Deliverable 5.4b

Explanatory notes on the redox potential mapping at EU scale

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SUMMARY

The present document is a supplementary material to the deliverable D5.4 “ Assessments of attenuation patterns for a number of relevant European settings” 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* ”. It is part of the task 5.5 “overview map”.

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

The task 5.4 is centered on the denitrification aspects. The D5.4 report contains a presentation of the denitrification concept, the methods used in UK, Denmark, The Netherland/Flanders and Cyprus. Based on this information completed by literature review a simple common approach was proposed to define the oxic, anoxic, mix and to map this information at large scale (D5.4). The present note is giving information on the application of the method proposed with D5.4 and on the way the map available on EGDI was built. This document does not meant to give a detailed interpretation on the results obtained.

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1 INTRODUCTION

An important policy consideration for integrated land and water management is to understand the spatial distribution of nitrate attenuation in the groundwater system, for which redox condition is the key indicator.

Different methods exist to evaluate the denitrification potential in groundwater such as i) geological – determined by sediment/rock chemistry i.e. the presence of electron-donor minerals, ii) isotopic using $\delta^{18}NO_3$ and $\delta^{15}NO_3$ tracers, iii) hydrochemical indicators, based on dissolved redox sensitive ions and gases (Eh, O_2, NO_3, NO_2, Fe, Mn, SO_4, CH_4, H_2S or N_2). The methods can be combined and results refined by geochemical modelling.

At the large-scale and using data acquired within various groundwater monitoring networks and for different purposes, data quality and quantity may not be sufficient to allow a strict determination of the presence of denitrification. In the GEOERA HOVER project, the determination of the redox transition from nitrate containing water to iron-reduced water with no nitrate was preferred to a strict delineation of denitrification status due to the need for a pan EU overview of this information using data available in various countries. There was also a need for a simplified approach to map reduction potential in a common way without the need for further extensive data collection.

Based on the existing data in each of the participating countries and previous experiences in mapping nitrate attenuation patterns a classification tree was proposed using a minimum number of parameters (D5.4). The classification tree is based on nitrate concentration, presence at defined concentrations of Fe, O_2 and NH_4. After being tested in some regional scale case studies, the method was applied at national scale in France, Denmark, UK, Latvia, Spain, and Cyprus and in catchments in the Netherland, Croatia/Slovenia.

After distinguishing between groundwater containing nitrate and groundwater without nitrate, the first step of the method allows for the classification of groundwater with iron (anoxic) or without iron (oxic)"). Water types having both iron and nitrate at either low or relatively high concentrations at the same time are classified as “mixed”. The method can either end here or if needed continue in a second step for mixed samples. The second step considers NH_4 and O_2 concentrations.

After applying the methodology to individual sampling points the results were aggregated to lithological units. The results of these calculations and how the redox potential map was build are described in this report.

2 SHORT PRESENTATION OF THE METHOD PROPOSED FOR REDOX POTENTIAL ESTIMATION

2.1 Type of product to be prepared

Within the HOVER project we propose a simple method to be applied in different case studies in order to propose a Pan European map of Redox conditions in groundwater, a map that could be extended by time with new case studies or national scale applications of the proposed method.

The method use data that are expected to be available in many countries and be applicable at groundwater body scale. Due to the great variability of methods used for monitoring and aquifer types the method proposed does not pretend to give precise and accurate information on redox processes in aquifer but should permit to distinguish oxic to anoxic environment and mixed conditions.

2.2 Description of the method

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

The more reliable parameters to be used are NO_3 and Fe. NH_4 and O_2 could be additional parameters of interest but are not key parameters of the decision tree. Thus, it is proposed 2 mandatory steps and 2 additional steps. The additional steps are depending on data availability (use of NH_4 or O_2). The data preparation shall involve a check of homogeneous use of units and detections limits, filtration status etc. (e.g. oxygen can be measured as mg/l, molar concentrations or saturation %). Caution: the Fe concentration may be very different if water sample is filtered or not. Great care should be taken to raw data for this element. Only filtered samples are reliable.

Data can be selected from a major sampling campaign or aggregated to the mean or median in the same monitoring point for a specified period of time.

Using these 4 parameters we can propose a first classification tree (*Figure 1*).

