depth. The reason for the image seen in Figure 5.8 is differences in groundwater recharge, hydraulic barriers and other variations in hydrogeological flow conditions. In outflow/seepage areas with upward gradient, even very old groundwater can be found close to the terrain. Therefore, the best straight line also does not go through the age 0 years at depth 0 m b.s. In Denmark thus no age depth relation is established, as on the contrary, such a relation would be considered rough and erroneousness, see also figures below flow the multiscreen wells.

When working with these data, it must be kept in mind that the age is only a reflection of the actual age-distribution in each monitoring point, where the relative short screens in the monitoring wells reduce the age span in cases where hydrogeological mixing play a minor role.

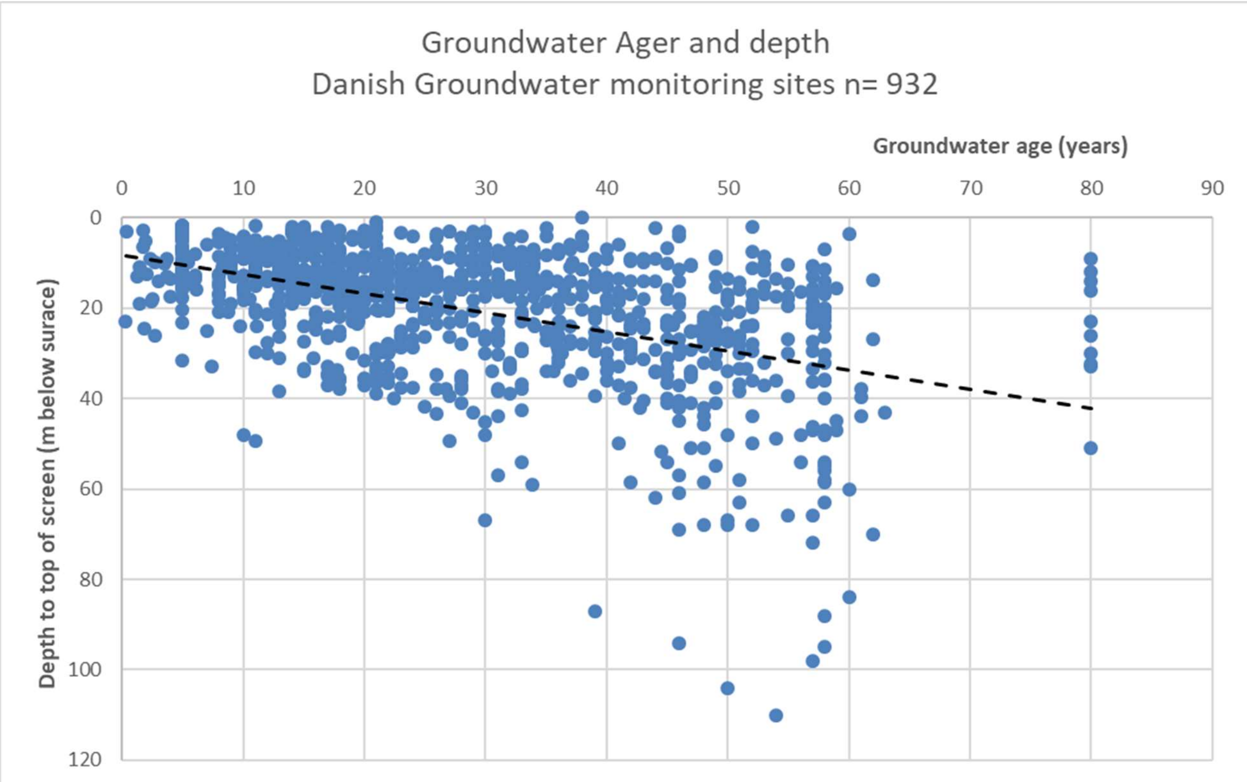

Figure 5.7 Groundwater age/residence times (apparent CFC or 3H/3He tracer ages) of groundwater sampled at different depths of 932 monitoring points assuming piston flow. The best straight line through all points is shown to illustrate the challenges. (Thorling et al., 2019)

The most comprehensive and detailed data sets and study on groundwater age distributions in nitrate contaminated wells in Denmark are available from the Rabis Creek site (Postma et al., 1991, Engesgaard et al., 1996, 2004, Hinsby et al., 2007, Jessen et al., 2017). The Rabis Creek site is sampled as part of the GRUMO program.

5.2.3 PLAP

The travel time of different pesticides and their degradation product at the PLAP fields varies a lot with climate, crop and soil conditions. It is, hence, too complex to estimate the travel times of compounds. In Rosenbom *et al.* (2015), three types of leaching scenarios are today not fully understood: i) long-term leaching of degradation products of pesticides applied on potato crops cultivated in sand, ii) leaching of strongly sorbing pesticides after autumn application on clay till/loam, and iii) leaching of various pesticides and their degradation products following early summer application on clay till/loam. Rapid preferential transport through macropores in the clay till/loam bypassing the retardation of the plow layer seem to dominate the leaching of pesticides, their degradation products and e.g. nitrate-N at these fields, making the clay till fields more prone to leaching of compounds than sandy soils.

5.2.3.1 Age dating

As noted in the PLAP-report Rosenbom et al., 2017 Appendix 9 groundwater in PLAP is too young to be given an age and as noted in Gimsing *et al.* (2019) the commonly accepted definition ‘‘the (highly) idealised groundwater age is the time difference that a water parcel needs to travel from the groundwater surface to the position where the sample is taken’’ does not account for mixing of different ages and the complexity in transport pathways in time and space (Suckow, 2014), why no evaluation in PLAP is including this type of “age”-data.

5.3 Information about attenuating processes in the subsurface

5.3.1 Denitrification mapping

In Denmark the National groundwater mapping has taken place since late 1990s until 2015. The main purpose of this mapping effort was to map vulnerability towards nitrate in drinking-water areas. The Danish Environmental Protection Agency is responsible for the mapping, and after delineation of nitrate vulnerable abstraction areas, the municipalities are responsible for action plans in these areas. More than 2.7 bio. DKK has been used on this task. (Danish EPA, homepage)

An important part of this mapping is identification of the redox-interface and assessment of the stability of the extent of nitrate in the aquifers.

The national guidance documents for the geochemical mapping for the national groundwater mapping program operates with 4 water types (Hansen and Thorling, 2018) (figure 5.8).

- Oxygen-rich groundwater: O_2> 1 mg/L and Fe ≤ 0.1 mg/L and Mn ≤ 0.1 mg/L (water type A).
- Anoxic nitrate reducing zone: NO_3> 1 mg /L and O_2 ≤ 1 mg /L, (water type B).
- Reduced groundwater: NO_3 ≤ 1 mg/L, O_2 ≤ 1 mg /L and SO_4> 20 mg /L, (water type C).
- Strongly reduced groundwater: NO_3 ≤ 1 mg/L, O_2 ≤ 1 mg /L and SO4 ≤ 20 mg/L, (water type D).

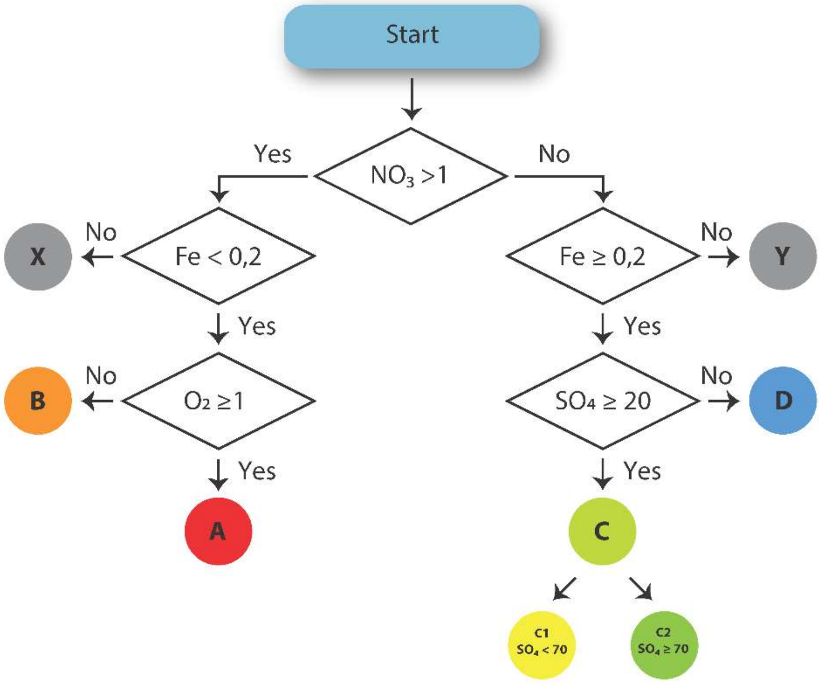

Figure 5.8 Algorithm for assigning redox water type used in Denmark, from Guidance on mapping of groundwater chemistry (Hansen & Thorling 2018).

Water type A is found in the water samples from the fully oxidized layers were nitrate is present and no denitrification takes place. Water type B is met in layers where nitrate reduction takes place, in anoxic groundwater. Water types C and D are met after the nitrate reduction processes are completed, and less than 1 mg/l nitrate is left in the groundwater and iron and sulfate reduction are the dominating processes.

In relation to this, GEUS has produced a national map for the depth to the *first upper redox interface.* The map is a 100 m grid, compiled for display in scale 1:400.000, figure 5.9 and can be downloaded from GEUS' Webshop. The map is used for a wide variety of groundwater planning and management issues as task in connection with the WFD. (EU, 2000). Due to geological heterogeneity, consecutive redox interfaces may be found in typical Danish geological settings (Kim et al, 2019).

The map illustrates depth to the redox interface in meters below ground. The interface marks the transition from oxidised to reduced conditions in the subsurface. Based on approx. 13.000 observations of colour changes in sediment cores, a model has been developed describing relations between explanatory variables and depth to the redox interface. The machine learning method "random forest" has been used to develop the model. The map shows the best estimate of the location of the interface in a 100 m grid resolution. The applied method additional provides an estimate of the uncertainty. The method is described further in (Koch et al., 2019)

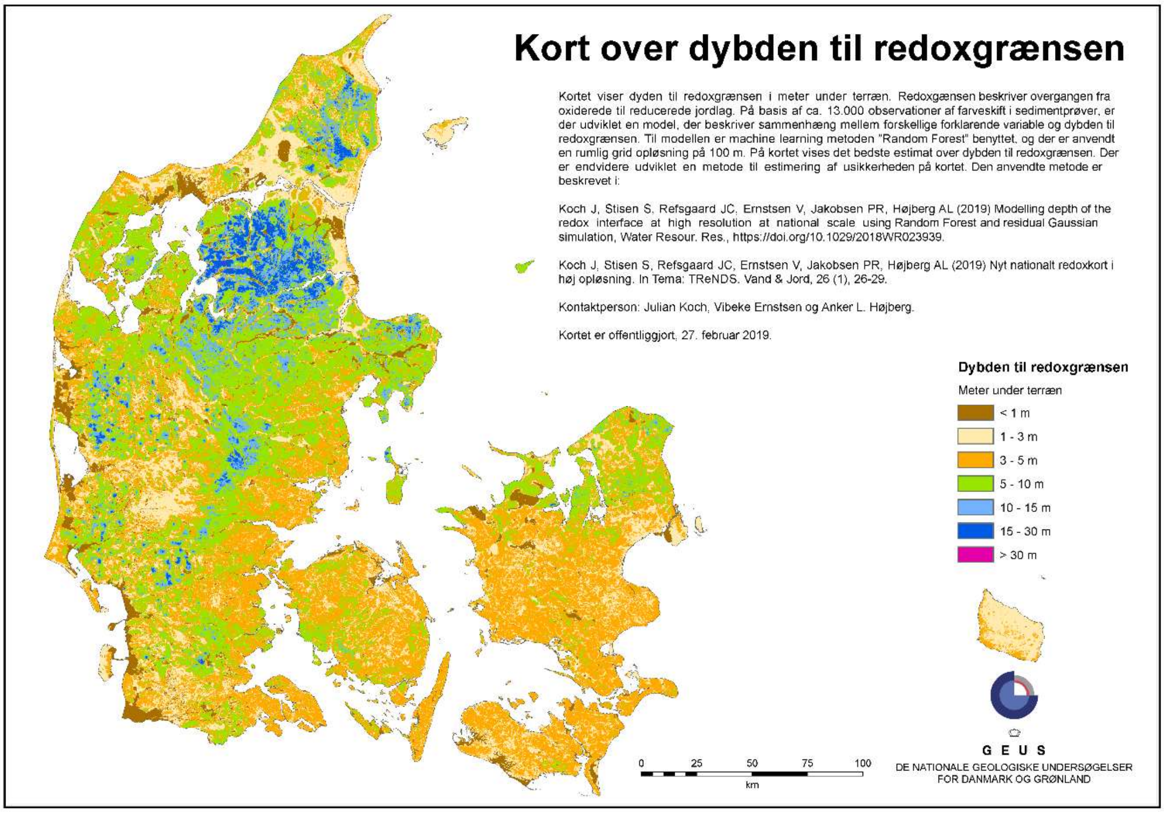

Figure 5.9 Danish National map for the depth to the uppermost redox interface (Koch et al, 2019).

5.4 Temporal variations in variations in the depth and thickness of the redox zones

Objectives and relevance

In order to improve the description and understanding of variations over time of the vertical distribution of the redox zones and their interfaces, and thus of the distribution of nitrate in particular in the groundwater aquifers, groundwater is monitored in 5 special multiscreen redox wells, each with 15 to 23 short (10 cm) screens as monitoring points. Changes in the penetration depth of nitrate and oxygen are of great importance to the environmental state of associated surface water systems, since the greater the extent of the nitrate-containing layers, the greater the risk that the associated surface water systems receive groundwater with nitrate. At the same time, the extent of the oxidized layers has a significant impact on how much of the drinking water resource is affected by nitrate.

The nitrate reducing zone's ability to reduce nitrate depends on the geochemical properties of the geological layers. When the nitrate reducing zone (with water type B, see below) has a great extension of several meters, it is an indication that the nitrate reduction processes are slow in that aquifer and that the content of reactive nitrate reducing agents is low. The reduction capacity of the aquifers, and not least the rate of turnover of nitrate, is of great importance for the drinking water supply. In areas of low reaction rate and / or low reduction capacity, there is a high risk of nitrate breakthrough. Thus, increasing nitrate concentrations may occur in water works wells when nitrate reduction is too slow relative to the altered flow conditions in the reservoir caused by the water abstraction.

A better understanding of the temporal variations in the spatial distribution of the redox zones may also support the interpretation of time series for especially nitrate, sulfate and other redox-sensitive parameters established in the monitoring program, thus supporting one of the primary objectives of the monitoring, namely to assess the effects of national environmental measures in for the objectives set.

Data basis

During the period 1999-2018 data for a number of redox-sensitive substances have been collected from the redox wells: oxygen, nitrate, nitrite, iron, manganese, sulfate, chloride as well as pH, conductivity and redox potential. The figures 5.10 to 5.15 show the geological strata series together with monitoring data from all monitoring points in the boreholes. Until 2011, the wells were sampled one to several times each year. Since then, sampling has become less frequent.

Data processing

The redox zones shown in the figures are due to the high data quality based on a slightly adjusted version of the criteria in figure 5.8:

• Oxygen-rich groundwater: O_2> 1 mg/L and Fe ≤ 0.1 mg/L and Mn ≤ 0.1 mg/L (water type A).
• Anoxic nitrate reducing zone: NO_3 > 1 mg/L and O_2 ≤ 1 mg/L, (water type B).
• Reduced groundwater: NO_3 ≤ 1 mg/L, O_2 ≤ 1 mg/L and SO_4 > 20 mg/L, (water type C).
• Strongly reduced groundwater: NO_3 ≤ 1 mg/L, O_2 ≤ 1 mg/L and SO_4 ≤ 20 mg/L, (water type D).

Oxygen is a crucial parameter for the water type determination. Therefore a manual interpretation of the redox water type takes place for water samples where, for example, oxygen analyzes are lacking. The interpretation is based on the sample's other content of redox-sensitive parameters with special emphasis on the content of nitrite, manganese, iron, sulfate and nitrate (Hansen and Thorling, 2018).

The age of the groundwater

The age of the groundwater in the individual monitoring points is shown in Table 5.3. Note there is no simple linear increase of age with depth.

Table 5.3. Redox wells at Albæk, Kasted, Grindsted, Vejby and Siberia. Groundwater age in monitoring point determined by the CFC method. Note that the lower screen number is no. 1. (Thorling et al., 2019)

ID.	Albæk	Kasted	Grindsted	Vejby	Sibirien
DGU nr.	18.310	78.796	114.1736.	186.854	238.900
Monitoring point no	Age (years)	Age (years)	Age (years)	Age (years)	Age (years)
23			6		
22			8		
21			10		
20		20	8		
19		20	5		
18		27	10		
17		36	14		34
16		36	22	<5	33
15	21	44	21		24
14	17	45	19		28
13	17	51	19	13	31
12	18	48	25		25
11	18	50	27	17	23
10	22	50	28	40	11
9	17	40	29	56	36
8	24	40	31	55	39
7	26	40	31		37
6	31	49	35	55	44
5	32	52	33	57	45
4	39	60	40		45
3	45	61	38	50	44
2	43	61	33	57	47
1	47	61	55	36	48

5.4.1 The Redox Well at Albæk in North Jutland - DGU nr. 18.310

Figure 5.10 shows an overview of the water types in the redox well at Albæk with monitoring points in the interval 34-41 m u.t. In 2018, all monitoring points contained oxygenated and nitrate-containing groundwater (water type A). In 2018, the nitrate concentration in all monitoring points was between 14 and 33 mg/l (see Figure 5.15). The entire aquifer, which consists of fine to medium grain sand, is currently expected to be nitrate-containing.

The oxygen-rich environment means that denitrification is not expected, and the nitrate content of the groundwater remains unchanged as it flows from the soil surface down into the groundwater reservoir.

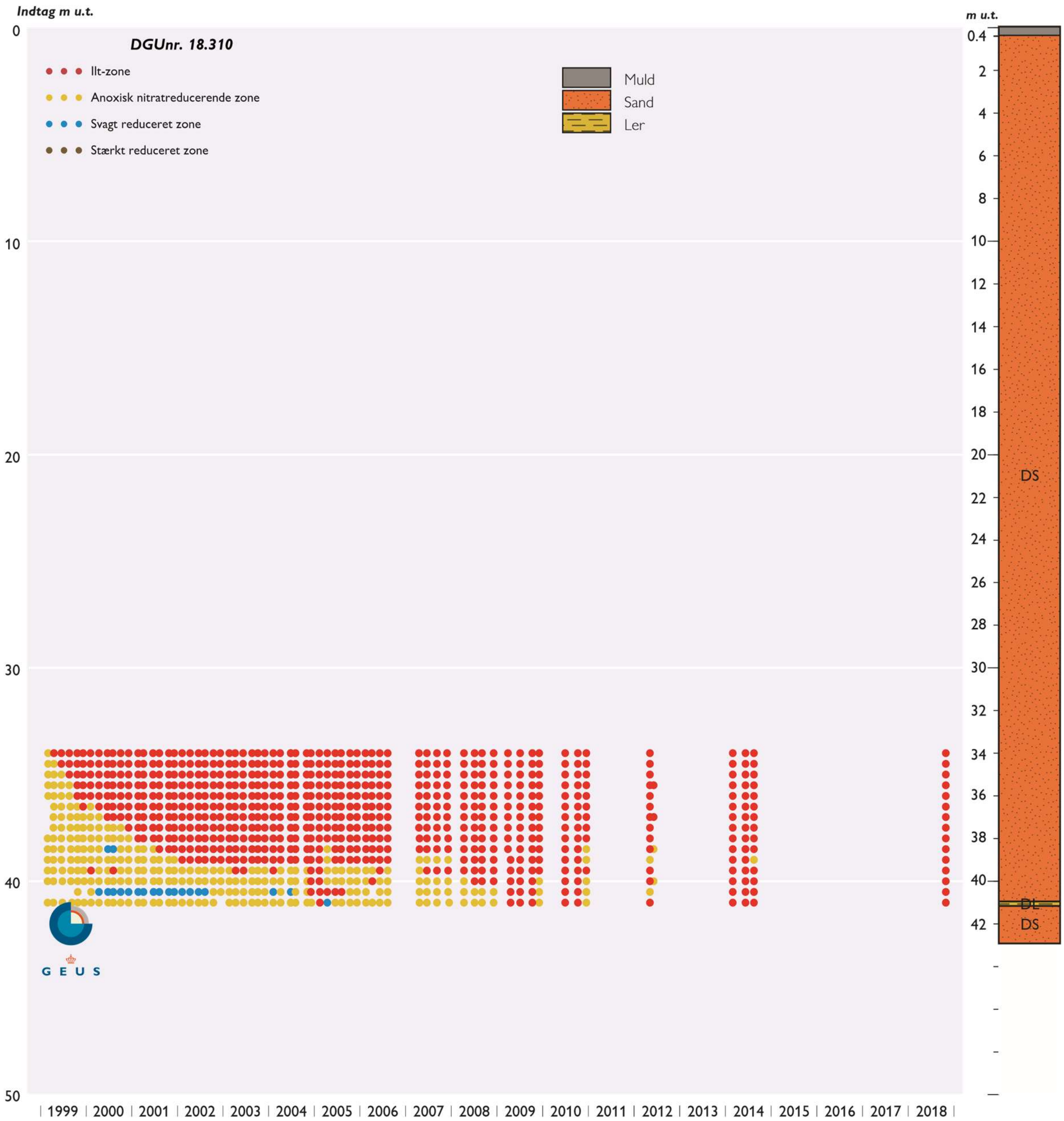

Figure 5.10 Albæk in Northern Jutland, DGU No. 18310, with redox zones for the period 1999-2018. Groundwater table is approx. 15 m b.s. The geological profile is shown at the far right of the figure. (Thorling et al., 2019)

5.4.2 *The Redox Well at Kasted north-west of Århus - DGU nr. 78.796*

Figure 5.11 shows especially the redox well at Kasted, where the redox zones have remained relatively stable, with no major changes from 1999 to 2018. The groundwater level is at approx. 9 m b.s. The top approx. 15 meters of the aquifer is nitrate- and oxygen-containing water type A, followed by an approx. 10 m of oxygen-free and nitrate-containing zone, with water type B and including slightly reduced groundwater, water type C. Thus, a significant part of the groundwater reservoir is nitrate-containing. In 2018, the concentration of nitrate in the oxygen-containing zone was 40-62 mg/l, and the content decreased to 7-27 mg/l in the upper part of the anoxic zone, after which the nitrate content increased to 48-54 mg/l in the lower part of the anoxic zone, Figure 5.15. In the oxygen-containing zone, the oxygen content in 2018 was between 5 and 9 mg/l. Relatively high concentrations of sulphate in the nitrate-reducing oxygen-free zone (120 mg/l) indicate that the reduction of nitrate here occurs, among other things by pyrite. The concentration of sulfate in the oxygen-containing zone in 2018 was between 21-81 mg/l. Aarhus Water has a well site approx. 500 m downstream of this well.

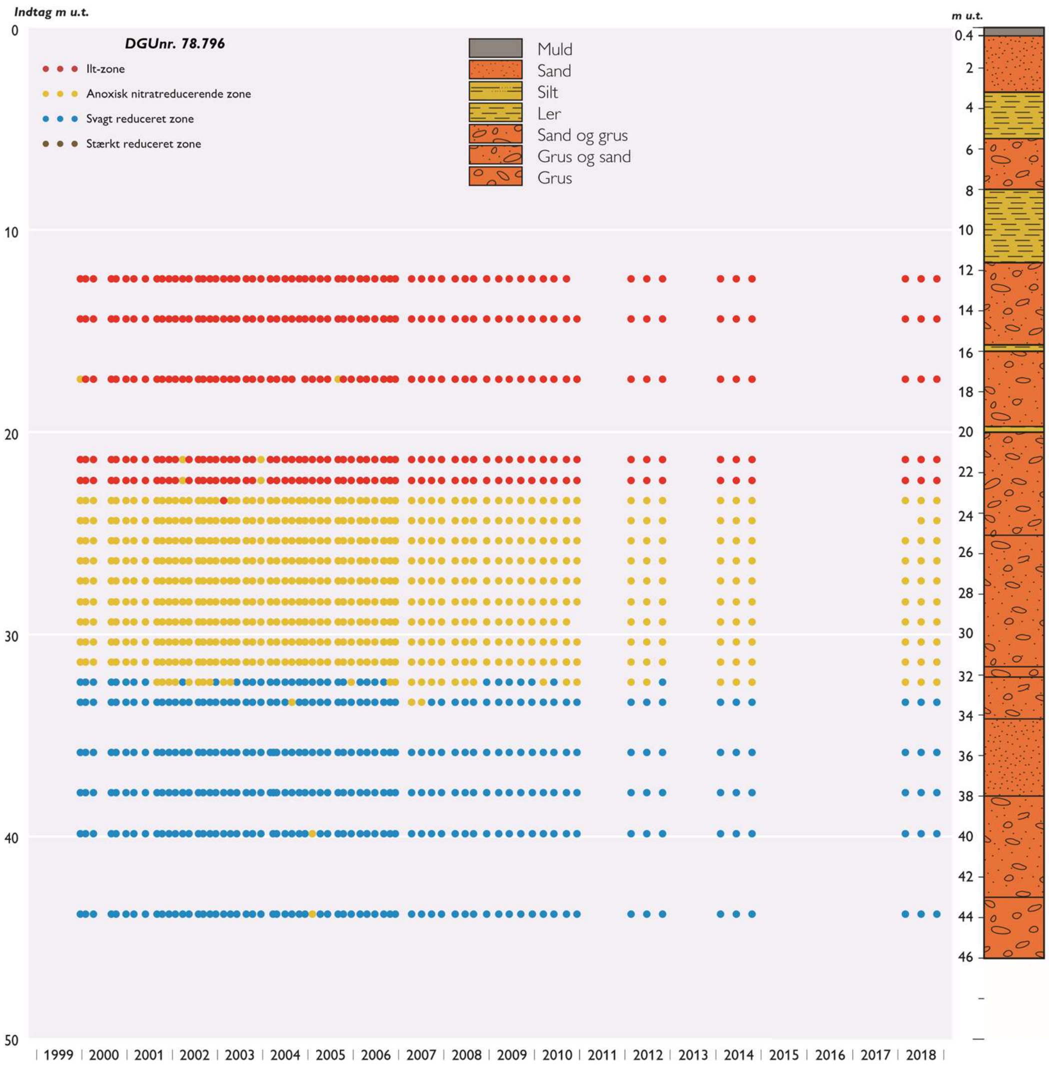

Figure 5.11 Kasted northwest of Aarhus, DGU No. 78,796, with redox zones for the period 1999-2018. Groundwater table is approx. 9 m b.s. The geological profile is shown at the far right of the figure. (Thorling et al., 2019)

5.4.3 The Redox Well at Grindsted in Mid-Jutland - DGU nr. 114.1736

Figure 5.12 gives an overview of the water types in the redox well at Grindsted with monitoring points in the interval 13-39 m b.s. It is evident that the spatial distribution of the redox zones in the well at Grindsted has varied somewhat in the period 1999-2010. During the period 2012-2018, the distribution of the different redox zones has been more stable, with the largest changes in water types A and B in 20-23 m b.s. The upper, oxygen and nitrate-containing zone, water type A, is estimated to extend from 3 m b.s. down to approx. 23 m b.s. and constitute the top 20 m of the groundwater reservoir. After this, approx. 3 m oxygen-free nitrate-containing zone, water type B, which is followed by a 10 m slightly reduced zone without oxygen and nitrate, water type C. In the deepest monitoring point 29.5 m b.s. occasionally, strongly reduced groundwater, water type D.
In 2018, the concentration of nitrate in the majority of the oxygenated groundwater reservoir was between 45 and 55 mg/l. In 2018, the concentration of sulfate was fairly constant down through the groundwater reservoir, by 35-45 mg/l.