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

- water supply wells with long screens – mixing of deep anoxic water with shallow oxic water due to pumping
- low pressure environment – very low nitrate in oxic environment due to low nitrate in leakage from the surface
- semi-reductive aquifer – Redox conditions variable in space and time, depend on pumping/water level conditions e.g. highly fluctuating water tables may temporarily activate or deactivate reductants

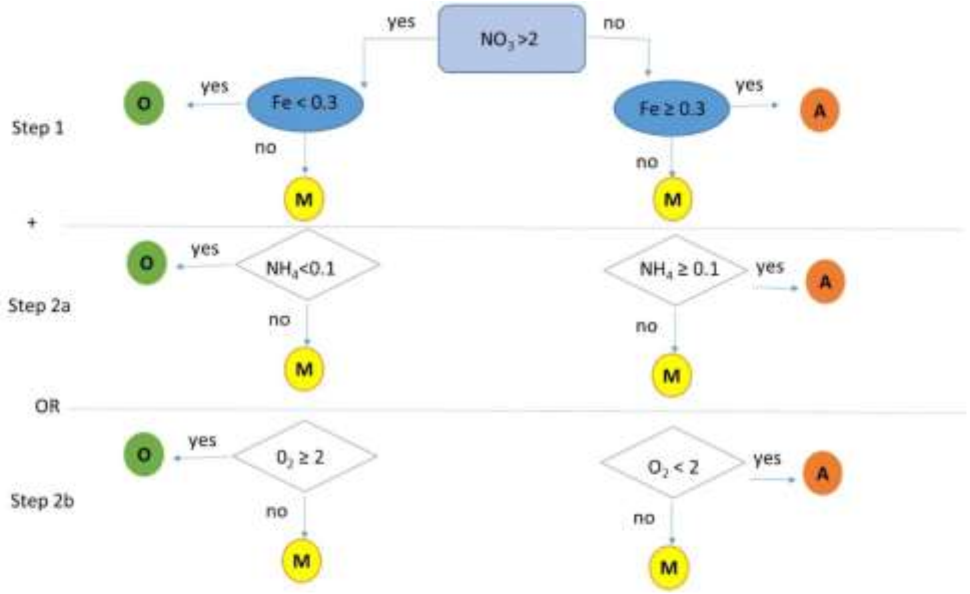

Figure 1: Proposed redox classification tree

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

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

2.3 Data collection

Once the method has been approved, it was necessary to define the dataset and associated metadata to be used by each partner. Moreover, a simple calculation method had to be proposed so that each participating country could process the data in the same way in a short period of time. After this, the EU map could be initiated.

For all countries except U.K., the results were reported at the monitoring point. The following parameters were defined for each monitoring point:

- Coordinates (WGS84 preferably)
- Groundwater body (European WFD code)
- Simplified lithology – was proposed alluvial, sedimentary-carbonated, sedimentary-sand, karst, Hard-rock, low-permeability formation
- NO_3, O_2, NH_4, Fe concentration
- Redox classification results – oxic, anoxic, mixed
- Depth of the screened interval (where this information is available)

As the information on the screen depth et depth evolution of the redox condition was not available in all countries and difficult to present in a 2 D map it was proposed to compile and plot only the data of the first groundwater horizon e.a. GWB horizon 1 or 2 or less than 100m from the WFD definition (CIS document 22, Guidance on reporting of spatial data)

3 APPLICATION OF THE METHOD AT NATIONAL AND GROUNDWATER BODY SCALES

3.1 Denmark

In Denmark the data covers the national groundwater monitoring network. However, only monitoring points with a depth of < 100 m are included. In Denmark the oxic layers are only found in the upper 5-10 m in clayey regions, but may go as far as 100 m in sandy hilly areas with huge unsaturated zones. Mostly only the upper 10-30 m of the saturated zone is oxic. Often the shift from oxic to reduced conditions takes place in an anoxic nitrate-reducing zone, where nitrate is present together with manganese, while oxygen and iron concentrations are very low. This Transition zone is created by nitrate and can in intense agricultural areas be up to 10- 15 m broad depending on the contents and reactivity of reductants (mainly organic matter and iron sulphides). Mostly it is only a few meters or less (Jakobsen et al. 2019, Postma et al. 1991).