Figure 5.12 Grindsted in Central Jutland, DGU No. 114.1736 with redox zones for the period 1999-2018. The groundwater table is located in approx. 2 m b.s. The geological profile is shown at the far right of the figure. (Thorling et al., 2019)

5.4.4 The Redox well at Vejby in North Zealand - DGU nr. 186.854

Figure 5.13 shows that in 2018 oxygen-free and nitrate-containing groundwater, water type B occurs in the upper 3 meters of the groundwater reservoir, down to approx. 14 m b.s. at Vejby. The nitrate content during this period was 3-20 mg/l, see Figure 5.16. In the deeper monitoring points, the water type has been unchanged, slightly reduced, water type C, since 2006, with the only exception being the monitoring point at 29.5 m b.s. That for a period has been strongly reduced. The concentration of sulfate is 10-40 mg/l in the nitrate-containing zone and rises to 50-60 mg/l in the deeper monitoring points, with the exception of the groundwater in the deepest monitoring point in 27.5 m b.s., where the concentration of sulfate is below 40 mg/l.

The groundwater table in 2018 was located for approx. 11 m b.s. and simultaneous measurements in 16.4, 21.5 and 29.5 m b.s. suggest that there is no good hydraulic contact between the layers.

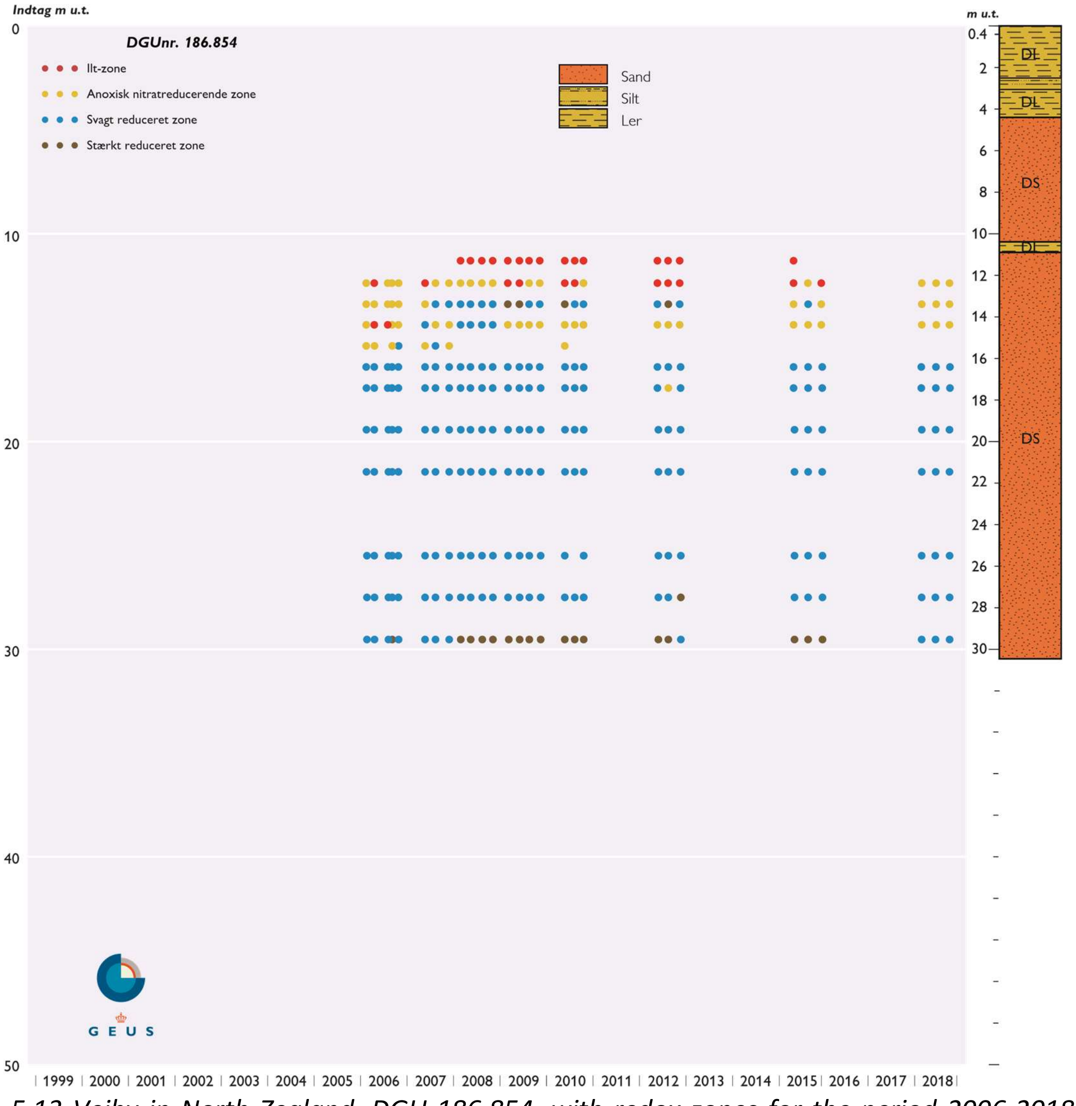

Figure 5.13 Vejby in North Zealand, DGU 186.854, with redox zones for the period 2006-2018. The groundwater level is located in approx. 11 m b.s. The geological profile is shown at the far right of the figure. (Thorling et al., 2019)

5.4.5 The Redox Well at Sibirien on Falster - DGU nr. 238.900

Figure 5.14 shows that there is nitrate down to approx. 21 m b.s. in the redox well at Siberia on Falster. In the top two oxygenated monitoring points, water type A, from 10-12 m b.s. nitrate concentrations of 82-190 mg/l and 2-6 mg/l of oxygen were measured in 2018. In the interval, 13-17 m b.s. there are alternating oxygenated and anoxic redox conditions throughout the years and the concentration of nitrate decreases to 23-58 mg/l, while the oxygen concentration is typically <3 mg/l. In 2018, the concentration of nitrate at 25 m b.s. increased significantly from < 5 mg/l to 110 mg/l, see Figure 5.15. This monitoring point was at the beginning of the monitoring period anoxic, water type B, in 1999-2003, after which it was slightly reducing, water type C, until 2012, when it again became anoxic. In 2018, the concentration of sulfate in 10-21 m b.s. ranged between 28 and 59 mg/l. The concentration of sulfate in deeper groundwater was up to 150 mg/l, except for the deepest monitoring point established in chalk, where the concentration was only about 30 mg/l.

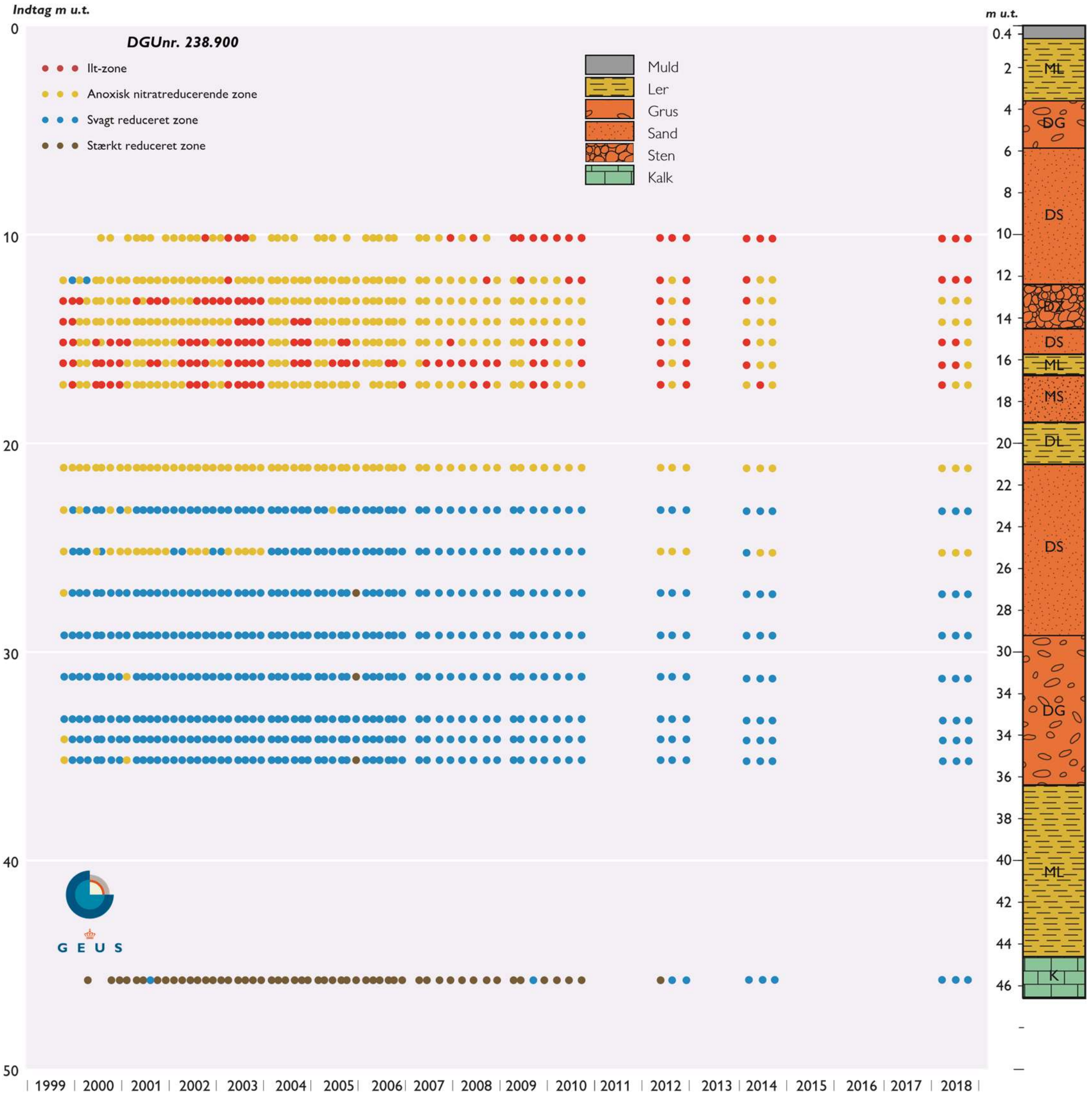

Figure 5.14 Sibirien on Falster, DGU no. 238.900, with redox zones for the period 1999-2018. The groundwater level is 9 m b.s. The geological profile is shown at the far right of the figure. (Thorling et al., 2019)

Nitrate trends in the period 2000-2008

Figure 5.15 shows how the annual average nitrate concentration has varied throughout the various redox wells during the period 2000-2018, divided into 6 year intervals.

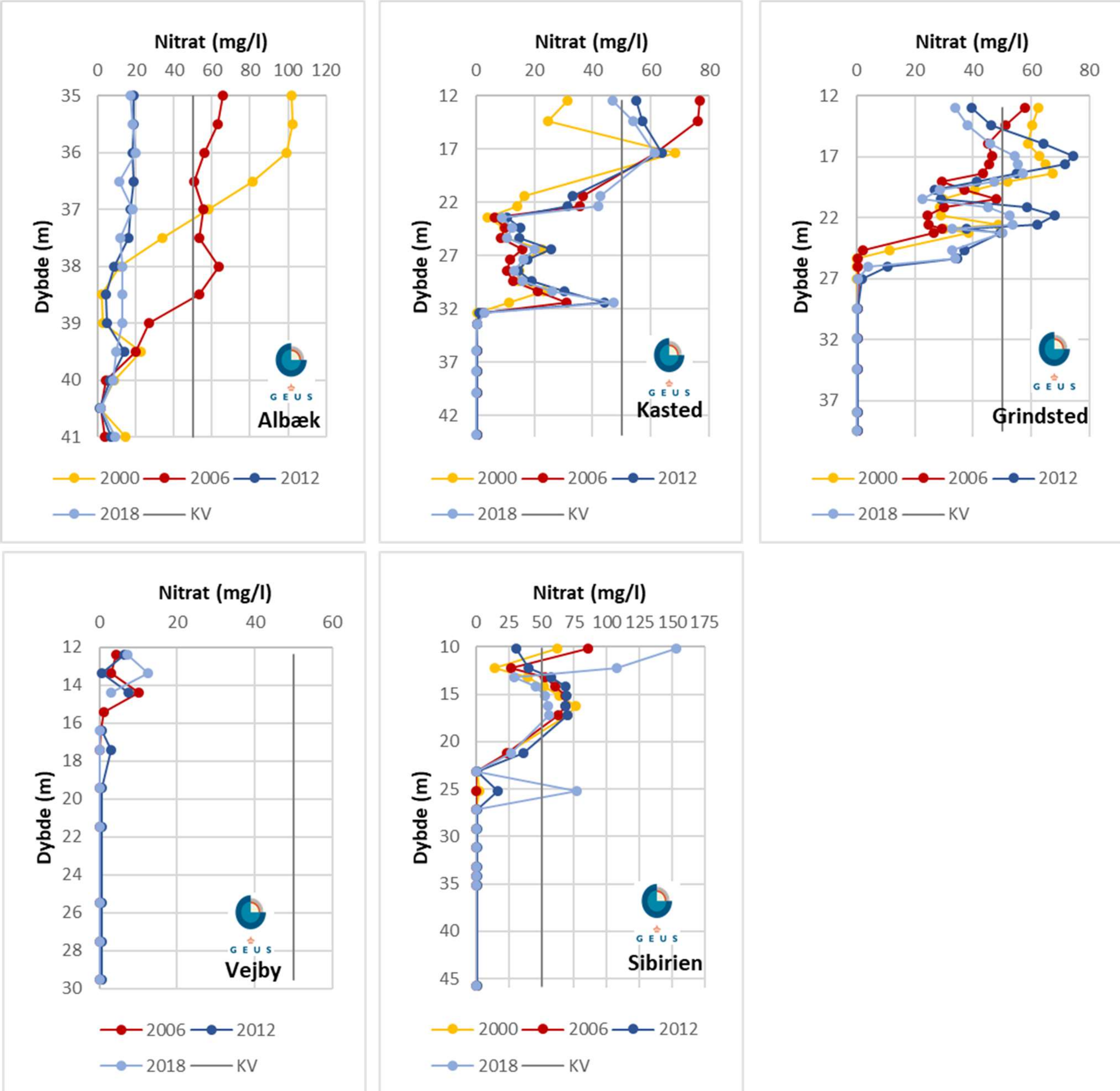

Figure 5.15 The distribution of the average concentration of nitrate at different depths in the redox bores. The distribution of nitrate is shown at an interval of 6 years for the period 2000-2018, with the exception of Vejby, where the measurement series is shorter. KV is the quality requirement for nitrate in groundwater and drinking water of 50 mg / l. (Thorling et al., 2019)

5.5 Combined analysis of transport and attenuating processes in the pilot area

Pesticides like MCPA being more or less completely degraded in the plough layer (Rosenbom et al., 2014) are ideal given their low risk of leaching to the groundwater. Having compounds being sorbed and/or degraded in the upper microbiological and organic rich zone (primarily the plough layer) are crucial for the reduction of the mass leaching through the variably-saturated zone. Such fate processes have normally a higher impact in sandy soil than fractured clay till soils, since the percolating water flow through a larger volume of soil. Having the preferential flow and transport making solutes/compounds move fast through the variably-saturated in discontinuities minimize the impact of these fate processes making the clay till/loamy fields much more prone to leaching of pesticides, their degradation product and inorganic compounds like nitrate-N (Ernstsen *et al.*, 2015).

5.6 Testing approaches to harmonized, processed data for supraregional evaluations

The PLAP-monitoring results have revealed for the Danish climate and soil conditions that the leaching of pesticides, their degradation products and inorganic compounds like nitrate-N is very complex and controlled by discontinuities/macropores/biopores/wormholes/fractures at the clay till/loamy fields. To be able to assess the leaching of different compounds in the future it will be imperative to have monitoring data like the PLAP-data from other EU-countries being an eye-opener in regard to leaching of compounds – by obtaining such high-quality data, shortcomings in our current understanding is delineated making it possible to address them in future research.

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Links:

Groundwater monitoring homepage
http://www.geus.dk/vandressourcer/overvaagningsprogrammer/grundvandsovervaagning

National redoxinterface map:
https://data.geus.dk/geusmap/?lang=da&mapname=denmark#baslay=baseMapDa&optlay=&extent=-11628.551440329175,5934760.653254077,1126628.5514403293,6515239.346745923&layers=redox_dybde_100m_grid

6 CASE STUDY UK

6.1 Description of Monitoring network

6.1.1 National scale groundwater quality monitoring data

In the UK there exists a large body of saturated groundwater quality data at the national scale held by the Environment Agency in England. A subset of this is reported online as the Environment Agency's OpenWIMS data (https://environment.data.gov.uk/water-quality/view/landing) Data are derived from observation boreholes and public water supply wells and consist of a wide range of denitrification indicator species (N-species, trace metals, O and S species, DOC and pH). This data has been used for trend and compliance analysis and reported extensively elsewhere (see, for example, Stuart et al. (2007)). In this case study, we report the use of this data to assess attenuation processes (see section 6.3), as well as the use of porewater profiles to assess unsaturated zone time lags herein.

6.1.2 Porewater profiles

In the past 40 years, extensive research has been undertaken into the transport and fate of nitrate in the unsaturated zone in the UK. A key component of this research has been the sequential coring of boreholes through the unsaturated zone at different sites to derive repeated concentration-depth porewater profiles for nitrate, tritium and other species. The profiles have been used to evaluate both travel times for nitrate and the extent of any denitrification in the unsaturated zone.

Boreholes were cored for specific research projects in the UK associated with nitrate pollution of groundwater (e.g. commissioned projects for water companies, university research, LOCAR, WRc investigations), and whilst this is likely to have resulted in some sampling bias, the major aquifers of the UK (Chalk, Permo-Triassic sandstones and Middle Jurassic (including Lincolnshire) Limestone) have all been investigated. BGS has collated the resulting profile data into national level databases as reported by Moreau et al. (2004) and further developed by Stuart (2005). Analysis of these profiles have significantly improved our understanding of contaminant fate and transport through the unsaturated zone across different hydrogeological settings.

Figure 6.1 shows the spatial distribution of nitrate porewater profiles in England in relation to the most important aquifers in the UK. In total the BGS porewater profile database holds 52,260 individual records of quality data, derived from 102 unique sites. The database has 389 nitrate profiles and 60 tritium profiles (Stuart, 2005). As well as sites in the Chalk, Permo-Triassic sandstones and Lincolnshire Limestone, profiles also exist for overlying Quaternary deposits (principally glaciofluvial deposits in East Anglia and silty loess sands in Jersey) and the Oxford Clay.

The porewater profiles held in the database have been used extensively for the development and validation of models of national and local scale models of nitrate transport and storage in the unsaturated zone (Ascott et al., 2016; Stuart et al., 2016; Wang et al., 2012). The rest of this chapter outlines the data further, and application of this data to models will be detailed in HOVER WP5 Deliverable 5.3.

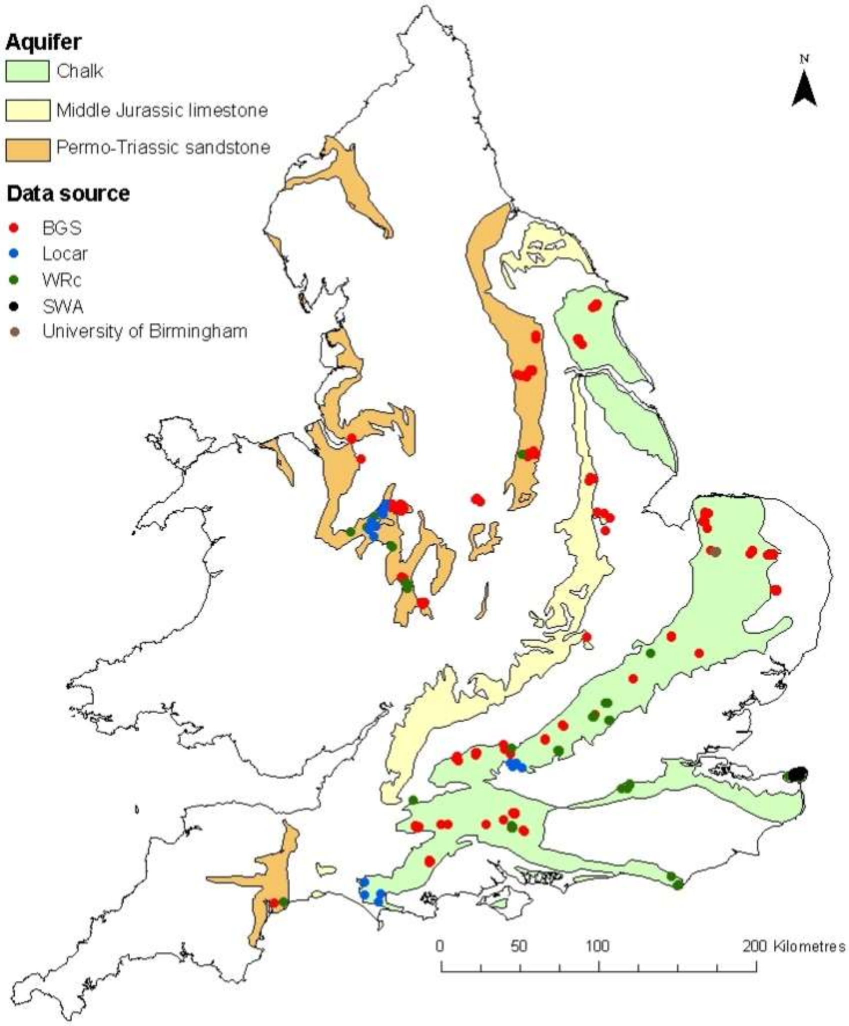

Figure 6.1 Locations of profile sites and major aquifers. Reproduced after Stuart et al. (2016).

6.2 Information about travel times in the saturated and unsaturated zones

Sequential nitrate and tritium concentration-depth profiles for the same site have been used to estimate travel times in the unsaturated zone. This is illustrated in *Figure 6.2* for a site in the Chalk, where the main peak has migrated from about 3 m depth to about 5 m over 2.5 years, a rate of downwards movement of about 0.8 m per year.

Table 6.1 shows the range of unsaturated zone velocities for the Chalk, Permo-Triassic sandstones and Lincolnshire Limestone aquifers derived using this approach, as well as effective rainfall and matrix porosity for each lithology. Estimations of unsaturated zone velocity using a simple piston flow model with effective rainfall and matrix porosity are reasonably close to measured values, with similar measured values also reported in Belgium (Brouyère et al., 2004) and France (Chen et al., 2019). Unsaturated zone velocities (c. 1 m/year in vertical direction) are several orders of magnitude lower than saturated zone velocities in horizontal direction, however it should be noted that this does not take into account bypass flow in the unsaturated zone.

It should be noted that in this research no estimations of saturated zone travel times have been made. However, saturated zone travel times have been estimated using regional groundwater models and particle tracking across the UK by the Environment Agency in the derivation source protection zones for public water supplies. For further information the reader is referred to Environment Agency (2014).

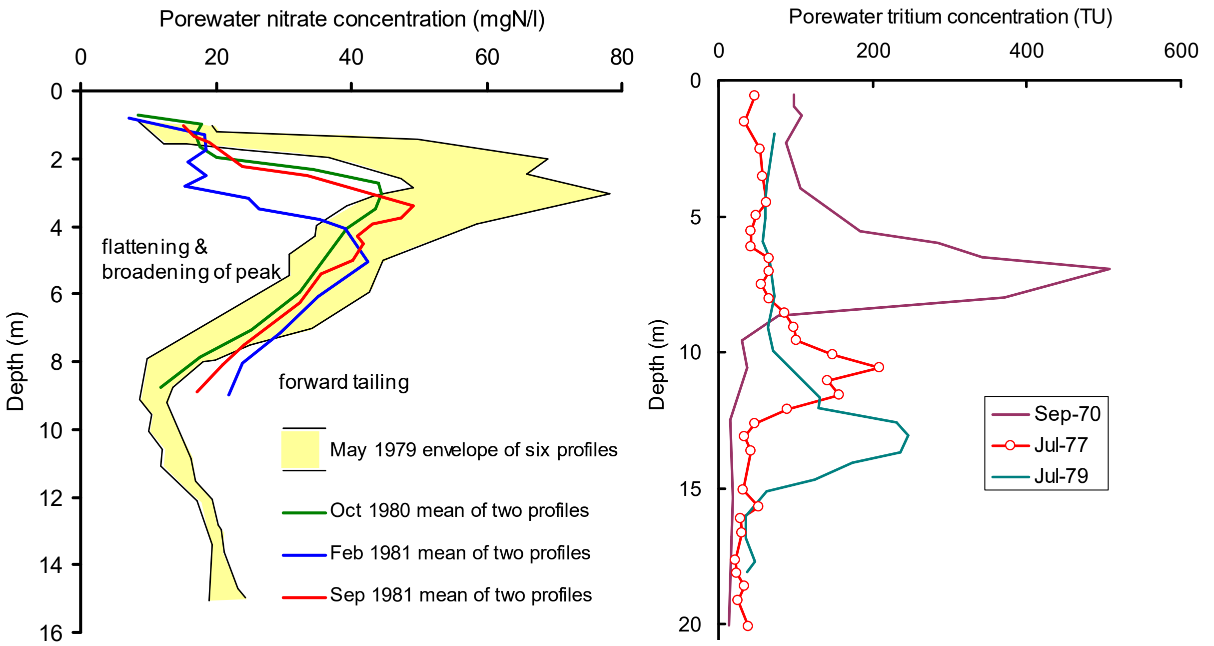

Figure 6.2 a) Typical early nitrate profiles for the Chalk and subsequent sequential reprofiling (from Foster et al., 1986) and b) Sequential porewater profiles for tritium (from Geake and Foster, 1989). Reproduced after Stuart et al. (2016).