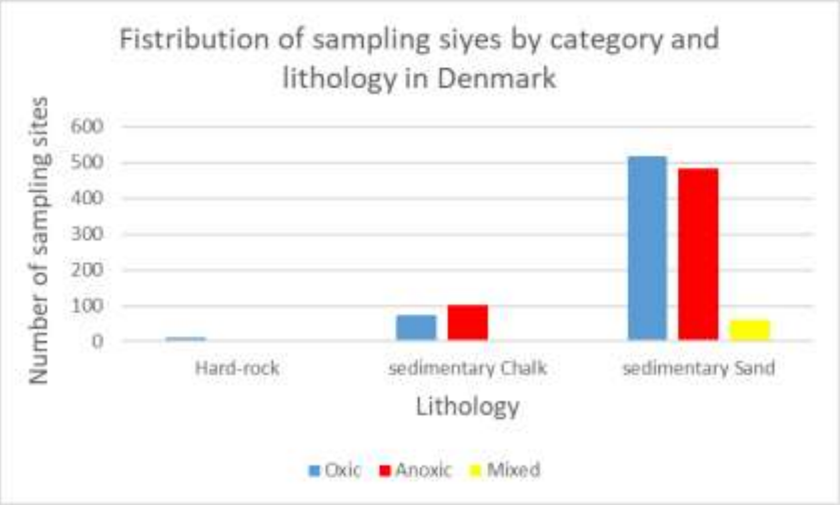

Figure 2: Distribution of sampling sites by category and lithology in Denmark

3.2 The Netherland

Information is available for the Dutch pilot site ‘Zand-Maas’. This area is equal to the groundwater body “Zand-Maas (Sand-Meuse). In addition, there is information for groundwater body ‘deklaag Rijn-West’. The lithology is sedimentary sand for both groundwater bodies.

Selection criteria are :
- Depth < 100 m MSL
- Fresh groundwater (chloride <300 mg/l)

The Netherland applied steps 1 and 2a and/or 2b to determine the redox. The results of the common redox classification for The Netherland are shown in *Table 1* and *Table 2*.

Table 1 - Redox results of groundwater body “Zand Maas” (equal to the Dutch Pilot site Zand-Maas)

Redox class	**Count of redox**	
anoxic	641	74%

mix	77	9%
oxic	148	17%
Total	866	100%

Table 2 - Redox results of groundwater body “deklaag Rijn-West”

Redox class	**Count of redox**	
anoxic	308	95%
mix	12	4%
oxic	4	1%
Total	324	100%

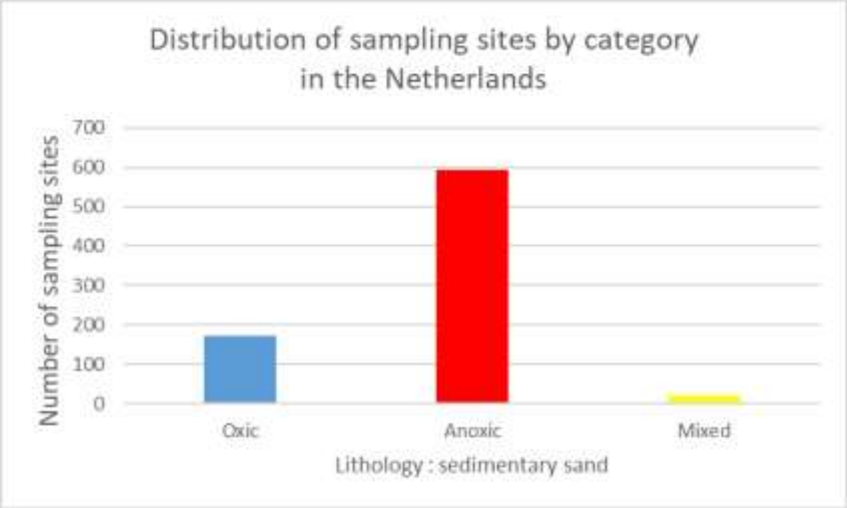

Figure 3: Distribution of sampling sites by category and lithology in The Netherland

3.3 Cyprus

In Cyprus denitrification is found to be active in areas of thick unsaturated zones and where clay layers predominate. Redox potential was classified in 59 boreholes (points) with depth of less than 100m and which are drilled in the most important aquifers of Cyprus. The number of points per aquifer lithology is shown in the Table 3 – Number of points by lithologies in Cyprus.