Table 6.1 Rates of unsaturated water movement for selected major aquifers (measured ranges from Chilton and Foster (1991), mean porosity values from Bloomfield et al. (1995) and Allen et al. (1997), mean unsaturated zone velocity values calculated. Modified after Stuart et al. (2016).

	Porosity (%)		Effective rainfall (mm year^{-1})		Unsaturated zone velocity (m year^{-1})	
	Range	Mean	Range	Mean	Range	Mean
White Chalk	25-45	33.1	150-350	250	0.3-1.4	0.76
Grey Chalk		27.9		250		0.90
Lincolnshire Limestone	10-25	18	150-250	200	0.6-2.5	1.11
Permo-Triassic Sandstone	15-35	26	200-350	275	0.6-2.3	1.06

6.3 Information about attenuating processes in the subsurface

6.3.1 Evidence for denitrification in the unsaturated zone

In addition to estimation of unsaturated zone travel times, porewater profiles have also been used to determine the extent of denitrification in the unsaturated zone. Applied to sites in the Chalk and Permo-Triassic sandstones, Kinniburgh et al. (1994) used profile data to derive a nitrate mass balance for the unsaturated zone. This was combined with measurements of gaseous and dissolved denitrification indicators to determine extent of denitrification. It was concluded that denitrification below the soil zone in the unsaturated zone is insignificant in relation to the nitrate fluxes passing through the unsaturated zone, and that all the nitrate will eventually reach the saturated zone. No evidence for autotrophic denitrification as a result of pyrite oxidation was found.

Other field studies have suggested that just 1-2% of the nitrate load to the unsaturated zone is denitrified (Rivett et al., 2008), and that there is also limited evidence for denitrification in unconfined saturated aquifers. As such low nitrate concentrations may be due to dilution, lack of pollution or to slow transport of plumes.

6.3.2 Saturated zone denitrification mapping

Stuart et al. (2018) used Environment Agency groundwater quality data in conjunction with mapping of the extent of aquifers below confining strata to derive maps of denitrification potential in groundwater at the national scale in England. The method used by Stuart et al. (2018) will also be detailed in deliverable 5.4 of HOVER, but this is briefly outlined here for the purposes of making preliminary comparisons between pilot areas in chapter 12.

The overarching approach developed by Stuart et al. (2018) is detailed in *Figure 6.3*. In the UK there are 2 principal settings where denitrification in groundwater can occur: (1) where bedrock aquifers are confined by other bedrock formations, and (2) where bedrock aquifers are overlain by low permeability quaternary (superficial) deposits. The approach aims to identify the potential for denitrification to occur within each of these two settings for different aquifers. This is achieved by use of a semi-quantitative scoring system for each aquifer and setting based on concentrations of indicator species to derive a "redox" score and monitoring point coverage to derive a "confidence" score. This is then supplemented by scoring of individual monitoring points in each setting to assist users in interrogating the maps.

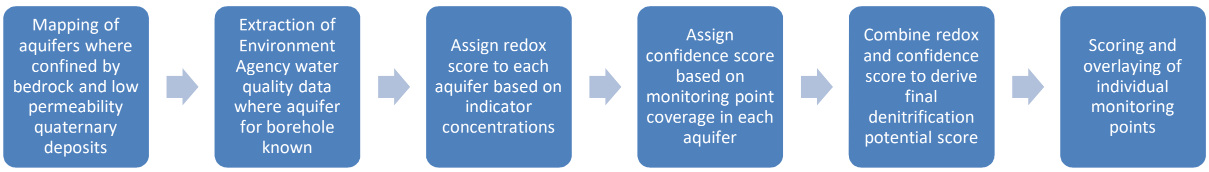

Figure 6.3 Schematic of the approach to mapping denitrification potential at the national scale developed by Stuart et al. (2018).

The first step was to map the distribution of aquifers where confined by other bedrock formations ("subcrop") or overlain by low permeability superficial deposits. Groundwater quality data were then extracted from the Environment Agency database, selecting only data from sites that report which aquifer the boreholes sample (some sites do not report the aquifer, depth of sample or confinement). For each site, the temporal mean of each determinant was taken, and then each site was then assigned one of two settings based on the location of the borehole: (1) outcrop overlain by low permeability superficial deposits or (2) confined by bedrock. Based on the available determinants in the Environment Agency database and the approach of McMahon and Chapelle (2008), a bespoke set of indicator species and concentrations were developed as criteria for low redox conditions which would favour denitrification. For each aquifer and setting above, a redox score was assigned based on how observed concentrations in boreholes compare to these criteria. The area covered by monitoring points was calculated for each aquifer and setting to assign “confidence” score. The redox score and the confidence score were then combined to derive a final denitrification potential score. Denitrification potential scores were also derived for individual points and overlain on the aquifers. This helps users interrogate the maps as they show the extent of monitoring coverage for each aquifer and category. Concentrations of four indicator species (TON, NH_4, dissolved Fe and Mn) relative to the criteria used for the aquifer-level mapping were used.

Table 6.2 shows the results of the denitrification potential mapping for selected aquifers at the aquifer-level. There is widespread potential for denitrification in groundwater across England, particularly in the Chalk where confined by bedrock or low permeability superficial deposits. However, it should be noted that the extent of denitrification is likely to be variable within individual aquifers. Figure 6.4 shows the final map product for the Chalk of England showing both the aquifer-level mapping and the overlying individual monitoring points. Individual monitoring points with high and medium denitrification potential map well to areas of the Chalk where confined by bedrock or overlain by low-permeability superficial deposits.

Table 6.2 Summary of evidence for denitrification potential in selected bedrock aquifers. Derived from Stuart et al. (2018)

Aquifer group	**Denitrification potential in subcrop bedrock**			**Denitrification potential in outcrop overlain by low permeability superficial deposits**		
	Low redox in confined zone supported by monitoring data	**Confidence from coverage**	**Potential**	**Low redox below superficials supported by monitoring data**	**Confidence from coverage**	**Potential**
Chalk	Yes	High	High	Yes	High	High
Upper Greensand	Yes	High	High	No	Medium	Low
Lower Greensand	Yes	High	High	No	Medium	Low
Corallian	Yes	High	High	No	Low	NC
Oolite	Yes	High	High	No	Medium	Low
Zechstein (Mag Lmst)	No	Medium	Low	Yes	High	High
Carboniferous	Yes	High	High	Yes	Medium	High
Dinantian (Lower Carb)	No	Low	NC	Yes	Low	NC

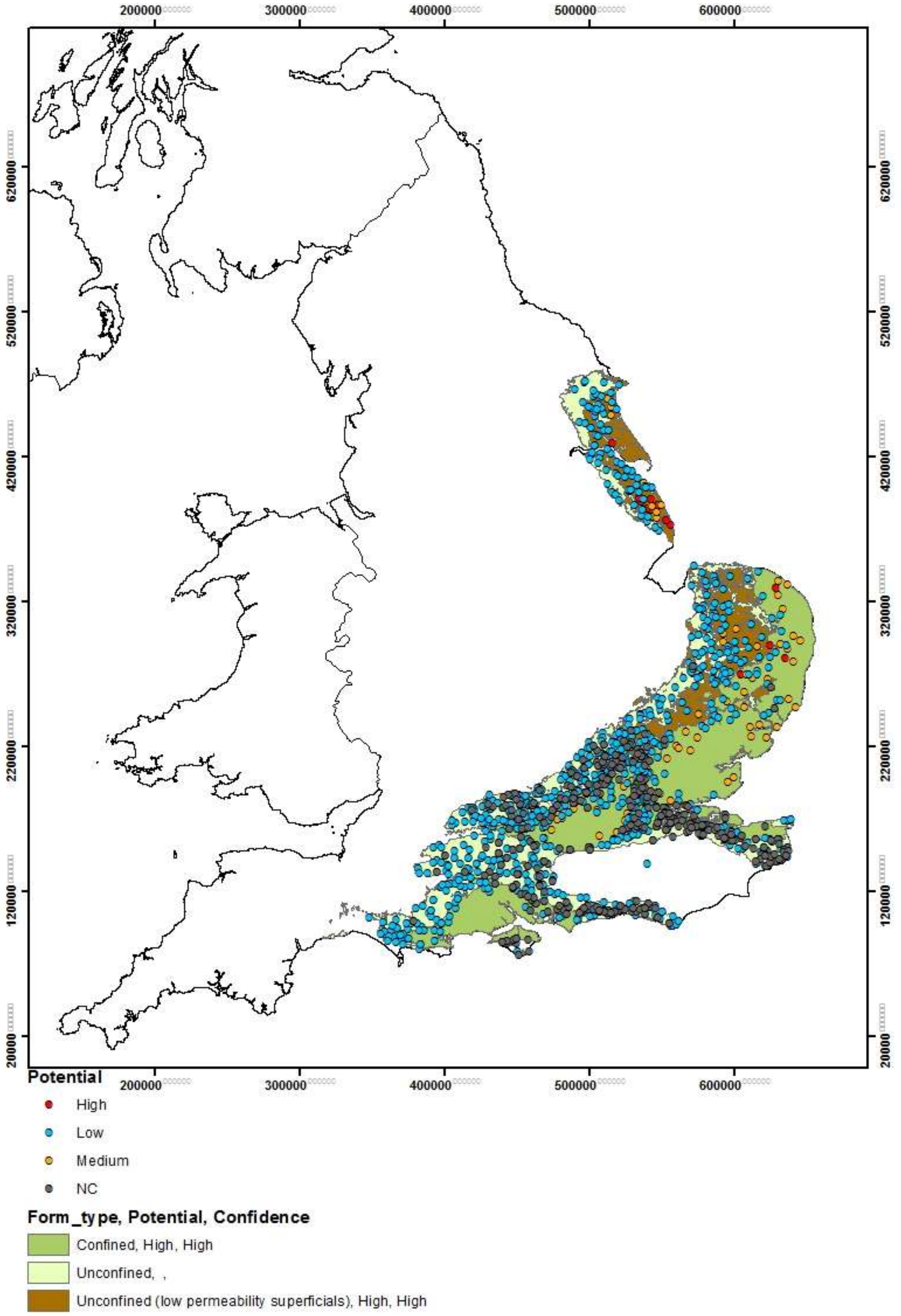

Figure 6.4 Denitrification potential map for the Chalk of England. Reproduced after Stuart et al. (2018).

6.4 Combined analysis of transport and attenuating processes in the pilot area

The sequential coring of boreholes at the same site and measurement of porewater concentrations has significantly improved our understanding of nitrate transport and attenuating processes in the unsaturated zone. Repeated nitrate and tritium profiles have shown that unsaturated zone velocities are c. 1 m/year in the Chalk, Permo-Triassic sandstones and Lincolnshire Limestone aquifers. These broadly agree with simple estimates of unsaturated zone velocities derived using effective rainfall, matrix porosity and a piston flow model. Estimation of a nitrate mass balance based on the profiles in conjunction with measurement of denitrification indicator species has shown that denitrification in the unsaturated zone (both heterotrophic and autotrophic) is likely to be insignificant, with just 1-2% of the nitrate load from the base of soil zone removed. The profile data collated in this research has been used extensively in the development and validation of models of nitrate storage and transport in the unsaturated zone, which will be detailed in D5.3. Groundwater quality monitoring data held by the Environment Agency in England has been used to develop national scale maps of denitrification potential in groundwater, which will be detailed further in D5.4.

6.5 Testing approaches to harmonized, processed data for supraregional evaluations

In this chapter, data used to characterize unsaturated zone travel times and denitrification in the saturated zone in UK have been reported. Chapter 12 provides an aggregation and overview of the different approaches taken in the HOVER WP5 pilots. Here we put the UK pilot in context, and briefly consider how the approaches could be used in harmonised supra-regional evaluations.

Both the UK and France have similar monitoring of unsaturated zone profiles to derive travel times. Going forward, it may be possible to evaluate unsaturated zone travel times across a number of pilot areas. Moreover, in countries where the unsaturated zone is less significant (e.g. Netherlands, Denmark), it may be possible to compare shallow saturated zone vertical velocities with UK/France unsaturated zone velocities. Combining the UK and France unsaturated zone velocity estimates in this deliverable with conceptual models of the unsaturated zone reported in D5.1 and the global modelling of nitrate transport by Ascott et al. (2017), it may be possible to present European maps of where nitrate in the unsaturated zone is likely to be significant.

The methodology used in the UK for mapping denitrification potential uses national scale datasets for groundwater quality. In these databases, the borehole depth, screen depth, extent of confinement and sometimes the aquifer is not known. It would therefore be challenging to adopt and approach similar to that applied in the Netherlands where a denitrification depth has been derived. The UK method is conceptually similar to classification-tree approaches such as that used in France, particularly the scoring and overlaying of individual monitoring points. It may be possible to adopt such an approach across a number of pilot areas.

6.6 References

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7 CASE STUDY FRANCE

7.1 Description of monitoring network

Monitoring of water quality

French waters have been under increasing scrutiny since the 1970s, and the European Water Framework Directive (WFD) of 23 October 2000 marked a turning point in the monitoring strategy. It requires in particular the establishment of monitoring programs of the state of the waters in all Member States.

In France, monitoring programs (of water status - watercourses, water bodies, transitional waters, coastal waters, groundwater) have been implemented in each watershed since 2007.

The technical coordination of the development of data production methods was entrusted to the ONEMA (French National Agency for Water and Aquatic Environments) and since 2016 to the AFB (French Agency for Biodiversity).

The establishment of monitoring programs has led to the establishment of a monitoring control network, to obtain a picture of the general state of the waters. The network is composed of 1940 stations on groundwater, spread over the entire French territory and represent the different types of water bodies. In groundwater, quantitative and chemical data are collected. Additionally, operational controls specifically track groundwater bodies that may not meet environmental objectives. They include 1608 stations on groundwater (including 702 stations from the monitoring network).

For groundwater, the assessment of the state of the water is based on the quantitative status and the chemical status. The good state is reached by a body of groundwater when its quantitative status and its chemical status are at least "good".

7.1.1 ADES: French National Data Base on Groundwater Public Service on Water Information

The French National Database for quantitative and qualitative data on groundwater resources has an open access web portal (Web access: www.ades.eaufrance.fr).

The ADES project is coordinated by the French National Geological Survey (BRGM) together with the main French major stakeholders (Ministries in charge of the Environment and Health) and the French National Agency for Water and Aquatic Environments, and since 2016 to the AFB (French Agency for Biodiversity).

ADES provides public access to water quality and groundwater levels collected, mapped results, metadata, and series of information updates. As a one-stop access point to relevant information, it is an essential tool for optimal management of groundwater resources, to enhance understanding of groundwater evolution and contribute solutions for local, national pressing societal and European requirements.

Groundwater monitoring networks

Data are collected from representative monitoring stations from over 70 000 stations scattered all over the country. These stations measure key components of groundwater quality (qualitometers), or groundwater level (piezometers). Some stations can insure both measurements.

Many partners take part in supplying ADES data base: ministry in charge of health (data on raw water groundwater quality, within the sanitation control program) ; regional services of the ministry in charge of Environment ; water agencies and water offices in overseas regions ; water suppliers ; territorial collectivises ; private companies (within under the regulations of Installations Classified for the Protection of the Environment and polluted sites) ; French National Geological Survey (BRGM) with the regional services.

In ADES, two networks gather nitrate and pesticides data:

- National network for qualitative monitoring of groundwater;

- National monitoring network of the Nitrates Directive for groundwater.

National network for qualitative monitoring of groundwater (RNESQ)
The Water Framework Directive has defined two types of quality control on groundwater bodies:
- the “surveillance control network” (RCS) is comparable to a patrimony knowledge network (monitoring of all groundwater bodies),
- the “operational control network” (RCO), designed to monitor the impacts and policies implemented on groundwater bodies that may not achieve the "good status".

The frequency of measurements corresponds to samples taken at least twice a year in the case of unconfined aquifers and once a year in confined aquifers. It measures the classical physicochemical parameters (pH, temperature, conductivity, nitrates, chlorides, sulphates ...) and analyses the organic micropollutants (pesticides, PAHs, ...) and minerals (metallic trace elements, ...) on raw water (untreated).
The results of the analyses performed as part of the groundwater quality measurement network are available on the ADES website.

National monitoring network of the Nitrates Directive for groundwater (RNESOUNO3)
The monitoring of nitrate concentrations in French groundwater is carried out under the Nitrates Directive, Directive n ° 91/676 / EEC of 12 December 1991 to delimit vulnerable zones and to evaluate the implementation of the action programs. The points are selected for each campaign by the DREAL in collaboration with the Water Agencies. The points are part of existing networks, mainly in the WFD networks (monitoring networks and operational control networks) but also in the national monitoring network for sanitary control on raw water used for the production of drinking water and in local networks of local authorities.

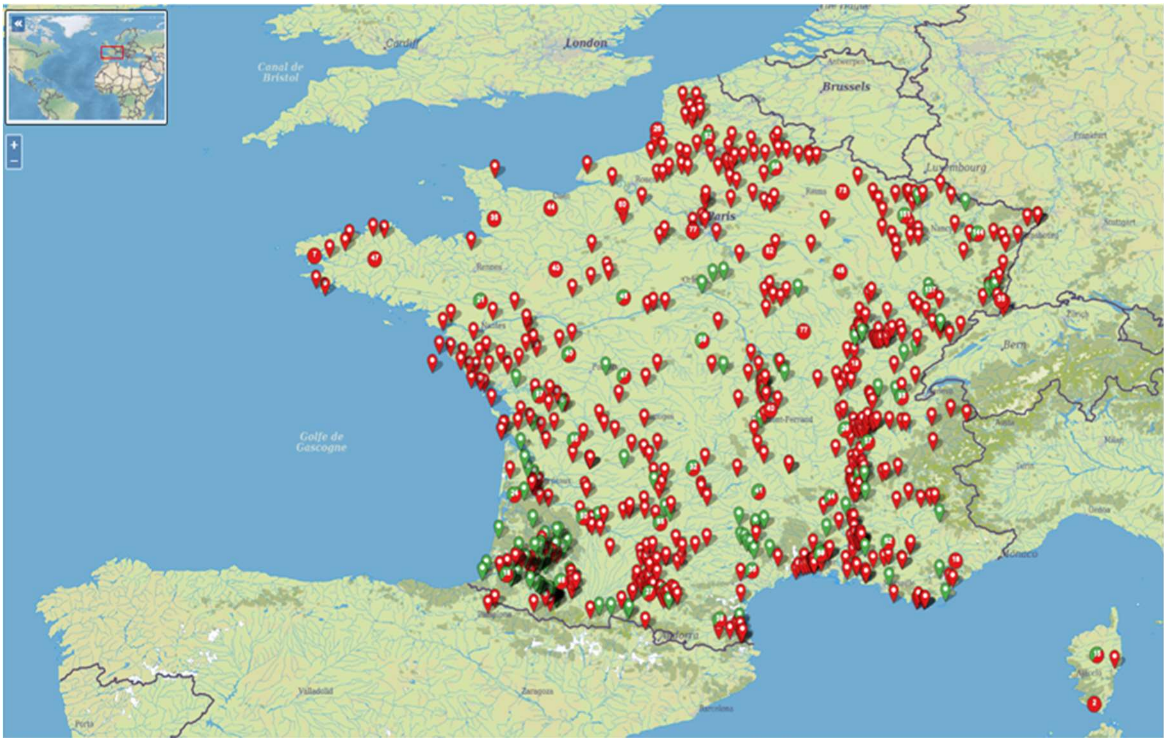

Figure 7.1 Illustration of the National monitoring network of the Nitrates Directive for groundwater (RNESOUNO3) in metropolitan territory and Corsica (screenshot taken from the ADES website)

The 2 networks summarized in a few numbers:
- Quality network: approximately 2600 water points;
- Nitrate network: approximately 3000 water points;
- The 2 networks together: approximately 3900 water points.

Of the 3900 water points, 1230 (32 %) are less than 20 mbs deep, the others are deeper. This distribution is consistent with the heterogeneity of aquifers. The average depth of the boreholes (50 mbs) is not a relevant indicator for French case study. The French aquifers have very variable depths, and this influences the borehole depths. Some boreholes are a few meters deep while others are more than one kilometre deep.
The technical sections of the boreholes, and therefore the position of the screens (their top, bottom, length) are not inputted into our national databases.
French aquifers are not necessarily captured in their entirety, it depends on the date of drilling, the habits and customs of drillers and owners and especially the geological and hydrogeological contexts.
Considering the 2 combined networks, 2744 water points (70 %) are used by water production plants and only 174 water points (5 %) are used just for monitoring water quality. The other uses are mainly divided between agricultural (5 %), collective (4 %), industrial (2 %) and domestic (2 %) uses.

7.1.2 Recent BRGM studies at national scale about nitrate and pesticide pressure-impact

For the territory of metropolitan France, two recent studies exist at French national level to assess and characterize the pressure-impact of nitrate and pesticide use:
- For nitrate: Gourcy et al, 2017 (BRGM/RP-67428-FR);
- For pesticide: Auterives and Baran, 2017 (BRGM/RP-67453-FR).

This work was difficult to achieve as there is no geological and hydrogeological and agro-pedo-climatic homogeneity at the French metropolitan territory. As an illustration of this heterogeneity, below is the map of simplified hydrogeological formations at the French metropolitan territory. The map (Figure 7.2) represent the first aquifers that can be affected by nitrate and / or pesticide pressures.
These types of studies also exist for the French overseas departments (Guadeloupe, Martinique, La Réunion, Mayotte).

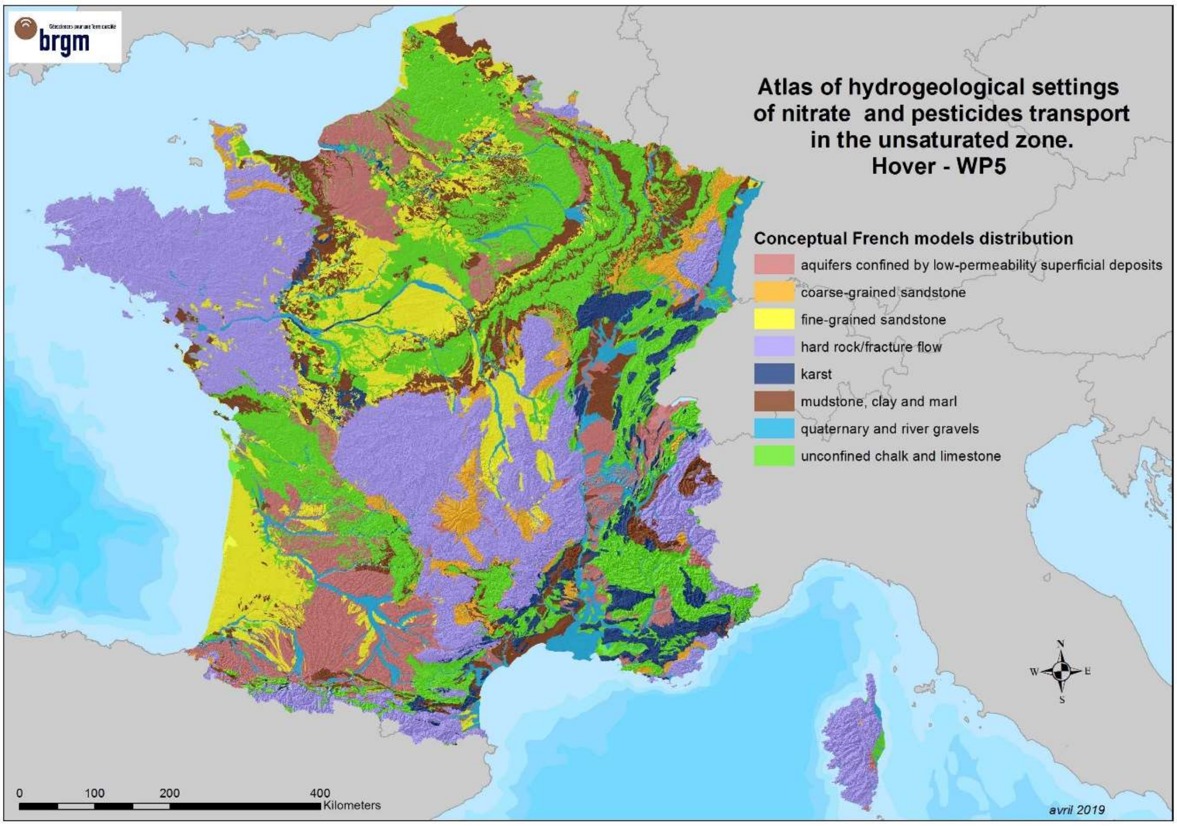

Figure 7.2 Main types of aquifer and no-aquifer formations identified as concerned by the nitrate and/or pesticides problematic in metropolitan France and Corsica.

7.1.3 Complementary local studies to national monitoring networks

There exist in France a large amount of local studies, notably for groundwater resources (springs, boreholes) used to supply drinking water to the population in order to better characterize and know the underground resources, often using multidisciplinary approaches, for springs or boreholes with concentrations close to or above the limit value of 50 mg/L in nitrate, in order to set up relevant catchment protection areas, to implement agri-environmental measures. We can also mention action plans against diffuse pollution at the scale of the watershed. Nevertheless, there is no synthesis of all these local studies and all the quality data resulting from a specific and localized study that does not belong to a monitoring network, are not necessarily available in the database ADES.

7.2 Information about travel times in the unsaturated and saturated zones

7.2.1 Unsaturated zone experiments

Several types of experiments have been performed in the unsaturated zone. These experiments are usually based on surveys to establish soil nitrogen profiles at different depths. Soil profiles linking nitrate concentration, water content, tritium activities and sometimes some major elements or traces were performed. Experiment sites are located in sedimentary formations, generally in the basin of Paris; the map below shows their location (figure 7.3).

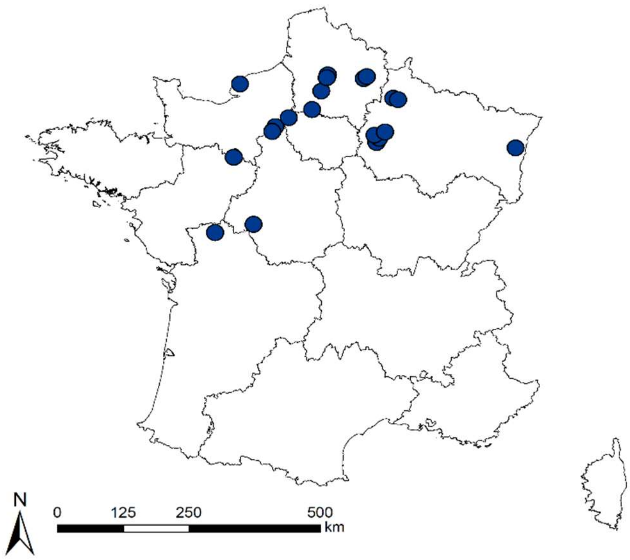

Figure 7.3 Location of the experimental study sites in French metropolitan territory where transfer speeds through the unsaturated zone were calculated by the BGRM.

Below is an example of a survey made in Northern of France in 2013. Soil profiles show that concentrations fluctuate in response to agricultural practices varying over the years and also in response to rainfalls. For the study plots, nitrate inputs to soil are less important today than in the past. However, they remain higher than those observed in the plot without fertilization used as a reference (follow period, Figure 7.4). Thanks to the data provided by farmers, values of nitrogen fertilization have been used to calculate the surpluses and deficits of fertilization, year by year and culture by culture on the plot. This work shows the impact of the fertilization on soil nitrate concentration over several years.

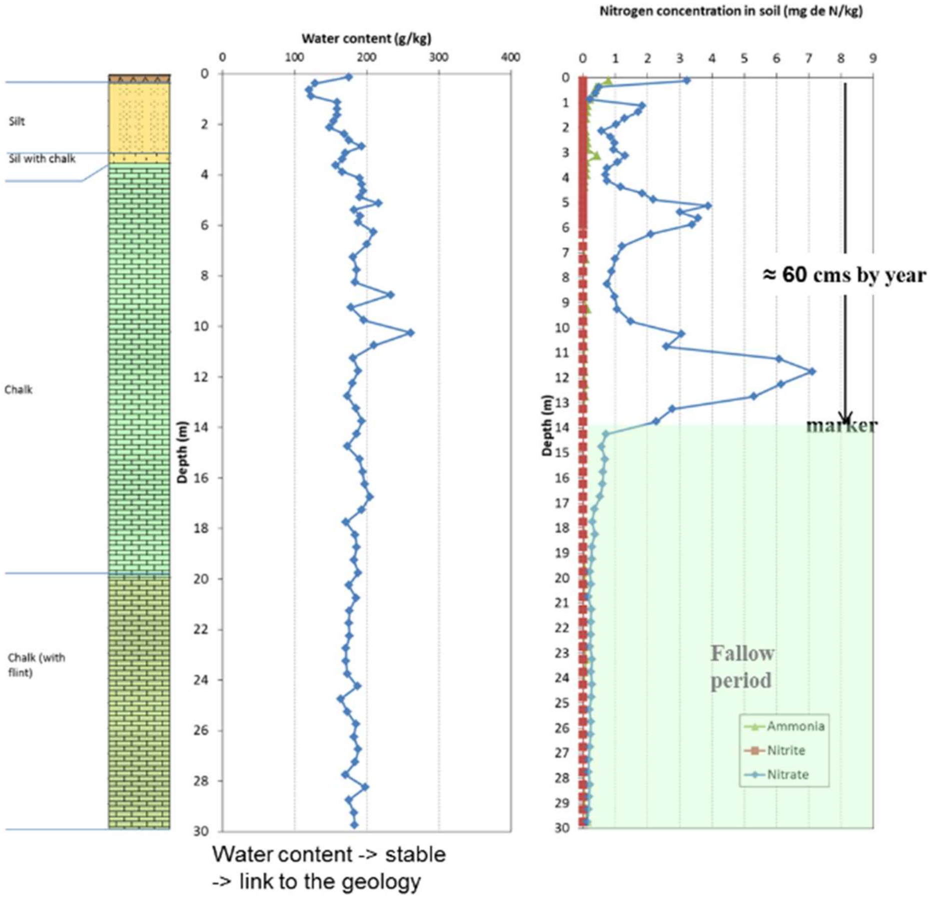

Figure 7.4 Geological log, water content and nitrogen concentration profiles in chalk of basin of Paris (from Surdyk et al., 2014, BRGM/RP-63714-FR).

The example of Brevilles (Figure 7.5) can also illustrate this work, it is extracted from Gutierrez and Baran, 2009. "The Brévilles spring is the main spring of a small aquifer of 12 km^2 in extension located 70 km west of Paris. The water table is mainly located in a sandy layer (''Cuise sands" – Upper Ypresian) overlying an impervious clay layer of 10 m thickness and overlain by heterogeneous marine clastic limestone of Lutetian age, becoming marly at the top of the formation. Bartonian sand and silicified limestone (millstones) occur in the highest places. Superimposed on the solid rocks are more recent loamy drift deposits of colluvium in shallow valleys, table-land loam covering part of the high ground, and stoneless drift soil covering the sand and clay around the site. Determining the impact of the unsaturated zone in the retardation and buffering of water flow is based on measurements made on cuttings recovered from the drilling. The samples collected during drilling were used for making water-content profiles. The deepest unsaturated zones were found at two piezometers (Pz2 and Pz3). Their water-content profile clearly showed a decrease of water-content variability with depth. Data covering the monitoring of pesticide transfer in soil, the physico-chemical characteristics of soils, profiles of water contents, tritium activities, and nitrate concentrations measured on rock samples collected by drilling, were compared in order to describe the transfer time in soil and within several meters of unsaturated zone. The profiles of water content, tritium activity and nitrate concentration are presented in the illustration below. These two parameters, tritium activity and nitrate concentration, allow a rough estimation of the transfer velocity at around 0.5 m/year for tritium (position of the peak at Pz3) and of about 1 m/year when considering a start of fertilizer applications in the 1960s or the fastest tritium peak at Pz2. Thus, the nitrate and tritium profiles provide evidence that nitrate is stored in the unsaturated zone and that some of it migrates with variable, but still slow, velocities."

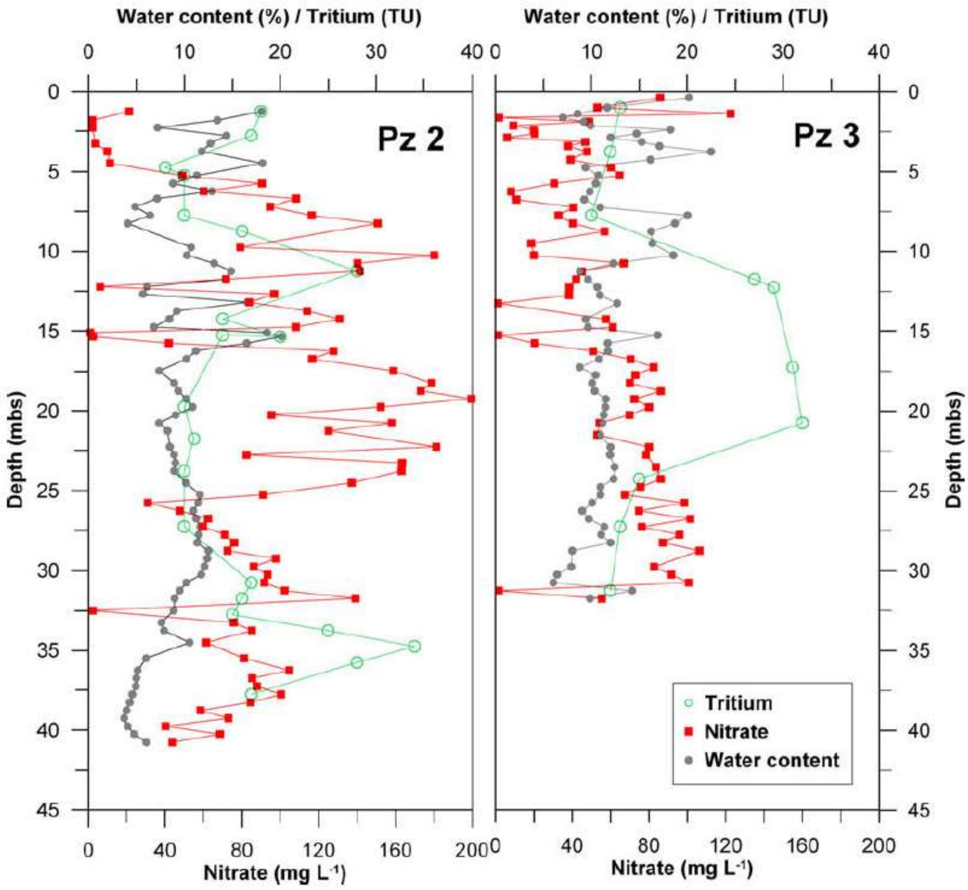

Figure 7.5 Water content, nitrate concentration and tritium activities versus depth along the unsaturated zone of Pz2 and Pz3 (from Gutierrez and Baran, 2009).

This type of experimentation on different types of geological formations with different climatic contexts leads to a knowledge of transfer speeds mainly for sedimentary formations (limestone, chalk, sands, etc.). To know the travel time, the transfer speed must be multiplied by the thickness of the unsaturated zone. This data can be obtained from the BRGM who has the piezometric maps and can calculate the unsaturated zone thickness using the digital terrain model.

7.2.2 Transfer times estimation in soil, unsaturated and saturated zones

On the French metropolitan territory and Corsica, the national report about the pressure-Impact of nitrate concentration is Gourcy et al., 2017 (BRGM/RP-67428-FR). The methodology applied to determine the transfer times is as follows.

One of the most important and delicate factors to estimate for groundwater is the pollutant transfer time through in soil, unsaturated and saturated zones. It can be estimated that nitrate transfer times in soil are low compared to transfer times in the unsaturated zone (ZNS) remainder and within the aquifers. The transfer times in unsaturated zones and in saturated zones are more or less important depending on the hydrogeological context and positioning of the measurement points within the basins (boreholes, springs, etc.). In this report, the time lag between pressure and impact has been addressed by two complementary methods; the estimation of the transfer times in the unsaturated zone and the apparent groundwater ages for the saturated zone, particularly in the fluvio-glacial zones.

7.2.2.1 Transfer time in the unsaturated zone

Several methods can be used for this estimate of the time of arrival at the saturated zone of nitrate aquifers from soils. Two methods have been selected and tested in France (Gourcy et al., 2017).

1st Method: Calculation of average residence time

This calculation of average residence time was initially developed for plant protection products. The method described by Rao et al. (1985) is based on the "piston" model, taking into account a real recharge coupled with delaying factors. These results are compared to field measurements, they are presented in the table 7.1 below.

Table 7.1 Table of transfer speeds in unsaturated zone for some lithological contexts derived from field data or calculations according to RAO et al., 1985

Lithology	Transfer speed (m/year) – field measurements	Transfer speed (m/year) – calculations
Limestone	1.5	0.8
Chalk	0.45 to 1.25	1.31
Sands	3	0.83
Sandstone	1.8	0.885
Regolith / granite	2.5	0.375

2nd Method: Transfer time in the unsaturated zone from literature

Estimates of nitrate transfer times in the unsaturated zone may come from literature data, from analyses of nitrate concentration profiles obtained for the unsaturated zone or from validated modelling according to aquifer lithology and climate. A summary of the data collected in the literature for the French regions is presented in the table below.

Table 7.2 Table of estimation data of nitrate transfer speeds (in m/year) in unsaturated zone according to lithological contexts and French regions from the literature (according to Gourcy et al., 2017; BRGM/RP-67428-FR)

French regions	**Lithology**						**Bibliographic references**
	Chalk	Lœss	Silts	Altered area of granites / arenites	Old alluvial and glaciofluvial	Flint clay	
Artois - Picardie	0.54 – 1.45		0.4 - 0.5				Surdyk et al., 2014 and 2016 ; Serhal et al., 2006 ; Serhal, 2006 ; Caous et al., 1984 ; Bernard et al., 2005.
Somme	0.5 - 0.7						Normald et al., 1999.
Alsace		0.2 - 0.3					Baran et al., 2007
Champagne -Ardenne	0.27 – 0.7						Kerbaul et al., 1979 ; Chabart and Baran, 2005 ; Landreau and Morisot, 1983 ; Balif and Muller, 1983 : Seguin, 1986 ; Crampon et al., 1993 ; Philiipe, 2011.
Nord	1.25						Lacherez-Bastin, 2005
Nord-Pas-de Calais	0.5 - 1.95						Baillon et al., 2001
Bretagne				2 - 3			Limousin, 2006 ; Legout et al., 2006 ; Molenat et al., 2013
Normandie	0.35 - 0.64 to 2.5 (karst)						Arnaud et al., 2009 ; Crampon et al., 1993 ; Jauffret et al., 1984
Rhône-Alpes					4.7 - 6.5		Rousseau et al., 2016
Touraine	0.45					0.75	Landreau and Morisot, 1983.

A map of average nitrate transfer speeds per work unit was developed in Figure 7.6.

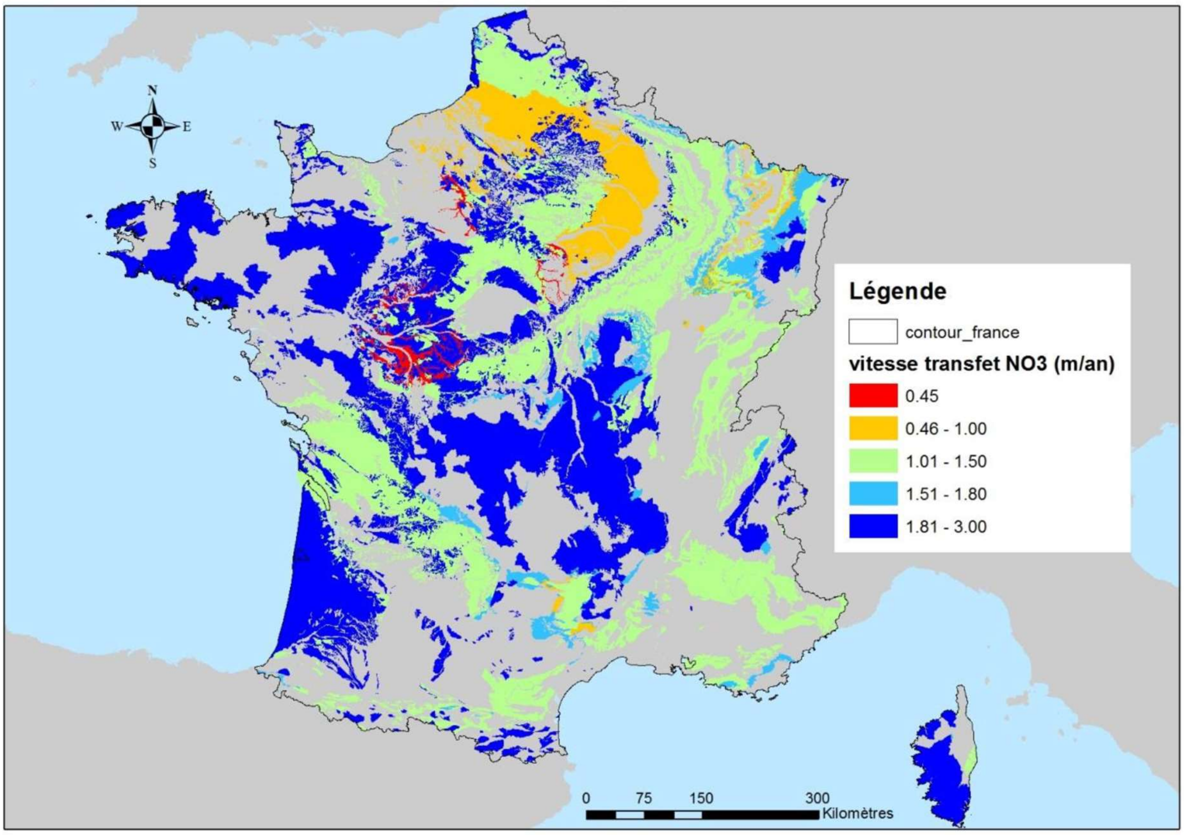

Figure 7.6: Average nitrate transfer speeds (m/year) in the unsaturated zone (from Gourcy et al., 2017; BRGM/RP-67428-FR)

By combining the thickness of the unsaturated zone and the of transfer time of nitrate through this same area, a transfer time calculated in years was obtained for 1613 units out of the 3631 covering the whole metropolitan territory and Corsica. The results of this calculation are shown in Figure 7.7. These transfer times only concern the matrix transport and therefore neglects a transfer through crack / fractures which is faster.

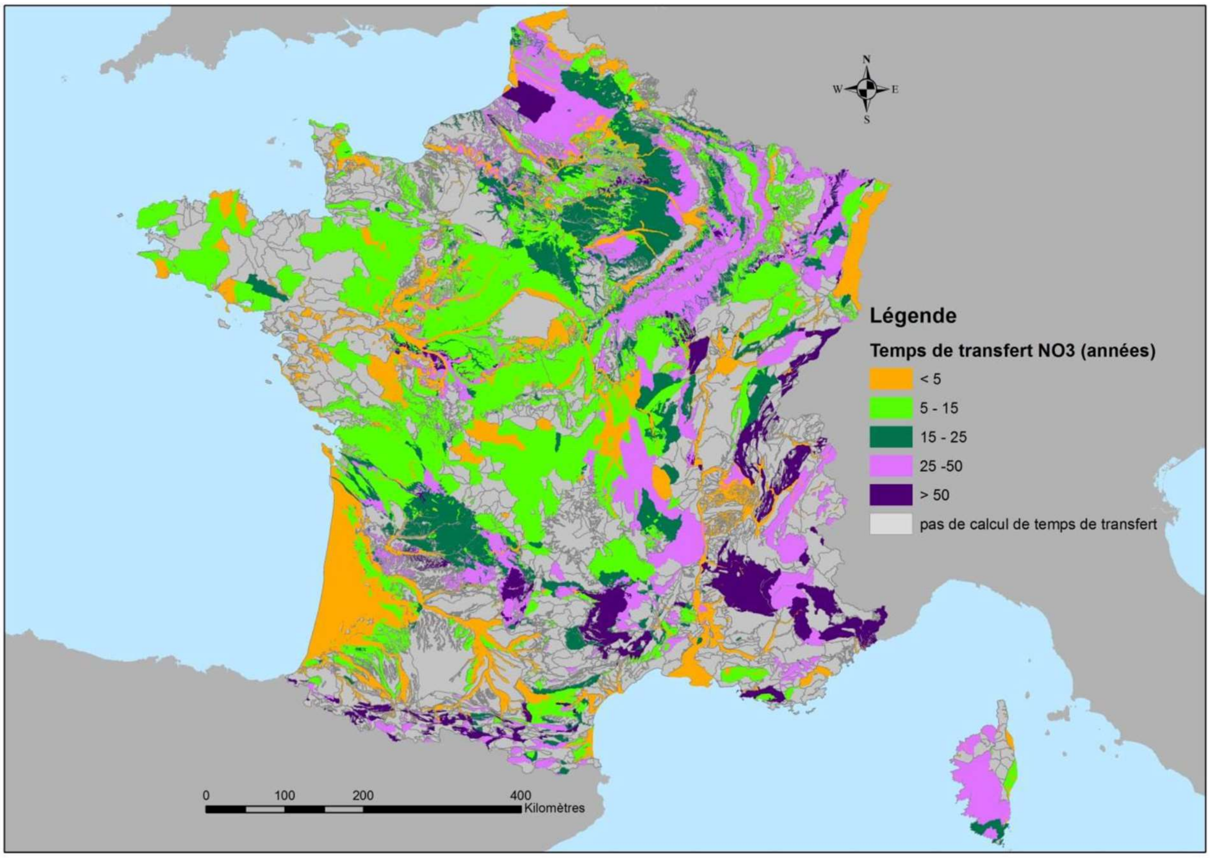

Figure 7.7 Nitrate transfer time (years) taking into account only the matrix porosity per unit of work (from Gourcy et al., 2017; BRGM/RP-67428-FR)

7.2.2.2 Geochemical tools used in France to determine average residence times and/or transfer times

To characterize the transfer times in the soil and in the unsaturated and saturated zones, the following geochemical tools were used in French BRGM studies to provide a better understanding of the flow of water and solutes in aquifers: concentrations of major dissolved elements, stable isotopes of the water molecule (δ^2H and $\delta^{18}O$), tritium activities and dissolved gases (CFC-11, CFC-12, CFC-113 and SF_6, Ar, N_2). These geochemical tools have been used per example in the plain of Ain to determine the average residence time of groundwater (Gourcy et al. 2011, BRGM/RP-59754-FR). These tools have been used also in different geological and hydrogeological contexts, per example the study (Gourcy et al., 2009) taken into account the whole volcanic island of Martinique, in French West Indie, in order to predict groundwater-quality trends in areas where the hydrogeological context is poorly known. The combination of ^3H, CFCs and SF_6 for the dating of water is a relevant approach in case of complicated mixing scenarios. This method can provide the requested information in terms of contamination trends and the vulnerability of aquifers. Groundwater transfer in the island is quite slow with apparent ages over 10 years. In similar volcanic and anoxic environment where microbial degradation may strongly affect CFC concentration in groundwater, the use of the $^3H/^3He$ tool in addition to already presented methods would improve age-dating estimation. In a poorly known hydrogeological context, the measurement of noble gases (N_2, O_2, Ar) would help better constraining the recharge condition and therefore also improve the apparent age estimation.

7.2.2.3 Transfer time in the saturated zone

The recent study Gourcy et al., 2017 (BRGM/RP-67428-FR) realised on the metropolitan territory and Corsica synthesized the bibliographic references relating to the transfer time in the saturated zone.

Within the aquifers, the transfer times between the recharge zone and the aquifer (approached by the boreholes / catchments where the measurements of nitrate concentrations or the springs, natural outlets) can be estimated by modelling or by dating the waters. Summaries of ages estimated by geochemical tools were performed on the Seine-Normandy basin (Lopez et al., 2012), Loire-Bretagne basin (Ayraud et al., 2008; Gutierrez et al., 2011; Molenat et al., 2013) and Rhône-Méditerranée basin (Gourcy et al., 2013). Further information has been obtained from publications or from PhD works (De Ridder, 2012; Aquilina and de Dreuzy, 2011; Jaunat et al,. 2012; Delbart, 2013; Delbart et al., 2014; Leray et al., 2014; Briand, 2014; Marcais et al., 2015; Sassine, 2014; Santoni et al., 2016 ; Sassine et al., 2017).

Thus, it has been possible to collect information on the apparent ages of groundwater for some 800 well-characterized water points (coordinates and indication of the water body). In many cases, for the same body of water (or BDLISA entity), there is a varied range of estimated age depending on whether the points tracked are in the recharge zone, fracture / crack zone, deeper zone of the aquifer or in the outlet (Figure 7.8). For the bedrock aquifers in Bretagne, the average ages considered are those of the recharge zone and the weathered zone, because these are the sectors most sensitive to agricultural pressures.

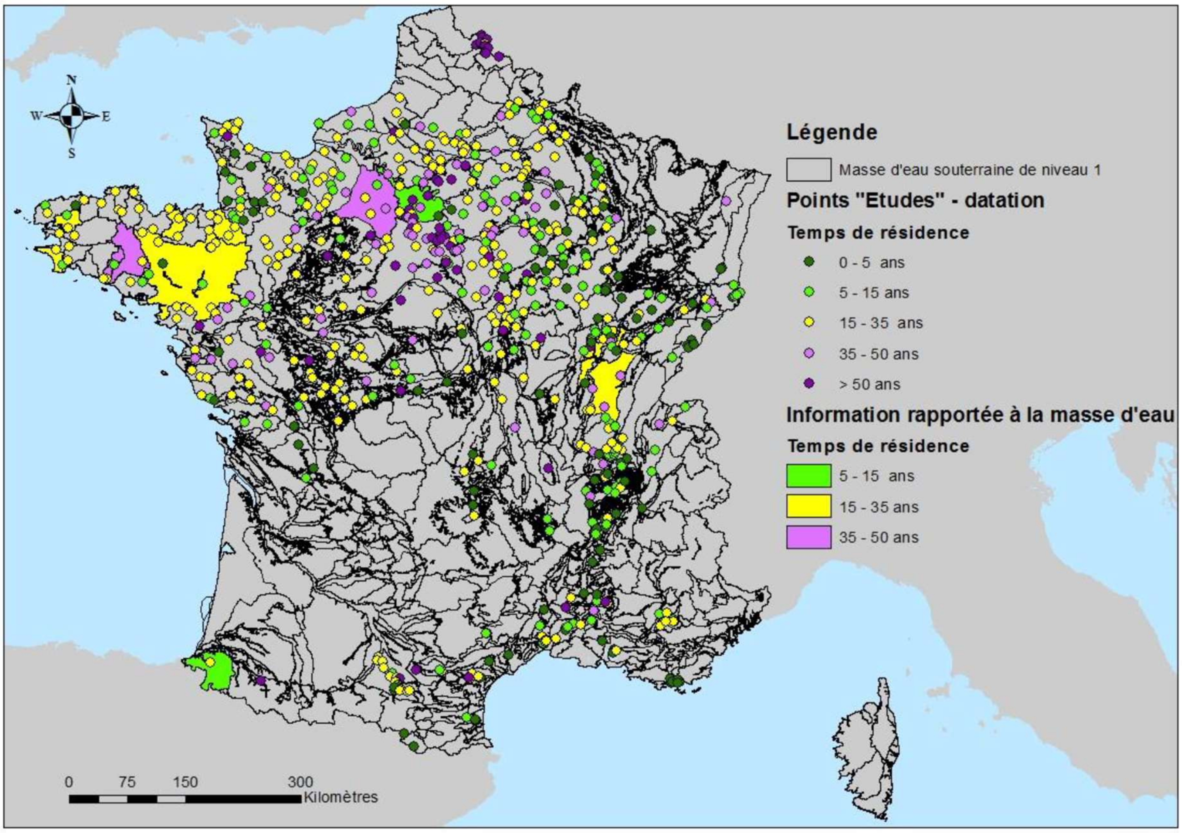

Figure 7.8: Apparent age ranges available at the water point and body of water (from Gourcy et al., 2017; BRGM/RP-67428-FR)

The apparent ages estimated by geochemical tools were, however, directly used for alluvial and glaciofluvial aquifers. For the other contexts, and when possible, the transfer times through the unsaturated zone have been taken into account in the calculation of the difference between nitrogen surplus and the arrival of nitrate in the saturated zone.