Table 3 – Number of points by lithologies in Cyprus

Lithology	**Number of points**
Alluvial	19
Sedimentary-carbonated	1
Sedimentary-sandstone	34
Hard-rock	4
Chalk/karst	1

Steps 1 and 2b of the classification tree were applied to all points. The majority of the monitoring points exhibit oxic conditions (98%) whereas anoxic conditions are seen in only one borehole (*Figure 4*).

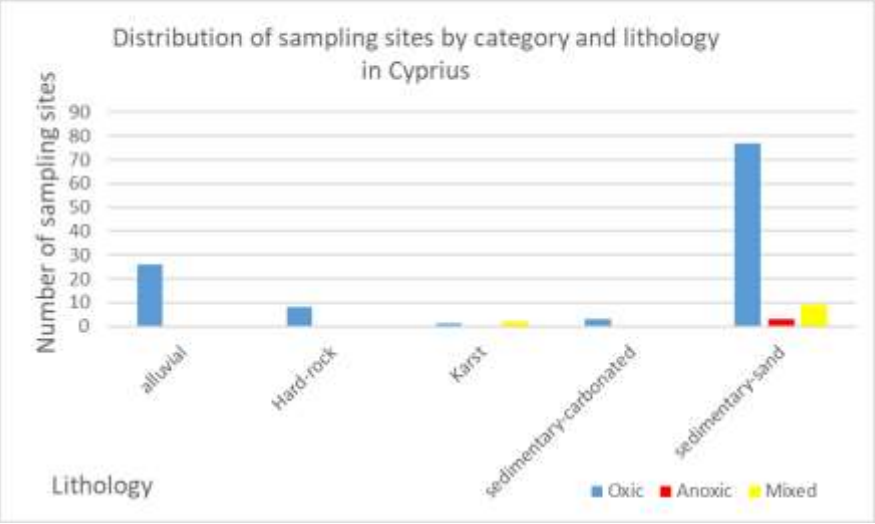

Figure 4: Distribution of sampling sites by category and lithology in Cyprus

3.4 Spain

The assessment of the redox conditions in Spain was carried out following the proposed classification tree. Data come from monitoring network within the period 1961-2010, which cover almost all the national extension (1083 sampling points located within 199 groundwater bodies). The mean value for the required parameters was calculated in each sampling point with a depth of < 100 m to obtain the redox classification. The lithology was deduced from the lithostratigraphic and permeability map of Spain (1:200.000). Figure 2 shows the results of the frequency and number of sampling points of each redox category by lithological units.

Most of sampling points are in oxic conditions and it seems not to be dependent on lithology although most of sampling points are located in alluvial domain. The percentages of observation points (%) in the different conditions are: anoxic: 2%; mixed: 5%; oxic: 93%. The mean depth of the oxic points is 36 m although nearly the 45% of the oxic points are at depths of 1.5 to 20 m. The mean depth of the mixed and anoxic points is 33 m and 55 m respectively.

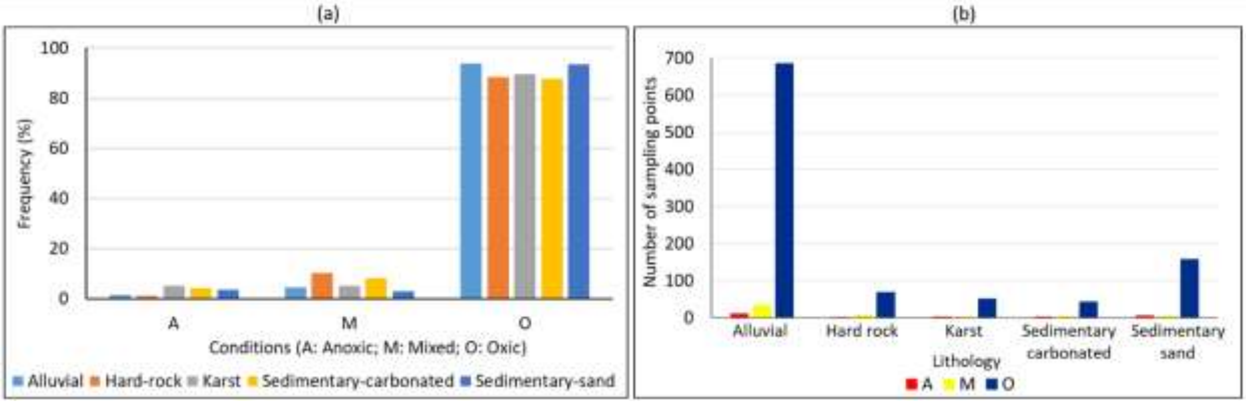

Figure 5: Distribution (a) and number (b) of sampling sites by category and lithology in Spanish groundwater

According to the frequency of appearance (*Figure 5*a), the observed anoxic conditions seem to be more common in carbonated aquifers (mainly karst), probably related to a higher thickness of these aquifers and higher depth of the wells.