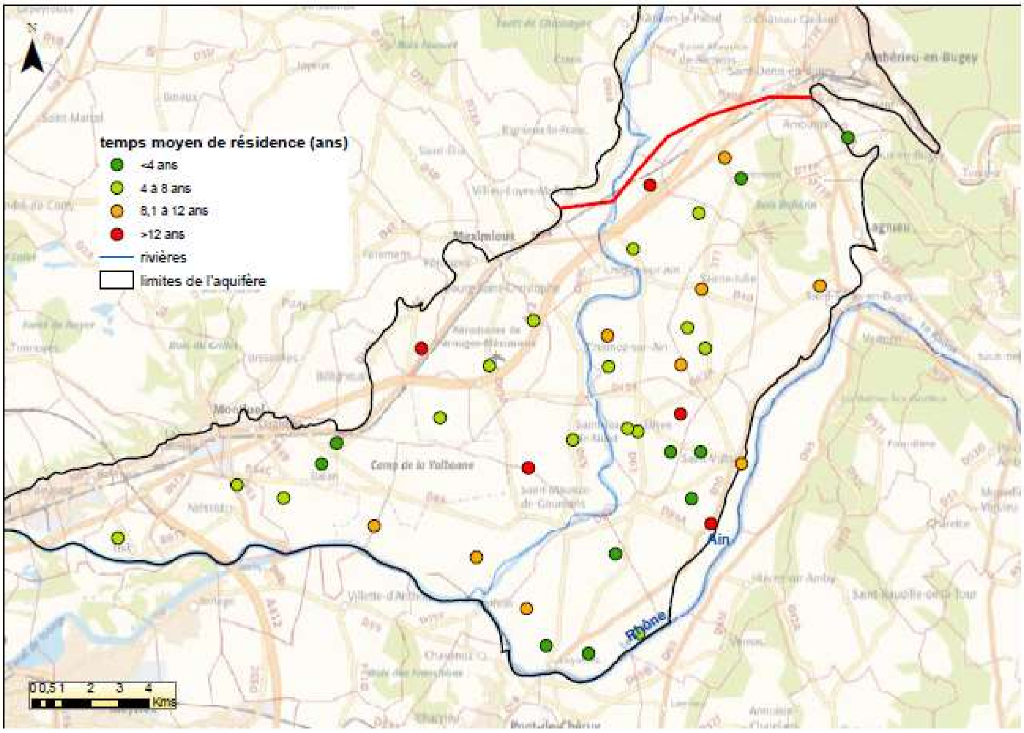

Figure 7.9 Map of average residence times for the alluvial aquifer (Plain of Ain) estimated using the exponential model from groundwater samples taken in 2008 and 2009 (from Gourcy et al. 2011, BRGM/RP-59754-FR).

7.3 Information about attenuating processes in the subsurface

We distinguish two types of mitigating factors for nitrate: attenuation through denitrification, and dilution or advective mixing. In this part, only the denitrification is presented, because mixing and dilution are already covered by the concepts used for calculating and estimating the apparent ages and average transit times.

7.3.1 Denitrification mapping

7.3.1.1 First approach in a BRGM report on a national scale

In Gourcy et al., 2017 (BRGM/RP-67428-FR), 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.

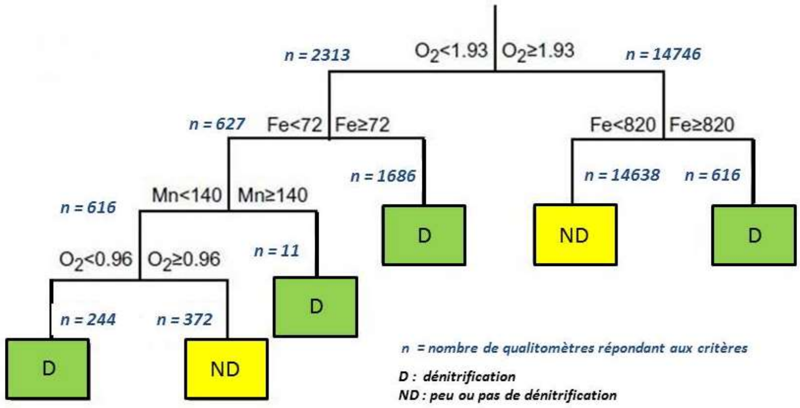

Figure 7.10 Classification tree applied to all the quality measurements in 2015 (modified according to Hinkle and Tesoriero, 2014). The locations of four different types of samples that have indication for denitrification (the green D's) are plotted as D1 to D4 in Figure 7.11

The results indicate 1532 water points likely to denitrify on the French metropolitan territory and Corsica. 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.

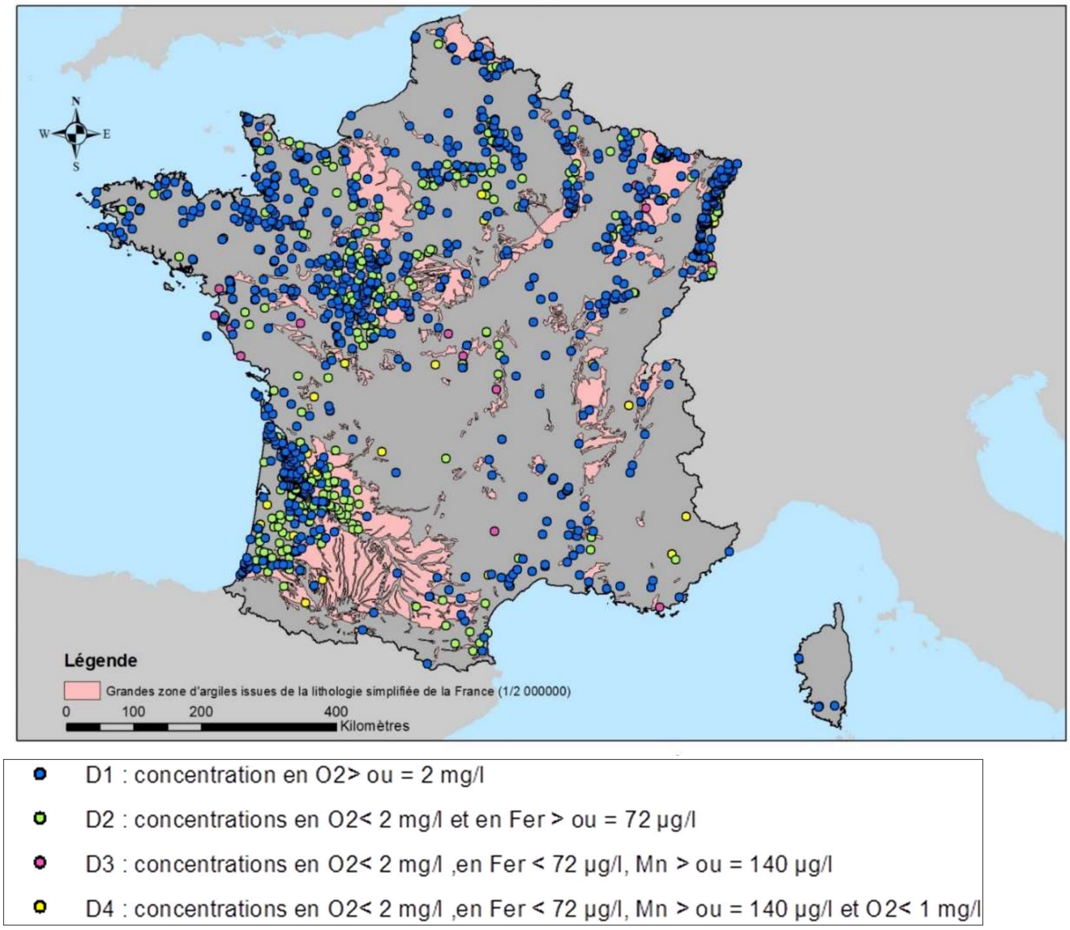

Figure 7.11 Location of points capturing potentially denitrified groundwater (from Gourcy et al., 2017; BRGM/RP-67428-FR). Points with no signs of denitrification are not shown on this map.

7.3.1.2 Local studies of nitrate reduction by agronomists

A lot of agronomic studies exist in France. We can cite for example Paul et al., 2015. They use nitrate contents and their ^{15}N isotopic signature to unravel denitrification processes. The concentration of chloride and sulphate, the content of mineral fertilizer, confirmed the reduction reaction of nitrate alone. These types of studies are not carried out by the BRGM.

7.4 Combined analysis of transport and attenuating processes in the pilot area

Based on experimental data, some work done to model the nitrate transfer in a context a possible denitrification. This modeling is based on the MARTHE model (Thiery, 2015), coupled with the agronomic model "MONICA" (MOdélisation des transferts de NItrates prenant en compte les Cultures et les pratiques Agricoles); it is described in Picot-Colbeaux et al., 2017 (BRGM/RP-66375-FR). A MARTHE-PHREEQC-RM coupling has also been realized (Thiery, 2015e).

The results of simulations show that the MARTHE-MONICA model can take into account, from the soil surface to the saturated zone, the flows and the transport of nitrate in solution while respecting the water and nitrogen balances of the soil and the subsoil. An example of modelling results is shown in Figure 7.12.

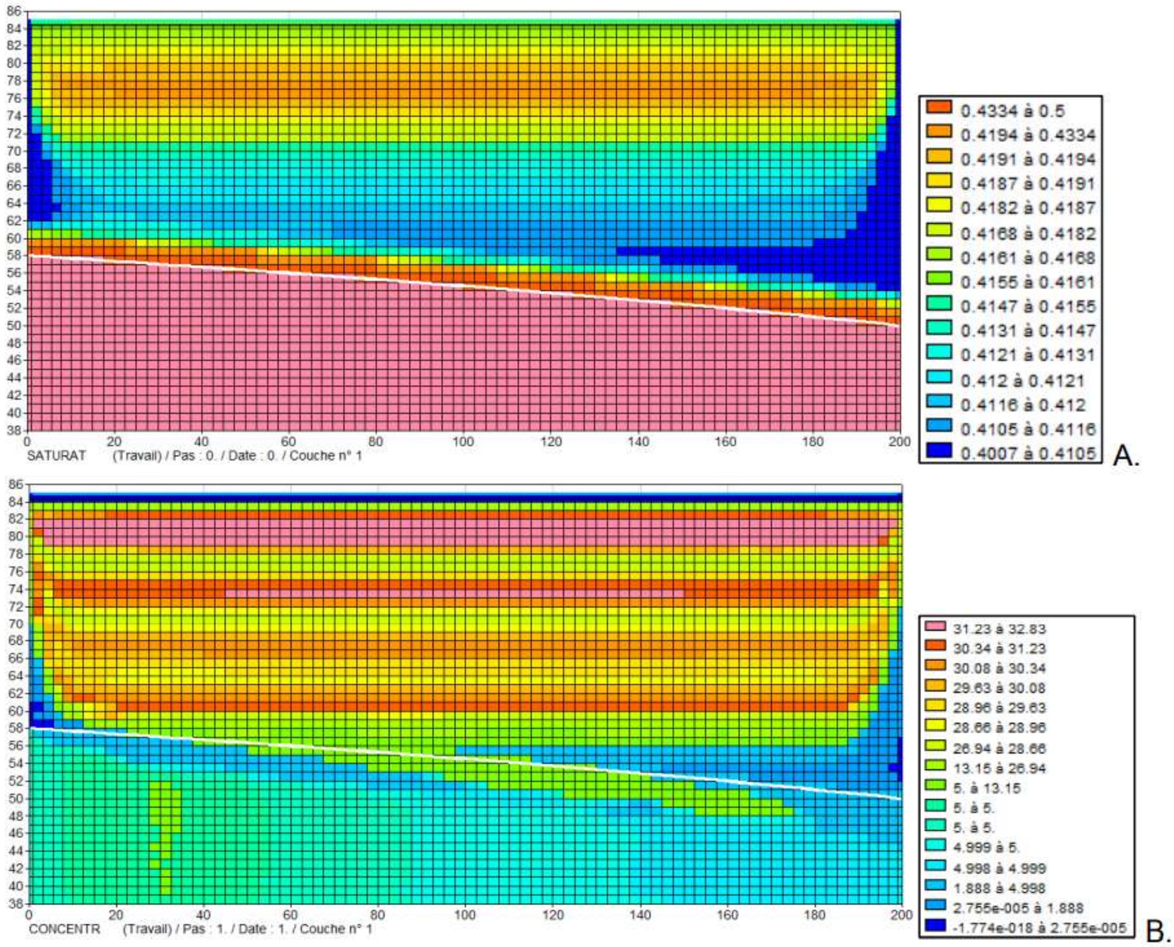

Figure 7.12 Initial state in vertical section of water content (A) and nitrate concentrations (B) in the MARTHE-MONICA model after 40 years (W-E orientation) (from Picot et al., 2017; BRGM/RP-66376-FR).

Because of the difficulty to acquire input data, modeling is rarely the preferred method in cases of strong denitrification when the study area is large (no more than one or two well catchments with one specific problem - area of the study area in km^2). Methods based on statistical and geographical treatments are preferred for harmonization and comparison at a European scale.

7.5 Testing approaches to harmonized, processed data for supraregional evaluations

Considering the size of the country and the variety of agro-geological context, no French national approach has already been able to be done. The maximum scale possible is a regional scale, and we have only one example for the Artois-Picardie region. The most important nitrate transfer modelling work currently concerns the North of France only (Buscarlet et al., 2012); the illustration below (figure 7.13) shows the results of simulated nitrate concentrations by comparing them to observed values. Otherwise, if one wants to work at the French national level, a simplified approach is preferable, with a statistical calculation based on the results of the experiments. These approaches developed by the BRGM in a national report about the pressure-impact of nitrate (Gourcy et al, 2017; RP-67428-FR) and pesticides (Auterives and Baran, 2017; RP-67453-FR).

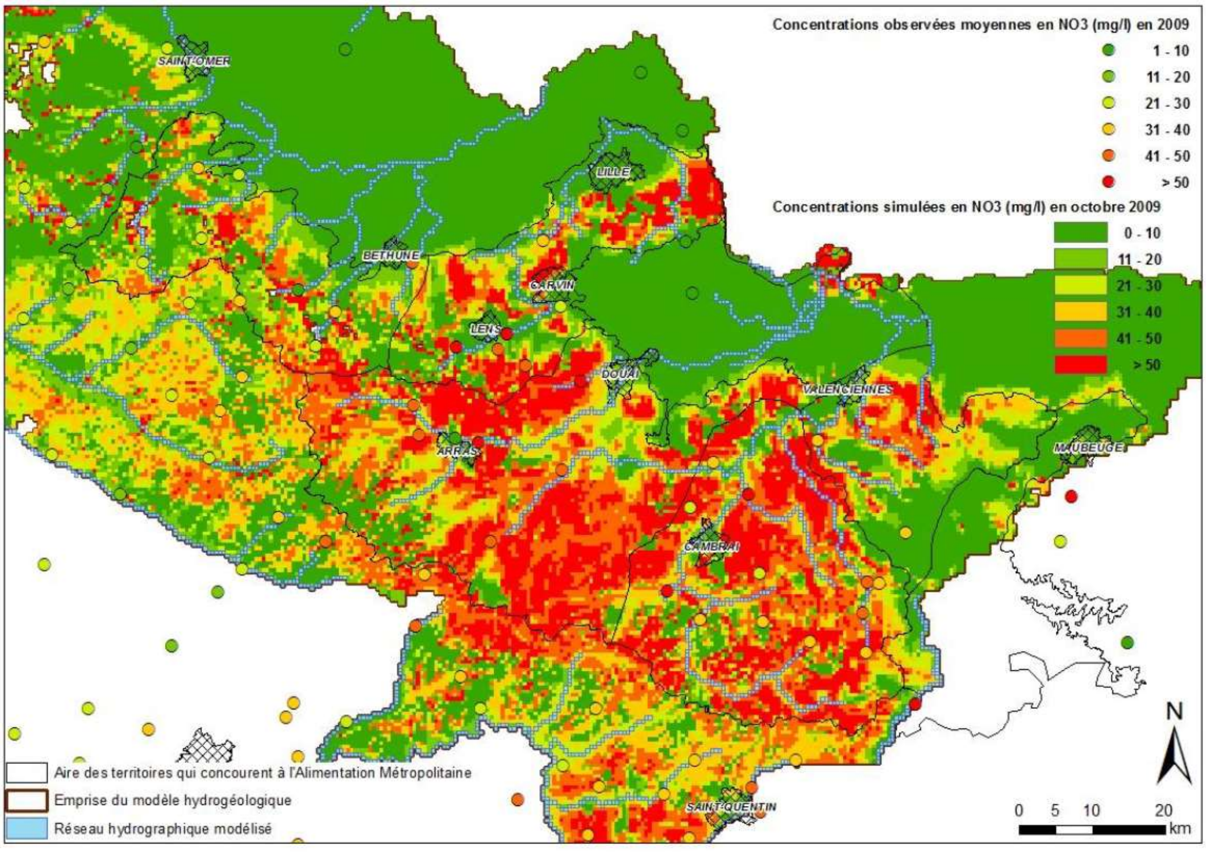

Figure 7.13 Comparison of the simulated and observed nitrate concentration for the month of October 2009, extract from Buscarlet et al., 2012 (BRGM/RP-61250-FR).

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8 CASE STUDY IRELAND

8.1 Description of Monitoring network

Groundwater quality data in Ireland is collected by a number of different state agencies. Since the 1960s groundwater quality data has been collected by the Geological Survey of Ireland (GSI) and local authorities for specific projects such as the protection of drinking water supplies and investigating the impacts of pollution events.

In the 1990s the Irish Environmental Protection Agency (EPA) set up the national groundwater quality monitoring network. The current groundwater quality monitoring network was updated substantially in 2006 to comply with Water Framework Directive requirements. Currently, the groundwater monitoring network comprises 293 monitoring points, of which 76 are springs (figure 8.1). A standard suite of 40 determinants, including field parameters, nutrients, major ions and certain minor and trace elements are analysed at each monitoring location within the monitoring network three to four times a year. These data are publicly available by request from the Environmental Protection Agency. For further details, the reader is referred to www.epa.ie.

In addition, Teagasc (Ireland's agricultural and food development agency) collect groundwater quality data from research farms and instrumented catchments for research purposes. This data is not publicly available. For further details, the reader is referred to www.teagasc.ie.

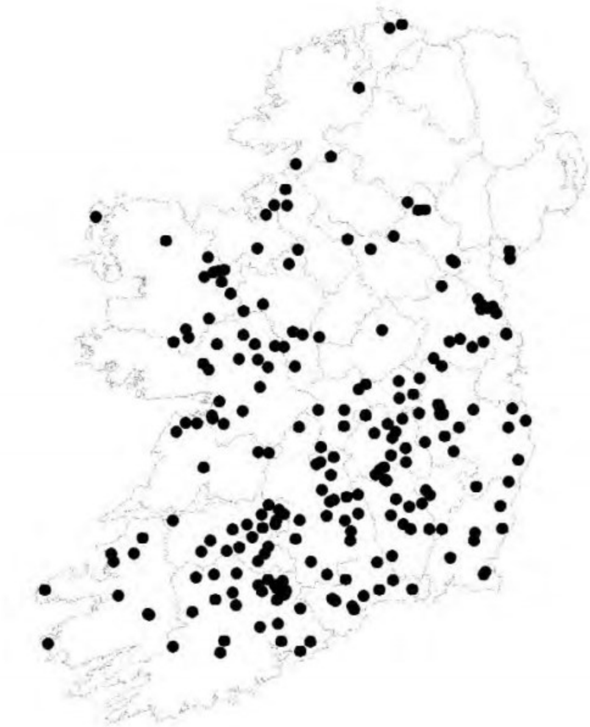

Figure 8.1 Location of monitoring points within the Irish EPA's national groundwater quality monitoring network

8.2 Information about travel times in the saturated and unsaturated zones

8.2.1 Age dating

Very limited groundwater age dating has been carried out in Ireland. It is generally assumed that given Ireland's (i) wet climate and (ii) fractured or karstic aquifers that most groundwater in Ireland is modern. Gallagher et al (2000) calculated the ages of groundwater near Belfast in Northern Ireland using ^{14}C groundwater dating techniques. The majority of their results identified modern water, but two boreholes yielded water with age estimates greater than 10,000 year before present.

8.2.2 Travel time estimation

In Fenton et al, 2009, researchers from Teagasc (Ireland's agricultural and food development agency) and Trinity College Dublin used a number of different techniques to estimate vertical and horizontal nitrate travel times. The aim of the research was to estimate the "lag time" between introducing mitigation measures and first improvements in water quality in different Irish catchments. Vertical travel times were estimated using a combination of depth of infiltration calculations based on effective rainfall and subsoil physical parameters and existing hydrological tracer data. Horizontal travel times were estimated using a combination of Darcian linear velocity calculations and existing tracer migration data. Total travel times to a virtual surface water receptor 500m away, assuming no biogeochemical processes, ranged from months to decades between the contrasting sites. The shortest times occurred under thin soil/subsoil on karst limestone and the longest times through thick low permeability soils/subsoils over poorly productive aquifers.

Fenton et al. (2011) outlines a modeling methodology to provide estimates of nitrate time lags (including unsaturated and saturated travel times) that could be anticipated in common Irish hydrogeological settings. The model does not account for denitrification along the nitrate transport pathway.

Vero et al (2017) presents a framework for determining *unsaturated zone* water quality time lags on grassland and arable catchments in Ireland. The model does not account for denitrification along the nitrate transport pathway. The modeling predicted that (i) trends would be observed at the base of the soil profile months to years after the modeled implementation of WFD measures, and (ii) the full effects may years to decades to be observed.

8.3 Information about attenuating processes in the subsurface

Irish aquifers are deemed to have low attenuation potential due to their fractured or karstified nature. Thus, it is generally assumed that denitrification occurring in surface and subsoil deposits is more significant than denitrification in the bedrock.

8.3.1 Denitrification potential in unconsolidated deposits

Research has been carried out on the denitrification potential of unconsolidated deposits in Ireland. One example is Jahangir et al, 2012, who investigated potential denitrification rates and ratios of N_2O / (N_2O+N_2) in in-tact soil cores collected from A, B and C soils horizons from an intensively grazed grassland plot in SE Ireland. They found subsoils could have a large potential to attenuate nitrate that has leached below the root zone, with the production of more N_2 than N_20, if available C is not limiting.

8.3.2 *Denitrification potential in the bedrock*

The Geological Survey of Ireland (GSI) developed a Potentially Denitrifying Bedrock map (GSI, 2011) to allow the Environment Protection Agency (EPA) and other decision makers to better assess the risk of surface water eutrophication from groundwater sources (EPA, 2013) as part of the implementation of the E.U. Water Framework Directive (WFD) (2008/98/EC).

In certain hydrogeological settings in Ireland, denitrification can occur. Denitrification reduces nitrate to nitrogen gas or, where the process is incomplete, the greenhouse gas nitrous oxide may be released. The GSI's Potentially Denitrifying Bedrock map (GSI, 2011) focuses on the denitrification of nitrate which occurs *in the bedrock* making use of electron donors present within the bedrock. This is in contrast to denitrification occurring *in the unconsolidated deposits* and shallow groundwater which has been shown to be significant in some settings in Ireland (e.g. Jahangir et al., 2012).

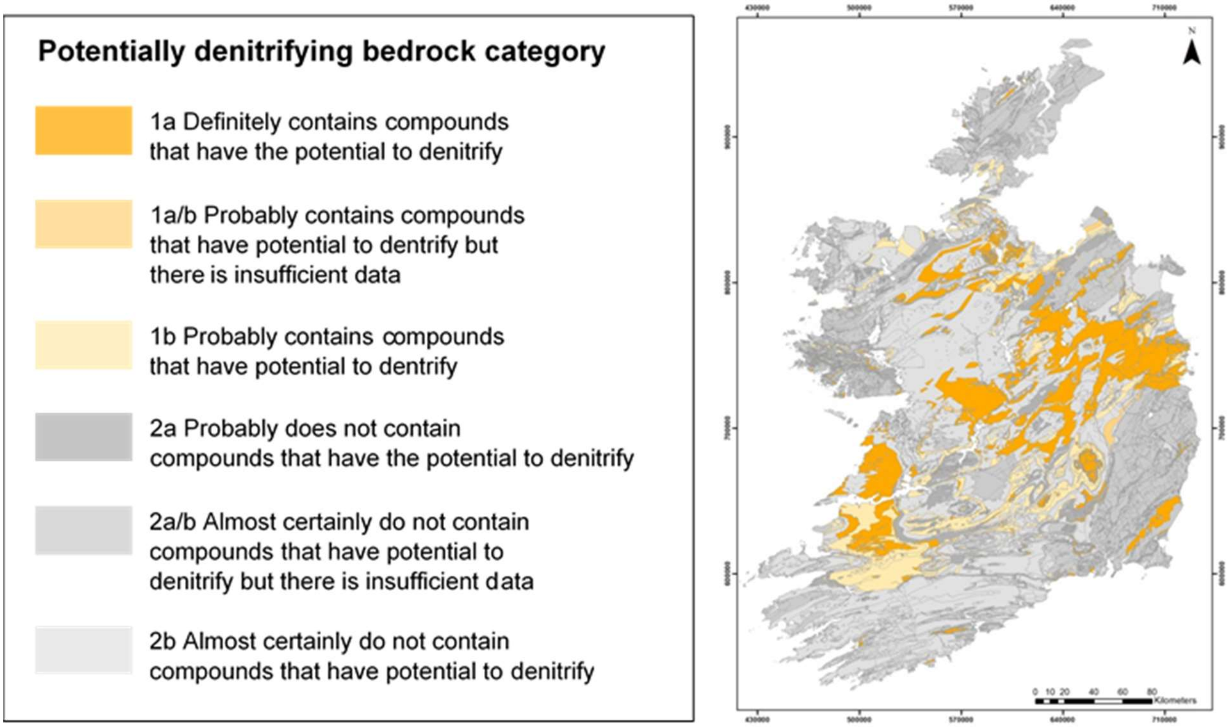

Figure 8.2 Geological Survey of Ireland's potentially denitrifying bedrock map

The GSI's Potentially Denitrifying Bedrock map (Figure 8.2) identifies bedrock units which are likely to contain electron donors such as organic carbon or metal sulphides (e.g. pyrite) and hence have the potential to reduce nitrate levels through microbially-assisted oxidation of the electron donor substances. The potential for denitrification is qualified through a scoring schema within the map, ranking bedrock units from "definitely containing compounds with the potential to denitrify" (1a) to "almost certainly not containing compounds that have the potential to denitrify" (2b).

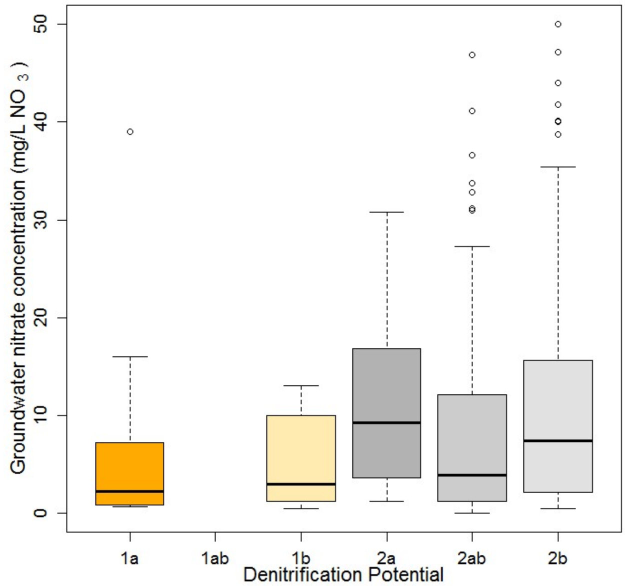

Figure 8.3 Box and whisker plot of mean groundwater nitrate concentrations for each potential denitrifying category. See Figure 8.1 for category descriptions.

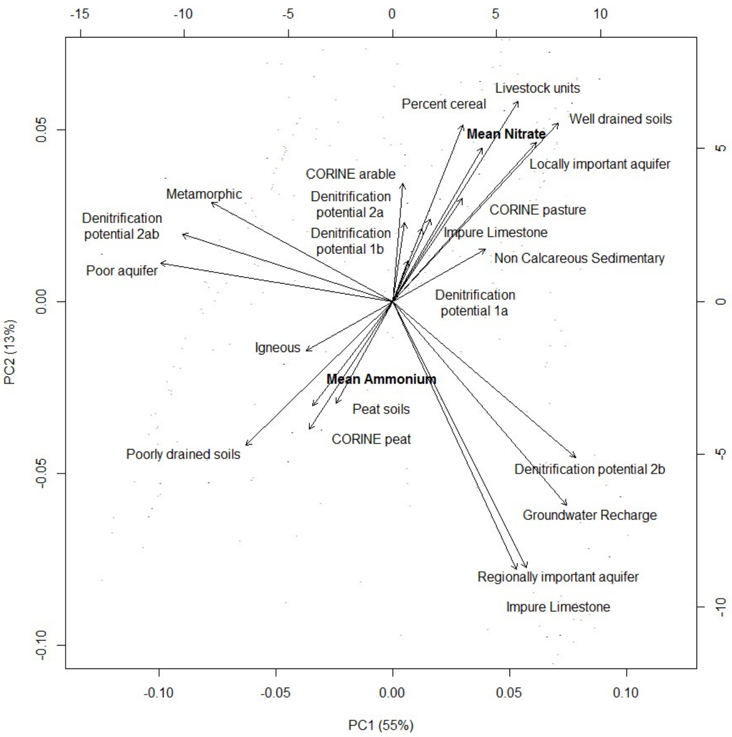

Figure 8.4 Principal component analysis indicates that soil type and land use have a greater influence on groundwater nitrate concentrations than potential denitrifying category.

A subset of groundwater monitoring data selected to minimize the influence of denitrification which may be occurring in the soils and unconsolidated deposits was analysed to appraise the GSI's Potentially Denitrifying Bedrock map (Tedd et al, 2016). Groundwater from aquifers which contain compounds that have the potential to denitrify (categories 1a and 1b) typically have lower groundwater nitrate concentration with a smaller range than groundwater from aquifers which do not (categories 2a, 2ab and 2b) (Figure 8.3). An analysis of variance (ANOVA) indicates that the difference in mean groundwater nitrate between the two groups is statistically significant (p value=0.023).

Multivariate analysis (principal component analysis) indicates mean groundwater nitrate concentration is associated with soil type (well drained soils), land use (cereal and livestock units) and aquifer type (locally important). In contrast mean ammonium is associated with soil type (poorly drained) and land use (peat) (Figure 8.4). The potential denitrifying bedrock category is a less significant parameter. This indicates that even for the subset of data, selected to minimise the influence of potential denitrification of soils and unconsolidated deposits, factors such as soil type and land use have a greater influence than the presence or otherwise of potentially denitrifying compounds in the bedrock aquifers.

8.3.3 Pollution Impact potential mapping

The Irish Environmental Protection Agency have produced a national suite of nutrient susceptibility maps which identify hydrogeologically susceptible areas. High hydro(geo)logically susceptible areas are areas from which nutrients have a high probability of reaching a water body of interest due to the underlying hydrogeological conditions. That is the areas that have significant pathway linkages from the source of pollution or pressure to surface water or groundwater receptors. Susceptibility maps are generated by linking data on soils, subsoils, groundwater vulnerability and aquifer types with nutrient attenuation and transport factors. These maps are now available for phosphate along the near surface pathway, and for nitrate along the near surface and groundwater pathways. Figure 8.5 shows the national sub surface nitrate susceptibility map.

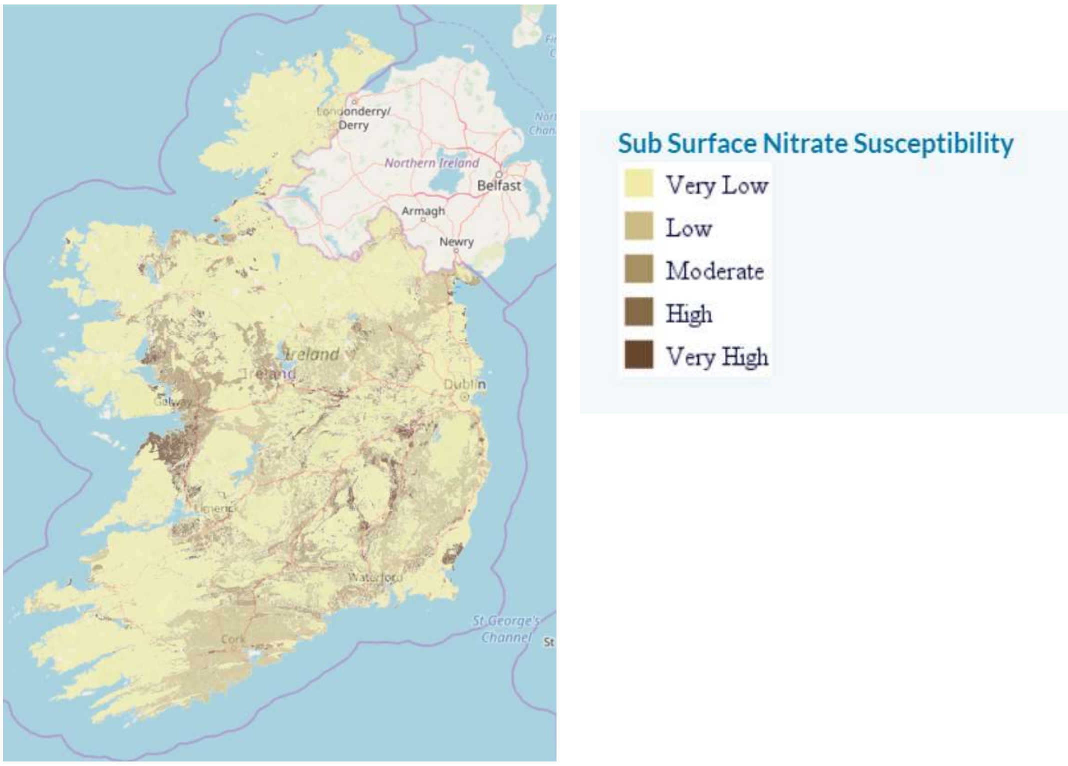

Figure 8.5 Nitrate susceptibility map

The susceptibility maps are combined with nutrient loadings data provided by the Department of Agriculture, Food and the Marine and the Central Statistics Office to produce Pollutant Impact Potential maps. For more information and further maps in the series the reader is referred to www.catchments.ie and Archbold et al, 2016.

8.4 Combined analysis of transport and attenuating processes in the pilot area

A number of site-specific investigations into the transport and attenuation processes of nitrate have been carried out in instrumented catchments in Ireland. Three examples are given here.

Jahangir et al, 2012, found the distribution of hydrogeochemical variables and their connection with the occurrence of nitrate provides better insights into the prediction of the environmental risk associated with nitrogen use within agricultural systems. Their research objective was to evaluate the effect of hydrogeological setting on agriculturally derived groundwater nitrate occurrence. Piezometers ($n = 36$) were installed at three depths across four contrasting agricultural research sites. Groundwater was sampled monthly for chemistry and dissolved gases, between February 2009 and January 2011. Mean groundwater nitrate ranged 0.7–14.6 mg/l as N, with site and groundwater depth being statistically significant ($p < 0.001$). Unsaturated zone thickness and saturated hydraulic conductivity were significantly correlated with dissolved oxygen (DO) and redox potential (Eh) across sites. Groundwater nitrate occurrence was significantly negatively related to DOC and methane and positively related with Eh and K_{sat}. Reduction of nitrate started at Eh potentials <150 mV while significant nitrate reduction occurred <100 mV. Indications of heterotrophic and autotrophic denitrification were observed through elevated dissolved organic carbon (DOC) and oxidation of metal bound sulphur, as indicated by sulphate. Land application of waste water created denitrification hot spots due to high DOC losses. Hydrogeological settings significantly influenced groundwater nitrate occurrence and suggested denitrification as the main control.

Orr et al. (2016) investigated the influence of hydrogeological setting on biogeochemical processes, aiming to characterise the dominant processes influencing nitrogen levels in groundwater in two Irish catchments underlain by bedrock aquifers with contrasting (physical and geochemical) hydrogeological properties, but having comparable nutrient loads and thin to no subsoil cover over much of their area. Their research considered the influence of spatial heterogeneity on biogeochemical processes within each catchment, both across the catchment and with depth. This was achieved through monitoring well tracer tests and the analysis of chemical and isotopic signatures of groundwater and surface water. They found that incorporating the knowledge gained concerning biogeochemical processes into water quality catchment management tools can prove fundamental in reducing the risk posed to groundwater and surface water receptors.

McAleer et al (2017) investigated two well drained agricultural catchments (10 km^2) in Ireland with contrasting subsurface lithologies (sandstone vs. slate) and land use. Denitrification capacity was assessed by measuring concentration and distribution patterns of nitrogen (N) species, aquifer hydrogeochemistry, stable isotope signatures and aquifer hydraulic properties. A hierarchy of scale whereby physical factors including agronomy, water table elevation and permeability determined the hydrogeochemical signature of the aquifers was observed. This hydrogeochemical signature acted as the dominant control on denitrification reaction progress. High permeability, aerobic conditions and a lack of bacterial energy sources in the slate catchment resulted in low denitrification reaction progress (0–32%), high nitrate and comparatively low N_2O emission factors. In the sandstone catchment denitrification progress ranged from4 to 94% and was highly dependent on permeability, water table elevation, dissolved oxygen concentration solid phase bacterial energy sources. Denitrification of nitrate to N_2 occurred in anaerobic conditions, while at intermediate dissolved oxygen; $N_2O$was the dominant reaction product. The denitrification observations across catchments were supported by stable isotope signatures. Stream nitrate occurrence was 32% lower in the sandstone catchment even though Nitrogen loading was substantially higher than the slate catchment.

8.5 References

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9 CASE STUDY MALTA

9.1 Description of Monitoring network

Regular monitoring data for groundwater in the Malta mean sea level groundwater system (MLSA = Mean Sea-Level Aquifer) dates back to the 1960's when monthly monitoring of all public groundwater abstraction stations started to be undertaken. Such monitoring included assessment of nitrate content – which was considered as representative of anthropogenic contamination mainly resulting from agriculture. The monitoring network was extended in 2005, as part of the implementation process of the EU Water Framework Directive, to include a number of private groundwater sources and hence increase its spatial representativity over the whole groundwater body.

The long-term results of these monitoring networks show an increasing trend in the nitrate concentration of groundwater, although trends have tended to be come not-significant in recent years. Furthermore, nitrate contamination is the single most important issue for the deterioration in status of groundwater in the Maltese islands, with groundwater bodies failing good status conditions because of nitrate levels exceeding the 50 mg/l quality standard established under the EU Groundwater Directive.

The importance of Nitrate as a groundwater contaminant has invariably led to a number of focused studies to assess this contamination. These studies include:

- BRGM 1991 – Assessment of Nitrate trends in the mean-sea level groundwater body
- WSC 1999 – Correlation of Nitrate and Chloride content in groundwater
- BGS 2008 – Determination of the sources of Nitrate in groundwater through the use of isotope fingerprints.

Furthermore, trends in the Nitrate concentration were also assessed in Malta's 1st and 2nd River Basin Management Plans (Malta Resources Authority, 2011 and Energy and Water Agency, 2016).

The most important study of the above was that undertaken by BGS (2008) which derived the "fingerprint" of nitrate contained in groundwater (based on the ratio of nitrogen and oxygen isotopes in the nitrate ion) and compared these to the "fingerprint" of nitrate contamination sources. This source fingerprinting exercise indicated that the main contribution to Nitrate contamination in groundwater comes from soil nitrate, and hence is attributable to over-fertilisation practices in agriculture. These results were key to support the development of Malta's Nitrates Action Programme (Government of Malta, 2011).

In addition to the above, a new unsaturated zone monitoring network is currently being developed to enable the sampling of percolating groundwater at different depths within the unsaturated zone. This network will enable the assessment of the nitrate content in the annual recharge (hence assessing the effective impact of the Nitrates Action Programme) and the attenuation of nitrate content as groundwater percolates through the unsaturated zone.

9.2 Information about travel times in the saturated and unsaturated zones

Investigations undertaken by Bakalowicz, et al. (2003) and BGS (2008) used environmental tracers such as Tritium, CFCs and SF_6 to assess groundwater dynamics and residence times within the MSLA. Both studies arrived at the conclusion that the average residence time of groundwater in the saturated zone is of the order of 40 years. In particular, both studies failed to detect the tritium peak, indicating that groundwater recharge to the mean sea-level aquifer occurred before the increase in tritium level due to nuclear weapons testing in the 60s and 70s.

Travel times through the unsaturated zone were expected to reflect the different hydrogeological properties of the different formations making up the stratigraphical sequence of the Maltese islands. In particular, slow travel times are expected in the Blue Clay formation (a marly impervious formation) and the Globigerina Limestone (a consolidated marly limestone overlying the main coralline aquifer formation). Geological investigations of these formations place percolating velocities in these formations as ranging between 0.5m – 3 m/yr. Higher flow velocities are expected in the lowest geological formation, the Lower Coralline Limestone, which being the main aquifer formation has moderate to high intrinsic porosities.

9.3 Information about attenuating processes in the subsurface

The long travel time of groundwater through the unsaturated and saturated zones facilitates the attenuation of infiltrating pollutants. In the unsaturated zone, the thin soil profiles overlying the bedrock are not expected to result in significant bacterial attenuation of the infiltrating nitrate. However, the long infiltration profile through the consolidated rock profile is expected to result the dilution and dispersion of contaminated recharge, whilst percolation through the Globigerina formation is also expected to contribute to attenuation.

Furthermore, once the percolating water reaches the saturated zone, the high groundwater storage capacity of the MSLA compared to the mean annual recharge also leads to the potential dilution of contaminated recharge with unpolluted uncontaminated resident groundwater, as the recharging water flows through the saturated zone.

Finally, at the abstraction point, consideration needs also to be given to intruding sea-water or saline waters from the freshwater-saltwater transition zone which is generally low in nitrate and hence leads to the further dilute of the nitrate content of the abstracted groundwater, albeit at the expense of an increase in its chloride content.

9.4 Combined analysis of transport and attenuating processes in the pilot area

Studies in the Maltese islands have to date primarily focused on the identification of nitrate sources, and less on transport and attenuation processes. A specific assessment was undertaken during the investigations undertaken by BGS (2008) which looked at transport rates in the unsaturated zone and concluded that primary porosity is by far more important than secondary (fracture) flow in the case of the MSLA. Hence, physical processes in the unsaturated zone are deemed to play an important role in the attenuation of inflowing contamination.

This lack of information is being addressed, as mentioned under section 9.1, through the recent launch of a new project which will use flexible time-domain reflectometry (FTDR) probes to assess groundwater recharge in the first 20 meters of the unsaturated zone (giving water contents of this unsaturated zone profile) and which is expected to provide invaluable information about the attenuation processes occurring in this important segment of the infiltration profile.

9.5 Testing approaches to harmonized, processed data for supraregional evaluations

The next steps in the assessment of monitoring data in Malta are focused on:

(i) the determination of the nitrate content of the mean annual recharge in the first horizons of the unsaturated zone, so as to enable the projection of the impact of this water on the status of the aquifer systems, and

(ii) the assessment of the diluting contribution of intruding saline-waters in groundwater abstraction wells, though a comprehensive assessment of infiltration mechanisms.

This information will enable the more comprehensive assessment of the status of the MSLA groundwater body and the development of corrected trends outlining the potential of the aquifer system to reach the good status conditions of the EU's Water Framework Directive.

9.6 References

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10 CASE STUDY CYPRUS

10.1 Description of Monitoring network

One of the most pressing issues in Cyprus, as in many countries around the globe, is groundwater nitrogen pollution induced by agriculture and stock-farming activities. For the period 2012-2015, six Cyprus aquifers have been identified as Nitrate Vulnerable Zones (NVZ) and action plans are being implemented since (http://www.moa.gov.cy/moa/gsd/gsd). In 2017, the Pentaschinos alluvial aquifer, was also designated as an NVZ. Moreover, for the purpose of the implementation of the Water Framework Directive 2000/60/EC, one river basin district was identified for the whole Cyprus. Furthermore, 20 groundwater bodies have been delineated (Republic of Cyprus, March 2005). This network consists of 95 monitoring stations (92 wells and 3 springs) and threshold values have been assigned for all groundwater bodies. For the scope of this project, however, the groundwater bodies of Cyprus have been classified in five aquifer types, referred to hereafter.
Cyprus Geological Survey Department (GSD), is actively involved in the implementation of Directive 1991/676/EEC on nitrate pollution of agricultural origin. Towards this end, the Department operates a groundwater monitoring network consisting of 221 boreholes, which are sampled twice a year for nitrate (NO_3). Borehole depth ranges from a few meters in depth up to 382 m with an average depth of 150m. Monitoring point distribution (on conceptual flow models) is outlined below and depicted in Fig. 11.1.

Hard rock/Fractures flow model.
Hard rock/fractured flow model aquifer develops in the ophiolite rocks of Troodos Massif and Limassol forest and occupies a total area of 2.404 Km^2. Groundwater flow is primarily controlled by secondary porosity caused by tectonic fracturing and uplifting. Borehole records indicate that favorable aquifer conditions decrease rapidly at 150 to 200 mbs (Afrodidis, 1991) leading to a fast draining system with high turnover rates, especially in gabbro, at the higher part of the aquifer (Udluft at. el., 2003a). The aquifer discharges through short-lived springs (Water Development Department, 2002) whereas deeper, regional flow recharges sedimentary aquifers in the lowlands. A total of 85 station are maintained in this aquifer.

Multi-layer aquifer
Multi-layer model aquifers include the Mesaoria, Kokkinochoria, Kiti-Tremithos, Germasogeia, Lemesos, Akrotiri, Paramali – Avdimou, Pafos and Chrysochou – Gialia aquifers, occupying a total area of 1894 Km^2. These aquifers commonly include an unconfined saturated layer, consisting primarily of gravels and deeper confined alternating layers of sand – sandstone and marl (Kitching et. al., 1980, United Nations Development Programme, 1970). A total of 108 monitoring stations are maintained in this aquifer type and the network is denser within the NVZs.

Confined carbonate
Confined Carbonate aquifers are dual porosity aquifers in which secondary porosity play a major role in groundwater percolation. In Cyprus, the Lefkara-Pakna aquifer is such an aquifer and it occupies an area of 1273 km2. A total of 14 monitoring stations are maintained in this aquifer.

Karst
Karst aquifer type covers an area of 541 km^2. A total of 14 monitoring stations are maintained.
Gravel aquifer

Gravel aquifer types, as defined in this project, only develops in one case to the northwest. It is a very small aquifer and it only covers an area of 2 km2. The Department does not maintain monitoring station at the area.

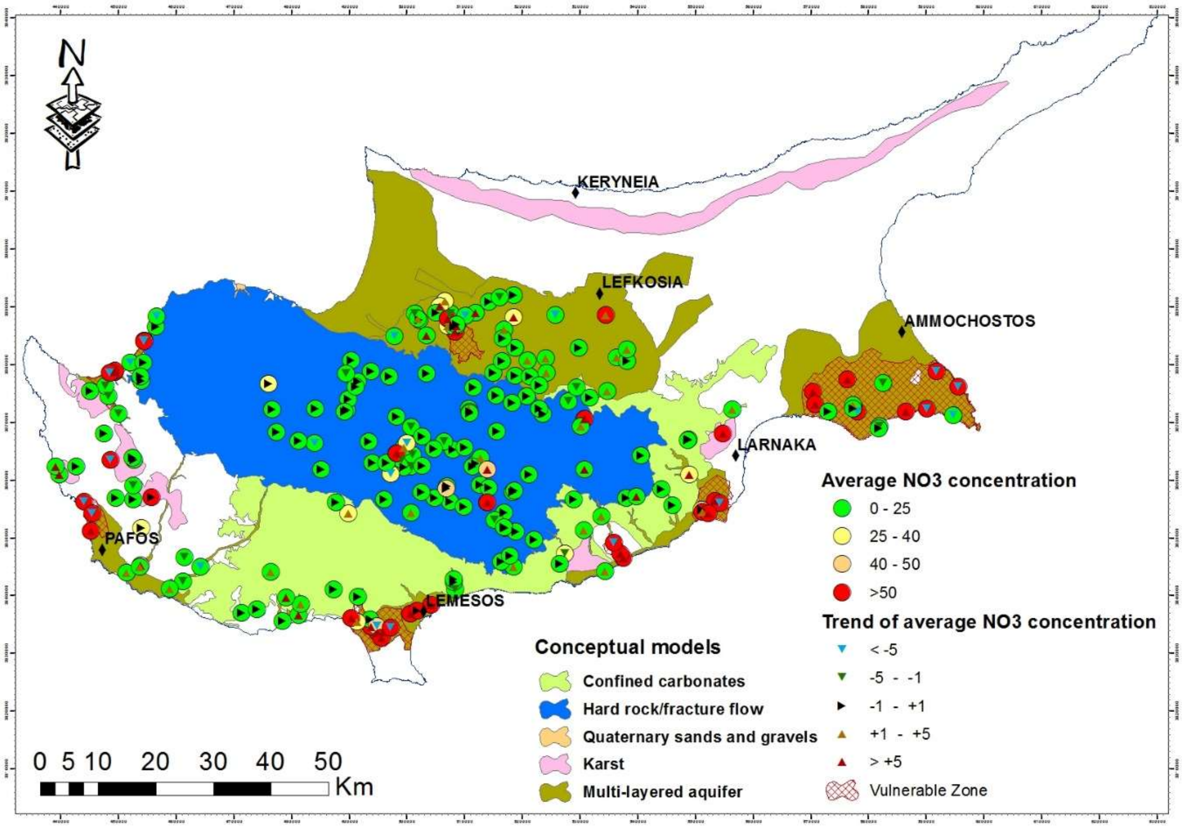

Figure 10.1. National monitoring network on implementing 1991/676/EEC. Base map depicting aquifer types and nvz (Report from the commission to the council and the European parliament on the implementation of Council Directive 91/676/EEC, http://www.moa.gov.cy/moa/gsd/gsd).

10.2 Information about travel times in the saturated and unsaturated zones

No systematic groundwater dating studies have been carried out in Cyprus. Groundwater was, however, modelled to be from actively recharged up to 10 years old, in upper and most dynamic part of the Troodos fractured aquifer (Fig. 11.2). This was also confirmed through ^{3}H and CFC age dating from which groundwater and spring water in the upper part of Troodos fractured aquifer was found to be very young (Boronina et. al., 2005, Jacovides, J., 1979, Udluft and Külls, 2003).

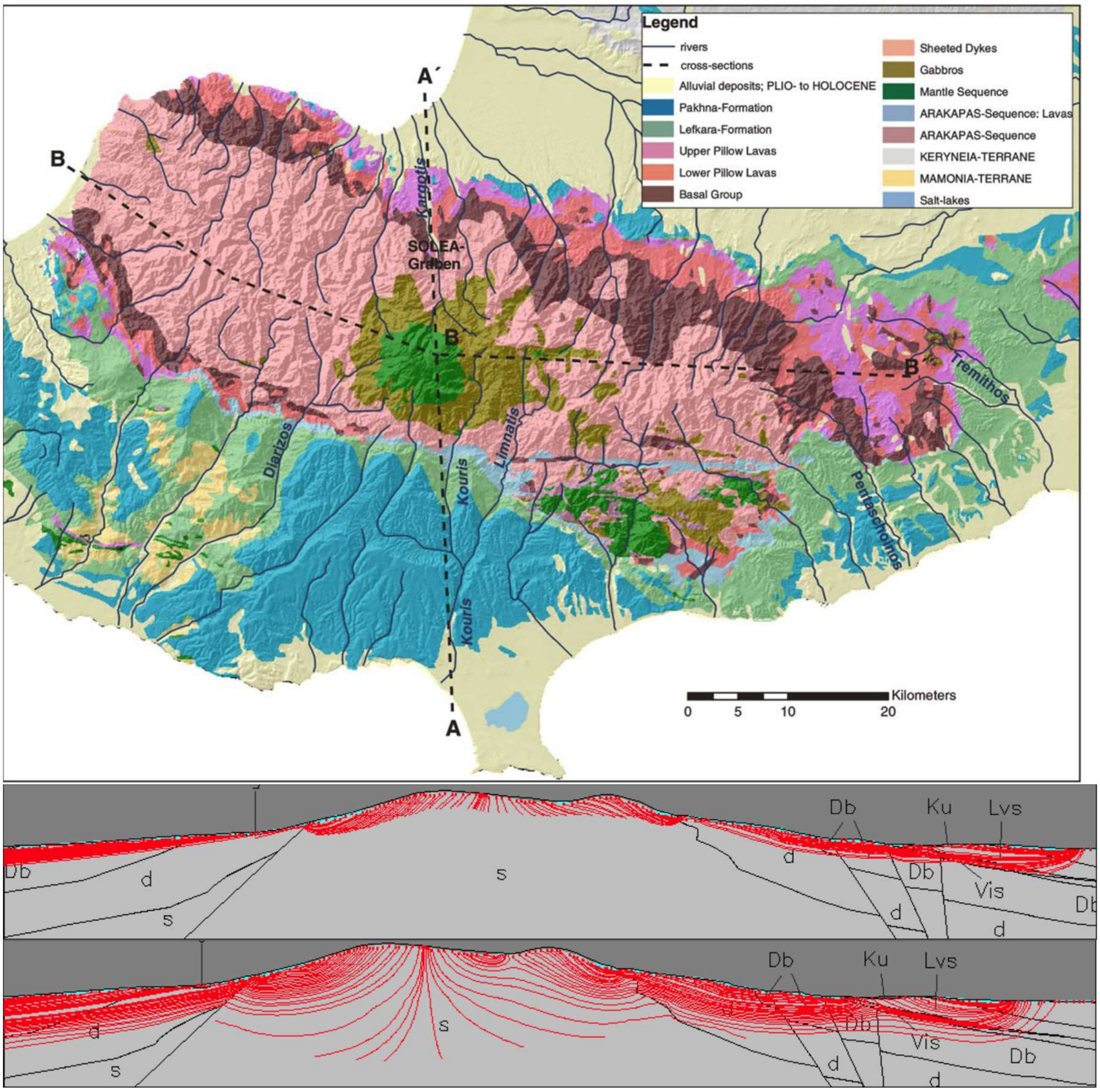

Figure 10.2 Modelled particle flowlines in the Upper Troodos for a time period of 10 and 100 years; upper and lower cross section, respectively. After Udluft et. all., 2003.

Groundwater age increases downstream of the ophiolites and was also modelled to be up to 100 years old, in the most extreme cases of regional flow from the intrusives in the higher elevations of Troodos, through the extrusives and to the sedimentary aquifers, in the lowlands (Fig. 11.2). Groundwater age was dated (through ^3H) to be over 50 years north and south of Troodos, thus partially confirming the model (Udluft and Külls, 2003). Similar results were found by Boronina et al. (2005) who found groundwater to be over 48 years old in consolidated sedimentary rocks to the south.
Furthermore, intermediate groundwater ages of 10-40 years old have been dated in clastic, multilayer aquifers to the north of Troodos, where river recharge is active and to the carbonate dual porosity aquifer, to the south (Udluft and Külls, 2003).

10.3 Information about attenuating processes in the subsurface

Nitrogen source and denitrification processes can be discerned by examining the ^{14}N and ^{15}N ratios of the nitrogen molecule. More specifically, $\delta^{15}N$ in nitrate (and $\delta^{18}O$) can be used to trace nitrogen source (modified from Hoefs 1997 and Clark and Fritz 1997 with data from Amberger and Schmidt 1987, Bottcher et. Al., 1990, Letolle, 1980). Furthermore, the combination of the isotopic composition of $\delta^{18}O$ and $\delta^{15}N$ can be used not only in distinguishing nitrate sources more reliably but most importantly, is to recognize the potential of denitrification (Amberger and Schmidt 1987, Bottcher et al. 1990, Durka et al. 1994).

In trying to identify the source(s) of the nitrate as well as to evaluate the denitrification potential of aquifers in Cyprus, GSD ran a project with total 100 groundwater samples, in September 2009, were analysed for $^{15}N/^{14}N$ and $^{18}O/^{16}O$ (Christophi and Constantinou, 2011). Upon sampling, pH, conductivity, dissolved oxygen and water level were measured and recorded. One liter of sample was collected in the cases of nitrate concentration equal or above 20 mg/l, whereas in lower concentrations, up to five liters were collected. Polyethylene bottles were used, and ten drops of chloroform were added upon collecting the samples. Samples were shipped for analysis to the lab Hydroisotop, in Germany.

The majority of the samples, 71% show nitrate isotopic composition that indicates mineral fertilizer as the primary source of nitrate, as 14% and 2% of the samples show manure and soil/manure as the primary source of nitrate respectively (Table 11.1). It is also clear that 20% of the samples show significant denitrification potential. Most of the denitrification samples tend to have lower nitrate concentrations than those with insignificant denitrification thus supporting the scenario of denitrification (Fig. 11.3 and Fig. 11.4).

In Germasogia and Akrotiri aquifers, two multi-layered aquifers as classified in the current project, all samples showed some trend in terms of denitrification. The former, showed significant denitrification potential whereas the latter showed no denitrification potential. However, in no other aquifer a definite trend was discerned. The low denitrification potential that is seen in Akrotiri aquifer might be attributed to the low clay content. Furthermore, there isn't any strong correlation between denitrification potential with water level, aquifer type (confined/unconfined) or the primary source of nitrate (Fig. 11.3 and Fig. 11.4).

Table 10.1 Tabulated the denitrification potential and primary nitrate source per aquifer type.

		Samples per aquifer type (conceptual model)				
		Confined carbonates	Hard rock / fracture flow	Quaternary sands and gravels	Karst	Multi – layered aquifer
Samples per models		2	7	0	4	87
Significant denitrification		1	0	0	0	19
Primary source of nitrate	Fertilizer	1	5	0	4	71
	Manure	0	2	0	0	14
	Soil/manure	1	0	0	0	2

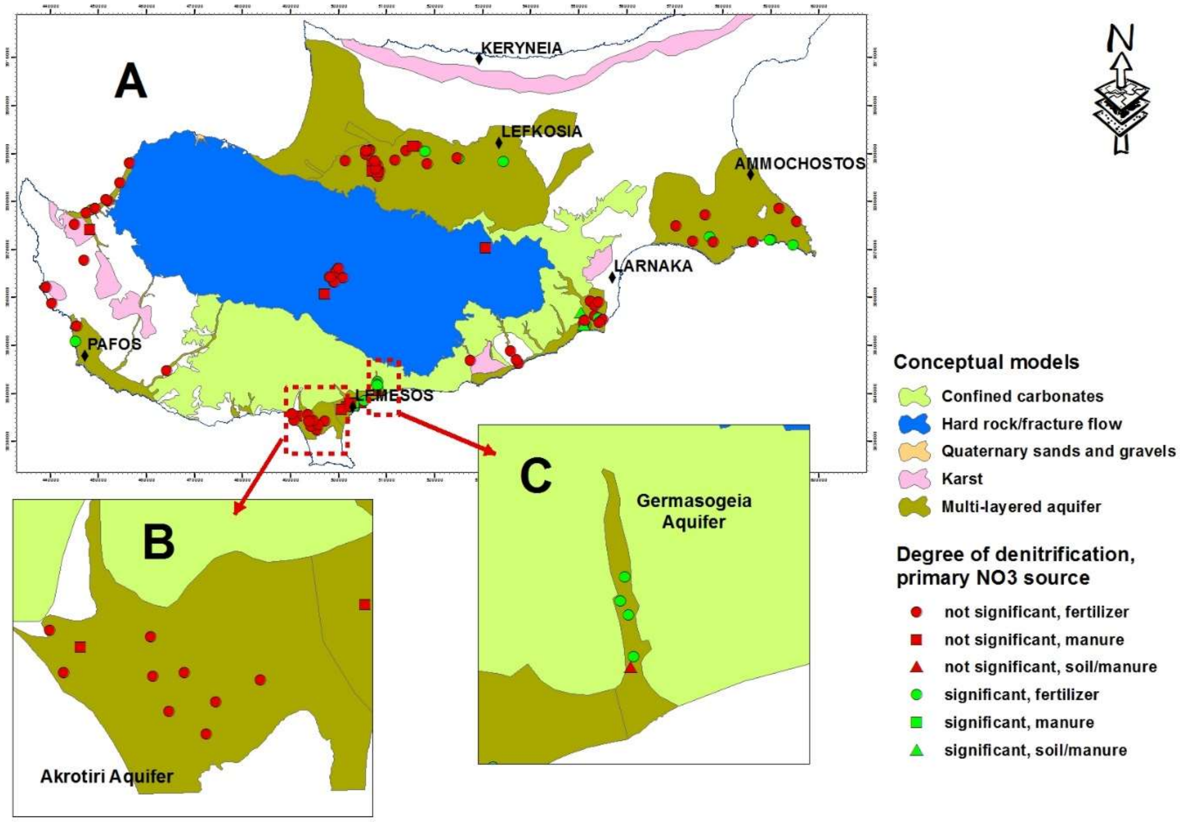

Figure 10.3 (a) depicting spatial of primary nitrate source and denitrification potential from 100 groundwater samples (after Christophi and Constantinou, 2011). (b) Germasogia aquifer and (c) Akrotiri aquifer.

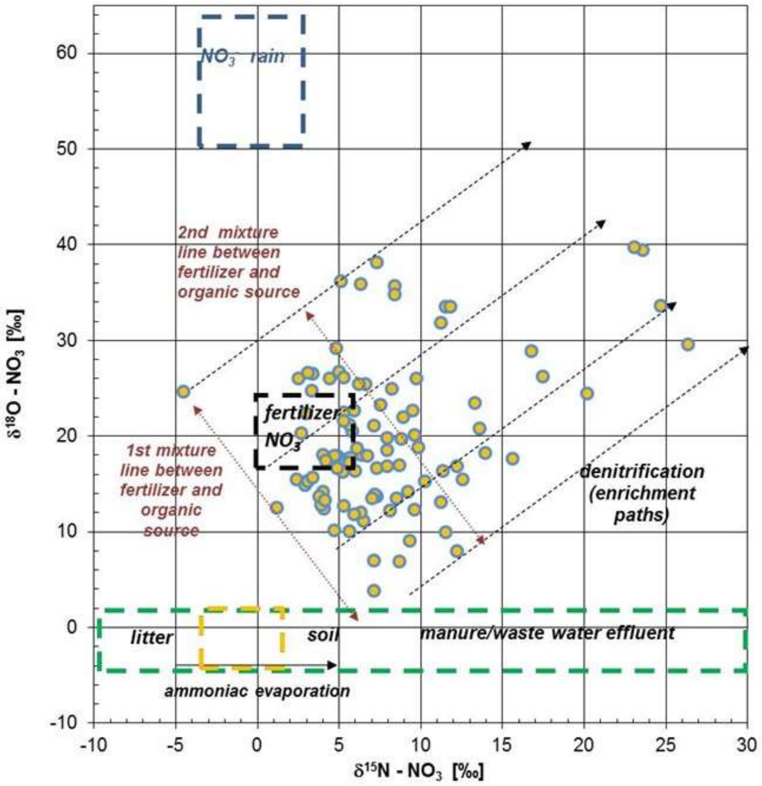

Figure 10.4 shows the isotopic composition of NO_3 in 100 groundwater samples from Cyprus (after Christophi and Constantinou, 2011).

10.4 Combined analysis of transport and attenuating processes in the pilot area

No data on transport and attenuating processes exist for Cyprus, as no systematic groundwater dating studies have been carried out. All relevant data are chapter 11.2. and 11.3.

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11 CASE STUDY LATVIA

11.1 Description of Monitoring network

Regular surveys of groundwater quality in Latvia have been conducted since 1959. The groundwater quality monitoring network was set up between 1970 and 1980, initially to assess the groundwater water quality and changes in confined aquifers, as these aquifers began to be used intensively for centralized extraction and supply of drinking water during this period not only in urban areas but also in rural areas. From 2004, the groundwater monitoring network includes also springs. This is an important improvement in the monitoring network, as springs with high water flow mostly represent water quality in much larger catchment areas than wells and are an important indicator of diffuse pollution (Ziņojums, 2016).

In Latvia, groundwater monitoring simultaneously fulfills the requirements of the Nitrates Directive and the Water Framework Directive (WFD, 2000/60/EC). The primary objective of nitrate monitoring in Latvia is to detect any nitrate contamination to ensure good drinking water quality throughout the country, as well as to reduce the impact of nitrate pollution on small and large rivers whose waters flow into the Baltic Sea. In the Nitrates Directive reporting period 2012-2015, 68% of all monitoring observation points represent confined aquifers, but in Latvian hydrogeological conditions (i.e., Quaternary sediments in Latvia consist mainly of glacial and its melting water sediments, which are variable in terms of composition and thickness), the monitoring of the deepest captive groundwater within the Nitrates Directive is not primary in Latvia (Ziņojums, 2016).

The groundwater monitoring program in Latvia is being adapted to the requirements of the two directives (Nitrates Directives and WFD), which are not equivalent. The WFD requires the identification of the background level of natural chemical composition and trends in the aquifers used in the main water supply of groundwater bodies, which in the case of Latvia are deeper confined water. However, it should be concluded that the current groundwater monitoring program is more adapted to fulfill the requirements of the WFD (Ziņojums, 2016).

Groundwater monitoring provides data on the status of the groundwater body. It is the main and strategic goal of monitoring in any year of the monitoring program period. Achieving good groundwater status in all groundwater bodies and assessing the risk of failing to achieve this goal is the main objective of groundwater resource management. Groundwater monitoring is primarily done at groundwater body level, while integrating river basin management into a common strategy for achieving environmental quality objectives (Ziņojums, 2016).

Groundwater status within the monitoring network is observed in 311 wells at 61 stations and 30 springs. Of these, quality (chemical composition) observations are provided at 53 stations in 218 wells and 30 springs (Figure 11.1), while in quantitative (water levels) observations at 60 stations in 305 wells. The frequency of monitoring observations during the six-year cycle of monitoring of river basin districts includes a detailed breakdown of monitoring stations by groundwater bodies and types of monitoring. Monitoring points that are monitored each year and observable parameters for groundwater quality can vary according to the annual monitoring plans developed. The frequency of groundwater monitoring is variable: the frequency of quantitative observations - two times a day (automatic level measurements) up to four times a year, and the frequency of groundwater chemical observations is four times a year, up to once a year (over a six-year period, it changes from one time in six years to one time each year) (Ziņojums, 2016).

Groundwater quality monitoring parameters traditionally are field measurements, key ions, nitrogen compounds and their ionic forms, heavy metals, chemical pollutants, and pesticides (atrazine, simazine, bentazone, MCPA, promethrin, propazine, 2,4-D, MCPB, isoproturon, aclonifene, bifenox, aldrin, dieldrin, heptachlor, heptachlor epoxide, dimethoate, cypermethrin, alpha-cypermethrin, trifluralin). Chemical pollutants are monitored only in urban areas, artificially replenishing groundwater resources, as well as in the areas of water extraction and associated potential cones of depression. Pesticides are monitored in agricultural areas, including monitoring stations that coincide with nitrate vulnerable zone. Primary pesticides are analyzed in the first sensitive and unprotected lower-lying aquifer, and in the case of pesticide detection, the deepest aquifers are sampled. Other observable parameters are observed at all monitoring points (both wells and springs) (Ziņojums, 2016). The frequency of monitoring observations and its determination in the following years may change, taking into account the new monitoring data obtained, experience gained, developed scientific projects in connection with the implementation of the WFD, and new requirements of EU and Republic of Latvia regulatory enactments. This will be assessed by developing a monitoring plan for each specific year (Ziņojums, 2016).

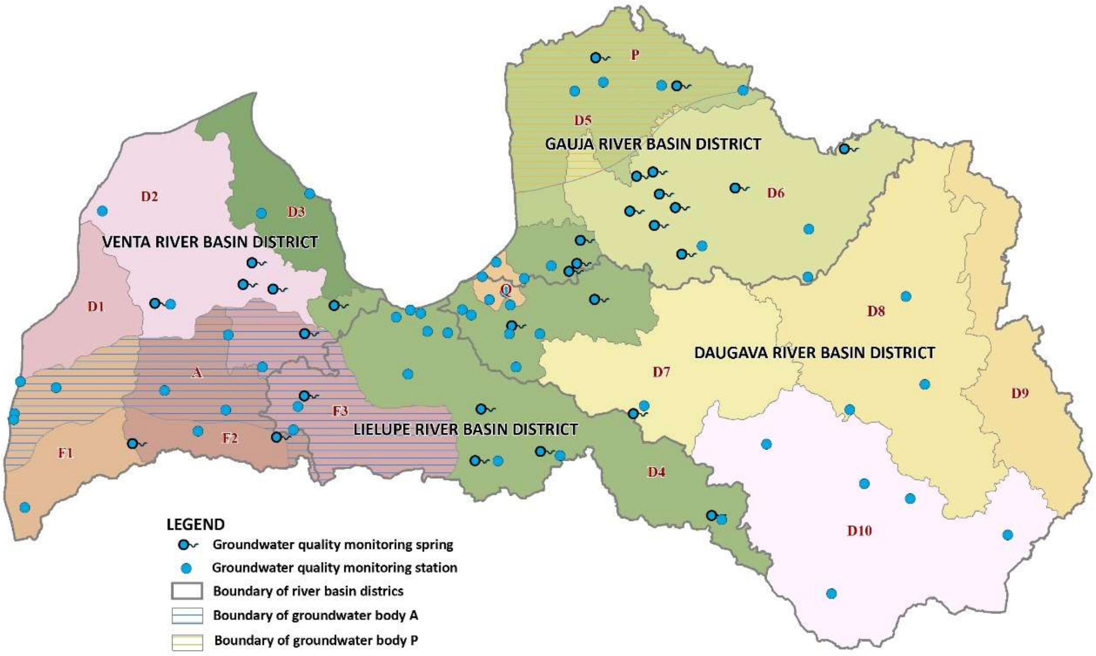

Figure 11.1. Groundwater quality observation network in Latvia

11.1.1 Nitrate monitoring in Latvia

The primary goal of nitrate monitoring in Latvia is to detect any nitrate pollution to ensure good drinking water quality throughout the country, as well as to reduce the impact of nitrate pollution on small and large rivers whose waters flow into the Baltic Sea. The national monitoring data were analyzed according to the breakdown of depths (0-5 m, 5-15 m, 15-30 m, >30 m depth and pressurized water) given in the guidance for Member States reporting. Taking into account the geological conditions of Latvia, the quality or natural protection of groundwater is influenced not only by depth of deposits, but mainly by lithological composition and subsequent water permeability of the rock layers. Quaternary sediments in Latvia consist mainly of glacial and its melting water sediments, which are variable in terms of composition and thickness. In the last reporting period (2012-2015), 68% of all monitoring observation points were representing captive groundwater. It should be noted that the number of monitoring points has also increased directly in captive groundwater compared to the previous reporting period (2008-2011) (Ziņojums, 2016).

Observations of NO_3^- during the period 2012-2015 were made in 81 monitoring stations and 199 monitoring springs, of which 169 are wells and 30 are springs (Table 11.1.). 72 monitoring points or 36% of all monitoring points for nitrate monitoring are located inside of nitrate vulnerable zone, of which 62 are monitoring wells and 10 are monitoring springs. Compared to the previous reporting period (2008-2011), the number of observation points for nitrate monitoring has increased by 25 (14% overall), while the number of observation points in the particularly sensitive area has increased by 16 (29% overall). Most of all observation points (83%) are common to both the current and previous reporting period. This allows objective evaluation of the changes in nitrate content over time and the evaluation of possible trends in the monitoring points. The average sampling frequency is twice a year (Ziņojums, 2016).

Table 11.1 Distribution of Nitrate Observation Points in reporting periods 2008-2011and 2012-2015 (Ziņojums, 2016)

Groundwater type (depth of aquifer)	**Number of monitoring points/wells and springs**		**Common monitoring points**
	Previous reporting period (2008-2011)	**Current reporting period (2012-2015)**	
0-5m *Phreatic groundwater (shallow)*	**29** 22 wells; 7 springs	**27** 19 wells; 8 springs	**24**
5-15m *Phreatic groundwater (deep)*	**27** 14 wells; 13 springs	**30** 16 wells; 14 springs	**26**
15-30m *Phreatic groundwater (deep)*	**5** 3 wells; 2 springs	**5** 3 wells; 2 springs	**5**
30m *Phreatic groundwater (deep)*	**3** 3 wells	**2** 2 wells	**2**
Captive groundwater	**110** 103 wells; 7 springs	**135** 129 wells; 6 springs	**109**
Total:	**174** 145 wells; 29 springs	**199** 169 wells; 30 springs	**166**

11.1.2 Nitrate monitoring results

In Latvia during the period 2012-2015 average concentrations of NO_3^- above the Nitrate Directive limit value (50 mg/l) have been observed only in groundwater within depth of up to 5 m. Compared to the reporting period of 2008-2011, the average nitrate concentration in layer up to 5 m depth has increased: the number of monitoring points with average nitrate concentration below 25 mg/l has decreased by 9%; but the number of monitoring points where the nitrate content exceeds the 50 mg/l nitrate limit has increased by 13% (Table 11.2.). Mean nitrate concentrations above 50 mg/l were observed at 4 monitoring points: 2 monitoring springs and 2 monitoring wells (Ziņojums, 2016).

Table 11.2 Distribution of observation points by average nitrate concentration classes by depth of surface deposition of aquifer (2012-2015) (Ziņojums, 2016)

Groundwater type (depth of aquifer)	Amount (%) of monitoring points (NO_3^-, mg/l)			
	<25	25-39,99	40-50	>50
0-5m *Phreatic groundwater (shallow)*	81	4	-	15
5-15m *Phreatic groundwater (deep)*	90	7	3	-
15-30m *Phreatic groundwater (deep)*	100	-	-	-
30m *Phreatic groundwater (deep)*	100	-	-	-
Captive groundwater	100	-	-	-

In deeper groundwater, there is a general decrease in average nitrate concentrations: at depths of 5 to 15 meters, there has been a 9% increase in monitoring points with mean nitrate concentrations below 25 mg/l and no monitoring point with nitrate concentration above 50 mg/l. In groundwater deeper than 15 meters, as well as in captive waters, contamination with nitrate has not yet been observed and the average concentration does not exceed 25 mg/l.

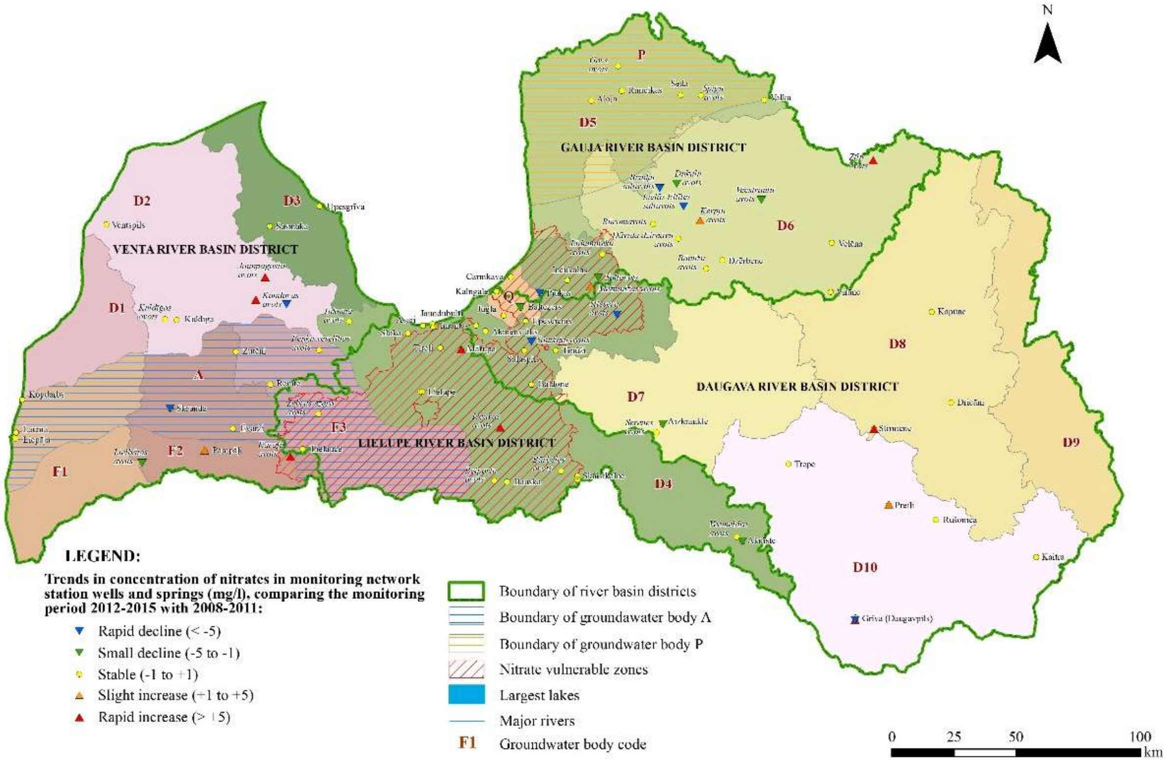

Figure 11.2 Trends in average nitrate concentrations of groundwater between the monitoring periods 2008-2011 and 2012-2015 (Ziņojums, 2016)

Trends in changes in the average NO_3^- content over the period 2012-2015 indicate that the most significant changes appear in groundwater at depths of up to 5 meters (Table 11.3.). Here, the number of monitoring points showing a rapid (<-5 mg/l) decrease in NO_3^- content compared to the period 2008 -2011 has increased by 15%. At the same time, there was a 12% increase in the number of monitoring points showing a slight upward trend (+1 to +5 mg/l) and a 12% increase in the number of monitoring points showing a rapid upward trend in NO_3^- concentrations (>+5 mg/l). Monitoring results confirm that shallow groundwater (up to 5 m depth) is the most exposed to agricultural pollution and therefore the NO_3^- content may change significantly over time depending on the intensity of economic activity. In general, there is a tendency for NO_3^- content to increase directly in shallow groundwater. In deeper groundwaters the number of monitoring points has increased significantly, and there has been a rapid decline in NO_3^- content. In pressurized waters the average NO_3^- content has changed from -1 to +1 mg/l compared to the previous reporting period.

Table 11.3 Trends in changes in nitrate concentration based on average a comparison of reporting periods 2008-2011 and 2012-2015 (Ziņojums, 2016)

Groundwater type (depth of aquifer)	**Amount (%) of monitoring point (NO_3^-, mg/l)**				
	<-5	**-5 to -1**	**-1 to +1**	**+1 to +5**	**>+5**
0-5m *Phreatic groundwater (shallow)*	15	4	51	12	18
5-15m *Phreatic groundwater (deep)*	18	25	46	4	7
15-30m *Phreatic groundwater (deep)*	-	-	100	-	-
30m *Phreatic groundwater (deep)*	-	-	100	-	-
Captive groundwater	-	-	99	-	1

11.2 Information about travel times in the saturated and unsaturated zones

In Latvia, the travel time of groundwater has been studied rarely. In 2002-2006 the travel time of the new groundwater after CFC method was determined during the joint study by the Denmark and Greenland Geological Survey (GEUS) and the Latvian National Geological Service (VĢD) on the impact of agriculture on groundwater quality in Latvia. However, data amount did not allow to do conclusions on the travel time of groundwater (Gosk et al., 2006). The latest studies were done from 2009 to 2012 during the project "Establishing a group of inter-branch scientists and a system of models for underground water research". Groundwater travel time studies with CFC and ^3H methods were carried out and provided new knowledge of the age of groundwater in the territory of Latvia. During this project the CFC concentration were analyzed in 39 samples – 19 samples in year 2010 and 20 samples in 2011. All samples were collected at depths of 5 m to 130 meters and one sample was taken from surface water (Baltezers basin). The results of the project (2009-2012) show that the values of $^{18}\delta$ are decreasing both towards larger sampling depth and closer to the groundwater discharge sites (such as within the shallower groundwater horizons near Riga). At relatively high depths, even reaching 70 meters, water replenishment takes place quite rapidly and the CFCs' stated lifetime in some cases does not exceed 40 years. The relatively small CFC dataset does not allow for the determination of direct legal relationships between the age of water residence and the signal of isotopes in them (Babre et al. 2012). Wide scattering of CFC-113 related ratio dating as well as remaining CFC ratios shows that some of CFC almost in all cases are affected after recharge (Bikše et al. 2011).
The information about travel times in the saturated and unsaturated zones will be updated in the near future based on the new monitoring (national delegated tasks) and ongoing project results.

11.3 Information about attenuating processes in the subsurface

Latvian groundwater is naturally free of elevated nitrate levels and is relatively well protected from surface pollution (Ziņojums, 2016). Monitoring of shallower aquifers (mainly within the Quaternary waters in the case of Latvia) allows to identify relatively recent anthropogenic impacts and to adjust eligible programs of measures (measures to improve the status of waters necessary for achieving good water quality) (LVĢMC, 2015).

A recent study by the University of Latvia and the LEGMC (Retike et al. 2016b) found that elevated nitrate concentrations in Quaternary groundwater were found primarily within the Lielupe River basin and adjacent areas of predominant agricultural activity (concluded after 2012 Corine Land Cover data). The excess of the threshold value of 50 mg/l was mainly observed in groundwater at less than 5 m depth and in this depth range the largest trends of both negative and positive changes have been observed (Ziņojums, 2016).

This confirms once again that in Latvia, pressurized water is relatively well protected from surface pollution. Also, in the current reporting period, Latvian groundwater is generally characterized by little time-varying nitrate concentration. The content of nitrate has increased in shallow groundwater but decreased sharply in deeper groundwater. Trends in nitrate elevation in shallow groundwater up to a depth of 5 m could also lead to higher concentrations of nitrate in deeper groundwater in the period 2016-2019 (will be analyzed during 2020), as the pressure on groundwater appears with a lag (Ziņojums, 2016).

From 2017 to 2018 the University of Latvia implemented the project "New data on nitrate loads on groundwater in standard sediments in Latvia", funded by the Latvian Environmental Protection Fund. The aim of the project was to obtain new data on the pollution of groundwater and associated surface water caused by agricultural activity in particularly sensitive areas and beyond, and to assess the impact of denitrification on the natural reduction of nitrate loads. In the framework of the project 147 water samples were collected, both groundwater and river and spring water from seven monitoring stations installed within the project (five monitoring stations were installed in a particularly sensitive area of nitrate and two stations outside to allow for an assessment of the differences in nitrate loads in the types of typical sediments). A project study has produced a large amount of data on surface water, groundwater and spring water on the basis of which conclusions have been drawn and recommendations have been made (Bikše et al. 2018a). The conclusions (Bikše et al. 2018a) were made, that the largest changes in nitrate values were observed in rivers during the year and the sampling time (season) is of great importance. In groundwater samples, nitrate is uncommon: only 1/3 of all 147 groundwater samples showed measurable values of nitrate (MDL=0.02 mg/l). The increased concentrations of nitrate in groundwater only correlate directly with the level of groundwater associated with other processes, denitrification and possibly changes in water flows, on a case-by-case basis. Groundwater levels are not directly applicable to the prediction of nitrate content (Bikše et al. 2018a).
The information about attenuating processes in the subsurface will be updated in the near future based on the new monitoring (national delegated tasks) and ongoing project results.

11.4 Testing approaches to harmonized, processed data for supraregional evaluations

Following the results of the state monitoring and optimization of monitoring network LEGMC ha updated and compiled the action plan for further monitoring of groundwater quality of Latvia. It is recommended to maintain pre-existing requirements for full analysis of the chemical composition of water four times a year (seasonally) in all wells of the Quaternary (Q) located in the nitrate vulnerable zone and groundwater body Q. It is also recommended that full chemical tests should be carried out at least once a year in wells of the Quaternary (Q) outside nitrate vulnerable zone, which has a good water supply (LVĢMC, 2018). The results of nitrate monitoring demonstrate that regular observations must be made in groundwater with a depth of not more than 15 m, but priority shall be given to groundwater which lies to a depth of 5 meters. (Ziņojums, 2016).

From the project carried out in 2018, it was concluded that the springs are generally more suitable for the assessment of diffuse pollution than shallow wells, but it is necessary to assess the water catchment area for each spring. If possible, groundwater should be monitored to a depth of 5 meters be extended to a larger number of drills outside a particularly sensitive area of nitrate, as the study does not justify the validity of the limits of an existing particularly sensitive area. Also, it was recommended to develop an effective protection map for groundwater by improving the current natural protection map, which takes into account the geological structure, the composition of the sediment blanket and the characteristics of filtration, terrain and, in particular, the type of land use (Bikše et al. 2018b).

The information approaches to harmonized, processed data for superregional evaluations will be updated in the near future based on the new monitoring (national delegated tasks) and ongoing project results.

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12 AGGREGATION AND OUTLOOK

12.1 Introduction

This D5.2 deliverable works towards the compilation of data that describe the transport of nitrate and pesticides in a harmonized way, integrating data that were collected within the pilot areas. In the chapters 3 to 10, we described the monitoring networks and data sets that are available for the pilot areas, evaluating different approaches and methods that are used to assess travel times and attenuation processes in these pilot areas. This chapter aggregates this information and presents the first ideas for a common, harmonized way forward that can be elaborated in D5.3 and D5.4. We believe that the overview of the different approaches followed over Europe for the estimation of transfer times and attenuation patterns is a crucial first step that achieves mutual understanding, and helps to identify similarities and differences that are inherently present given the varied hydrogeological settings present in Europe. The main results of the HOVER work on transfer times and attenuation of nitrate and pesticides will ultimately be presented in D5.3 that cover the modelling of transport, D5.4 that covers attenuating processes in the pilot areas and D5.5 that produces overview maps.

The following case studies were presented in the subsequent chapters of this deliverable:

Table 12.1 Overview of pilot studies in HOVER WP5

Case Study	Region	Nitrate	Pesticides
Netherlands	Noord-Brabant and Limburg age dated waters and gas compositions	X	X
Slovenia/Croatia	Transboundary Drava aquifer, unsaturated zone 18O/2H/3H recharge estimates and lysimeter data	X	
Slovenia	Lysimeter data	X	
Denmark	National denitrification map, groundwater age dating and pesticide permission monitoring including both the variably-saturated zone and the groundwater zone	X	X
UK	Unsaturated zone profiles, national scale denitrification mapping	X	
France	National scale transfer times nitrate, denitrification mapping		
Ireland	National assessment of unsaturated and saturated zone data	X	
Malta	Nitrate time series at water supply wells	X	
Cyprus	National scale nitrate and denitrification potential	X	
Latvia	National scale nitrate monitoring	X	

12.2 Definitions and applications of transfer times and time lags

The pilot areas present quite varying concepts of describing transfer times and time lags which is logical because of the diverse hydrogeological settings encountered over Europe. The UK, Ireland and France unveil long transit times through thick unsaturated zones that are present in many of their hydrogeological settings, including chalk and sandstone aquifers. As unsaturated zone flow is predominantly vertical and much controlled by the recharge rates and porosities, there is a significant delay between leaching of N and pesticides from the base of the soil zone and the first breakthrough in the groundwater itself. The French pilot clearly shows that these delays may be larger than the actual time groundwater flows in the aquifers towards receptors such as brooks, rivers and pumped wells. Therefore, much of the effort in France and the UK was put in acquiring estimates of vertical transit times in the unsaturated zone using repeated vertical profiling of porewaters.

In the Dutch, Danish, Latvian and Slovenian cases, however, unsaturated zones are much thinner and, generally, the delay in the unsaturated zone is short relative to the transfer times through the saturated zone towards monitoring screens and ultimately receptors such as springs or pumped wells.

Most of the efforts in these two first-mentioned countries therefore focused on age dating of the upper first 30 m of groundwater in order to obtain age-depth profiles and to relate concentrations of nitrate and eventually other solutes, such as pesticides and antibiotics, to the infiltration year of the groundwater ("infiltration year" approach; e.g. Visser et al. 2007, Hansen et al. 2010, Kivits et al. 2018). Using this infiltration year concept derived from the saturated zone travel times towards the monitoring screens, the leaching history of nitrate and pesticides could be related to the application history of nitrogen at farmlands. In principle, the same methodology is useful to study the transport of pesticides and emerging contaminants (see e.g. Kivits et al 2018, chapter 3 of this report), but care should be taken because of the pesticides being applied much more variable in space and time relative to nitrate, which promotes mixing and dispersion more than for nitrate. Moreover, the largely varying transport properties of pesticides and new substances (degradation rates, redox sensitivity op degradation, sorption behavior) asks for a dedicated, compound-specific analysis of the transport analysis including information on persistence and mobility of the specific solute, the climate and hydrogeological and biochemical settings.

A third concept of transit times relates to the transit time distribution of groundwater outflow to brooks, rivers or pumped wells. As groundwater mixes at these outflow points, the transit time cannot be described by a singular age or unsaturated zone delay, but conceptually needs to be described by a distribution (Maloziewski & Zuber, 1982; Juergens et al., 2010; Eberts et al., 2012). In order to assess these kinds of distributions one either needs a set of age tracers with complementary properties representing different age ranges (Visser et al., 2013; Massoudieh et al., 2014; Kolbe et al. 2018; Leray et al., 2012) or groundwater flow models that describe age or transport (Troldborg et al., 2008; Velde et al., 2010; Kaandorp et al., 2019/2020). Travel time distributions as a measure for transfer time have not been applied at the regional scale that was assessed in the pilot areas being described in this report, but local examples and conceptualization will be addressed under the D5.3 deliverable, for the Dutch and French cases.

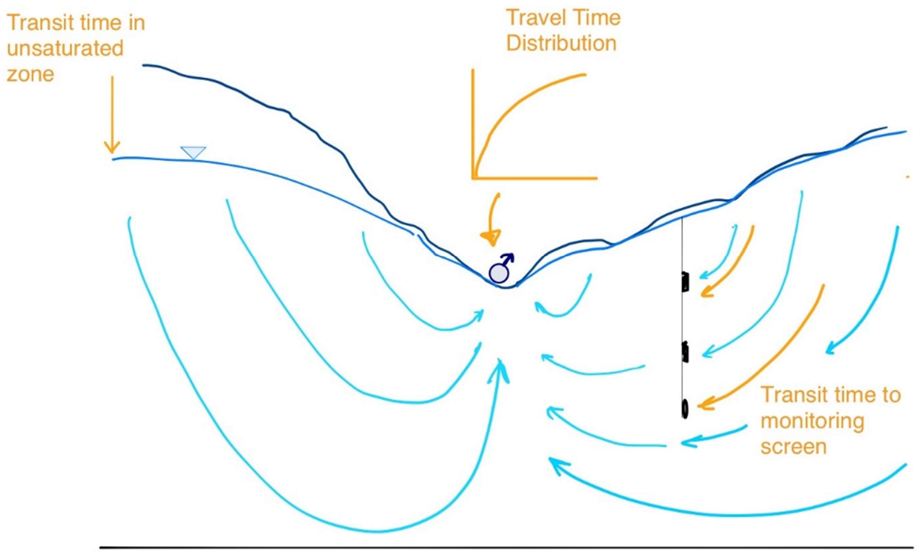

Figure 12.1 *Concepts of transit times used in this report. The approach to the right has been followed in Denmark and the Netherlands, applying the "infiltration year" approach. The approach to the left is followed in the UK and in France using unsaturated zone profiling.*

In summary, three main concepts of transfer time for nitrate can be distinguished (Figure 12.1):

1. Transit times of water that recharges the aquifer through the unsaturated zone
2. Transit times of water between the point of recharge (typically the water table) and the monitoring screen
3. Transit time distributions of water discharging at a well, spring or brooks and rivers.

Conceptually, one may argue that even the discrete age at a short monitoring screen may be regarded as an 'age distribution' (Weissmann et al., 2002) but for practical approaches this is often ignored without a loss of significant information (Visser et al., 2007; Hansen et al., 2010; Bohlke, 2002). However, once the monitoring screen has a substantial length and is pumped, the concept under type 3 is valid and the transit time should be regarded as a distribution of mixed water over the length of the monitoring screen, which conceptually is similar to the travel time distribution at a spring or groundwater discharge area (e.g. Juergens et al., 2008). This is actually what is done in section 7.2.2 and Figures 7.8 and 7.9, where the BRGM applied an exponential travel time distribution for interpreting their tracer data in pumped, long-screened wells.

A summary of the applied concepts is given in *Table 12.2* for the pilot areas that are part of the current deliverable. It shows that UK and French efforts were mainly targeted at regional and/or national scale assessments of transit times through the unsaturated zone, whereas Danish, Latvian and Dutch efforts were mainly targeted to regional and/or national assessments of travel times towards monitoring screens.

Table 12.2 Transit time concepts used in the pilot areas of this deliverable

	Transit time unsaturated zone	Travel time towards monitoring screen	Travel time distribution at the receptor
Netherlands		R	L
Croatia	L		
Slovenia	L		
Denmark		L, R	R
UK	R		
France	R	L	L, R
Ireland			
Malta	L		
Cyprus			R
Latvia		L	

R = Regional to National scale assessment, L = Local assessments for catchments or individual groundwater bodies, E = experimental scale of specific fields, lysimeters etc.

In all three types of transit time concepts, also the *concept of time lags* is incorporated, however with slightly or widely different meanings. In general, the concept of time lags is related to the time that passes between a certain impact in the recharging water and the moment that this is observed in groundwater.

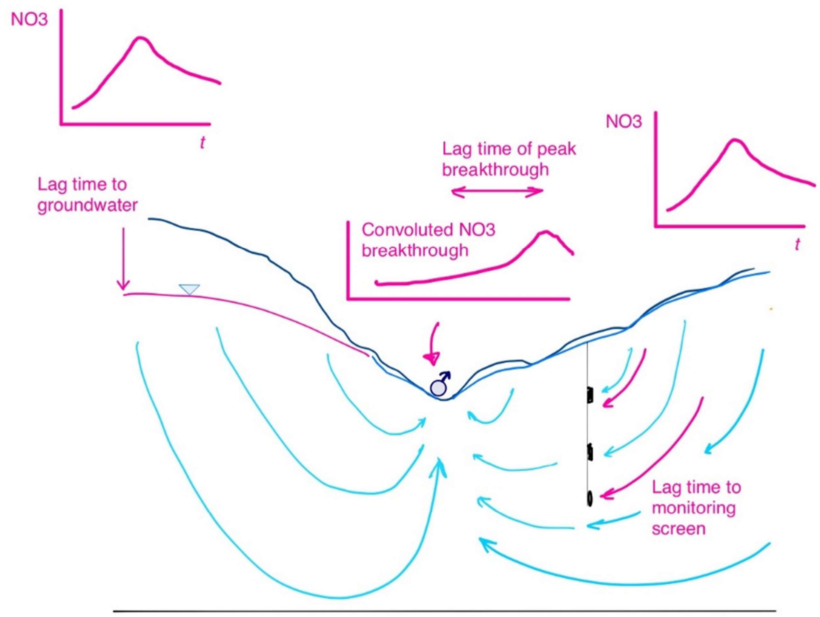

Figure 12.2 Concept for time lags as used in the pilot areas of this report. Time lags describe time that passes between a certain impact in the recharging water and the moment that this is observed in groundwater at the chosen observation point

For the three types of transit type concepts this would mean:

1. The time lag between leaching from the soil towards the breakthrough in the uppermost groundwater
2. The time lag between leaching from the soil / entering the water table and the actual observation of this water in the monitoring screen
3. The time lag between a specific part of the leached water from the soil and the entrance in the mixed water at the discharge point,

Note that types 1 and 2 differ considerably as for the first case the uppermost groundwater has a pathway towards any further monitoring screen for which the travel time is not yet accounted for (See Figure 12.1). Typically, in the Dutch and Danish concepts the first unsaturated zone time lag is considered negligible or very short and the depth and completion of the monitoring wells is well known as these where designed during the setup of the monitoring networks. The UK, Irish and French approach focused on the time lags in the unsaturated zone but do generally not specify the saturated zone travel time at the regional scale, as often the precise depths and confinement of the monitoring screens are not known, partly because the use of existing pumped wells for their assessment.

The third type of time lag is most difficult to define, as there is no discrete time that passed between recharge in the soil and the outflow, because several flow paths with a range of travel times are mixed at the point of outflow (Figure 12.2). For these cases, one could define the time lag as the time between the peak in nitrogen application and the observed peak in the pumped well, spring or river. Conceptually, this is a really different time lag as it is the result of convolution of the input signal and

the travel time distribution (e.g. Malosziewski & Zuber, 1982). Typically, the time lag observed in the breakthrough in a river, spring or pumped well is very different from the lag time of nitrate rich water entering the groundwater (type 1), or the lag time towards a specific monitoring screen (type 2) , as the breakthrough integrates travel times over a large depth range of the aquifer, which may contain nitrate concentration in the top layers, and old uncontaminated water in deeper layers (e.g. Broers & van Geer 2006, Visser et al., 2013; Juergens et al., 2008; Eberts et al., 2012).
Good studies that integrate these concepts for short screened monitoring screens, unsaturated zone delays and convolutions towards pumped wells, springs or rivers, are few, and all are applicable to local scales only (Baran et al, 2007). A good example using age tracers for integrating type 2 and 3 transit time assessments is Visser et al. (2013) and conceptually Broers & van Geer (2009), whereas examples using groundwater flow and transport modelling to integrate 1, 2 and 3 types are Velde (2010), Zhang et al. (2013), Kaandorp (2020) and Kolbe (2018).

Table 12.3 Types of monitoring applied in the pilot areas

Type of monitoring	nitrate	pesticides	^3H	$^3H/^3He$	CFC's	Noble gases
Unsaturated zone						
Unsaturated zone profiling	UK, F		UK, F			
Saturated zone						
Multi-level wells and short observation screens	NL, DK, LV	NL, DK, LV	LV	NL, DK	DK,LV	
Long screened observation wells	UK		UK/F/SL/CY/LV	CR	CR,LV	CR
Long screened pumped wells	F/CY/CR/UK	F	UK/F		F	
Monitoring of groundwater outflow at receptor, such as springs or streams	F/IR/CY, LV					

In line with the different concepts used and the hydrogeological settings encountered, the monitoring for nitrate and pesticides transport and chemical status of groundwater is divers for the pilot areas (Table 12.3). For GeoERA HOVER, it is important to find a common language once addressing transit times and time lags, and to find common ways to present our data, acknowledging that the monitoring design and concepts differ between countries in Europe.

Interestingly, the vertical transport velocities, that are assessed in the deep unsaturated zones of France and UK, averaging 1 m yr^{-1} for many settings, do not really differ from vertical saturated zone velocities in the upper parts of unconsolidated aquifers in Denmark and Netherlands, as can be derived from age-depth profiles, such as depicted in Figure 3.2. Dashed lines in Figure 3.2 represent age-depth relations based on a recharge rate of 250 and 350 m yr^{-1} respectively, and porosities of 0.35, yielding average transport rates of approximately 1 m yr^{-1} for the Dutch case as well (e.g. Broers 2004, Broers & van der Grift, 2004). As such, concentration-depth profiles in the saturated zones in Denmark and Netherlands resemble unsaturated zone concentration-depth profiles in France and UK (e.g. Broers & van der Grift 2004). Possibly, this is related by the fact that we are studying flux driven systems, for which the groundwater recharge rate is a key parameter, together with the effective porosity of the rocks. Once the ratio between recharge rate N and porosity ε is similar and the aquifer has considerable thickness, comparable vertical velocities may be anticipated for the systems studied. The observed correspondence may possibly be used to find overarching approaches to describe vertical transport in and towards groundwater in the next deliverables of HOVER.

12.3 Definitions and characterization of attenuation and denitrification

The diverse monitoring set-ups also reflect in the procedures to characterization of attenuating processes such as denitrification. In the Dutch and Danish, and probably Latvian and Slovenian, set-ups, the depth of complete denitrification is accessible because depth profiles of nitrate concentrations and transformation products, such as N_2, Fe and SO_4, can be obtained (e.g. Fig 3.4) and/or a redox classification tree can be applied (Figures 5.10-5.14). Once the age - depth patterns is known, the transformation processes can be distinguished clearly from the advective flow component. If water without nitrate is encountered in water that is in the age range where nitrate leaching was known to occur from historical records, and estimates of leaching are available, even a quantification of lost nitrate through denitrification is possible. Moreover, adding evidence from measuring profiles of nitrate and reaction products and complementary age dating allows also to estimate the depth range of ongoing denitrification.

For monitoring networks that partly exist of pumped wells or long-screened wells this is obviously not a feasible approach. Instead, characterization of redox using classification trees and semi-quantitative scoring methodologies are used in France and UK to evaluate the wells and wells of aquifers that are probably affected by denitrification. Assessments of N- and O-isotopes ($^{15}N/^{14}N$ and $^{18}O/^{16}O$) also gave indications for denitrification in Cyprus. Denitrification in these countries is concentrated in specific hydrogeological situations and lithologies. The classification tree approach, preferable incorporating gas measurements when feasible, is applicable in all types of monitoring systems and might be an applicable tool for common work in HOVER for mapping at a European scale. Table 12.4 gives an overview of the approaches followed to characterize denitrification in the HOVER pilot areas.

Table 12.4 Characterization of attenuation and denitrification

Type of monitoring	Redox classification	Application of (N2, CH4, H2S) or N-isotopes	Depth of complete denitrification	Depth range of ongoing denitrification	Linking time lags and denitrification
Unsaturated zone					
Unsaturated zone profiling	UK	UK			UK, F
Saturated zone					
Multi-level wells and short observation screens	NL, DK	NL	NL, DK	NL, DK	NL, DK
Long screened observation wells,	UK, F, SL	F, CR	F		
Long screened pumped wells	UK, F, DK	F, CY	F		
Monitoring of groundwater outflow at receptor, such as springs or streams					

Alternatively, an approach that considers aquifer reactivity could help identifying zones of enhanced denitrification. Nice examples that describes the relation between groundwater travel times, nitrate lag times and denitrification are Kolbe et al. (2018) and Zhang et al. (2013). The studies use conceptual and modelling approaches to assess the lag times in relation to denitrification depths in weathered crystalline aquifers and pyrite containing sediments, respectively, using a convolution and/or travel time distribution modelling approach as described in section 12.2. The random forest machine learning approach that was applied for the Danish National map of the depth of the uppermost redox interface (Figure 5.9) is a nice, advanced example of such an approach at the national scale. The general finding of these studies is that the depth of the reaction zone is controlling the concentrations of nitrate in the mixed discharge at the stream, with deeper reaction zones leading to higher nitrate concentrations and lower overall denitrification. Whether is it feasible to identify the depth of reactive layers as a proxy for characterization denitrification depth or denitrification potential at a regional or national scale will be further assessed under D5.4 of HOVER.

12.4 Outlook

The idea is to use the age and chemical concentrations measured in the monitoring networks to come up with indicators about transformation processes and depths that can be mapped for the pilot areas of HOVER. This includes incorporating the approach of the UK unsaturated zone mapping at a European scale in the EGDI. Additionally, for the pilot areas, we now propose a number of indicators that are relatively simple to obtain at a supra-regional scale and which summarize important aspects for nitrate and pesticides transport. Mapping would typically involve plotting of monitoring locations with symbols denoting classes of the indicators that we could commonly define. The dataset that we foresee to be compiled under the further work in HOVER could contain the following processed info for each monitoring well:

- Approximate GPS coordinates
- Age-depth gradient (years per meter depth) with an indication whether this is about unsaturated zone or saturated zone flow
- Applying a classification tree based on redox-sensitive indicators for monitoring points, e.g. based on oxygen, nitrate, ammonium, iron, manganese and sulfate, differentiating between the different types and depths of observation wells. This may lead to a number of possible outcomes, such as
    - The depth range with high probability of no denitrification below the soil zone
    - The depth range of ongoing denitrification (m - surface level. E.g. based on analysis as under Figures 5.10-5.14 and Fig. 3.4
    - The depth at which complete denitrification certainly is reached (m -surface level). This could be:
        - The depth at no nitrate is found, but the redox status or the measurement of reaction products (gases, N_2, iron, sulphate etc.) indicates complete denitrification
        - The depth at which the estimated age indicates young water, but no nitrate is observed
        - The depth of a known layer with high reactivity (weathered zone in crystalline rocks, pyrite containing layers, organic matter rich deposits)

The further mapping of these locations will be reported on in D5.4. During the next WP5 workshop in Madrid (scheduled for March 2020) the consortium will evaluate a number of possible scenario's for setting up a harmonized approach, that could incorporate the ideas mentioned above.

For the pilot studies were pesticides are studied, the work under D5.4 may include a combined analysis of redox conditions and groundwater age data, in order to find out if certain pesticides show clear signs of transformation processes in the subsurface (e.g. Kivits et al., 2018). For the Dutch data, it is foreseen to test an approach of jitter-jitter plots describing how both redox status and groundwater age are related, thus giving a framework for evaluating pesticides concentrations within that framework. Ultimately, this would yield information about the depth at which transformation of a pesticide is taking place in groundwater, and under which redox conditions this transformation may be completed.

In general, the feasibility of different approaches to come to such harmonized indicators will be tested in the pilot areas and be reported in deliverables D5.3 and D5.4. The current deliverable forms an intermediate step, conceptualizing the ideas and visualisation, towards such an approach and eventual map.

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