3.5 Croatia/Slovenia

Croatia

The classification tree methodology was applied in the Drava-Mura pilot, which includes 4 groundwater bodies. In total, 32 observation wells were included in analysis. The dataset was retrieved from the database of national groundwater quality monitoring. The list of points includes groundwater body code and the depths of screens do not exceed 100 m. All observation wells have screens in alluvial aquifer composed of gravel and sand with various shares of silt and clay.

The results of the analysis demonstrate that the majority of the pilot area is characterised by oxic conditions. Only one point shows anoxic conditions, whereas 11 points display mixed conditions. The oxic conditions prevail in the western part of the pilot. Further downstream, the conditions gradually change and mixed conditions become more frequent, especially in the deeper parts of the aquifer system.

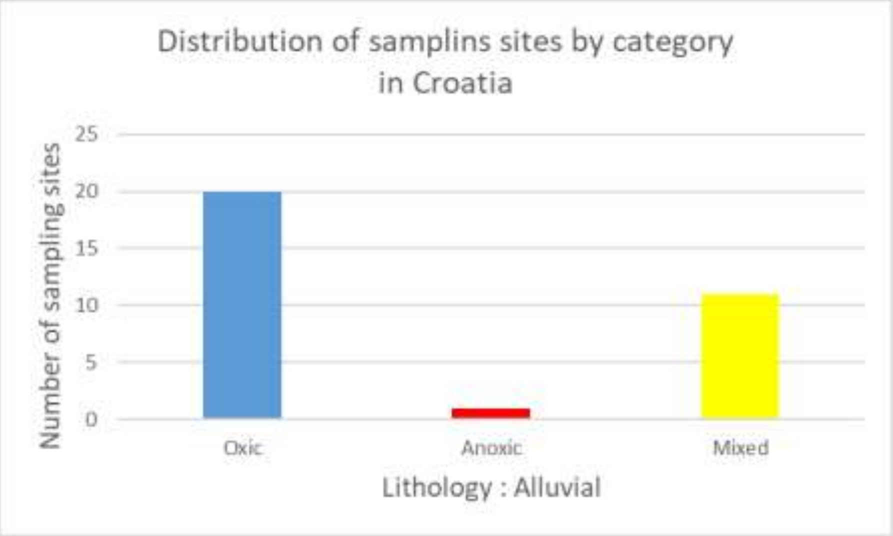

Figure 6: Distribution of sampling sites by category and lithology in Croatia

Slovenia

The results of the national groundwater quality monitoring and research groundwater monitoring in 2020 were used to determine the redox classification based on the common methodology. Groundwater samples were collected at 206 monitoring sites covering all 21 groundwater bodies as part of the national monitoring. Groundwater monitoring for research purposes was conducted at 80 monitoring sites covering the five alluvial aquifers and their periphery. Monitoring sites shallower than 100 m were selected. We collected the results of measurements for water temperature, pH, electrical conductivity, dissolved oxygen, oxygen saturation, nitrate, manganese, and iron.

The determination of the common redox classification was based on a proposed classification tree (Figure 1). We applied step 1 and step 2b which considers the oxygen concentration.

Table 1 shows the results of the frequency of occurrence (number of sampling sites) of each category (oxic, anoxic, and mixed) by lithologic units.

Table 4 : Frequency of occurrence (number of sampling sites) of each category (oxic, anoxic, and mixed) by lithologic units

Lithology	Number of points - total	Oxic	Anoxic	Mixed
Alluvium	139	123	11	5
Hard rocks	1	1		
Karst	38	37		1
Sedimentary: carbonates	21	8		13
Sedimentary: carbonates (limestone, chalk)	9	9		
Sedimentary: clay	12	5	4	3
Sedimentary: gravel	16	15	1	
Sedimentary: sand	50	31	7	12

As shown in the *Table 4* and *Figure 7*, 80.1% of the sampling sites (229) are in oxic groundwater conditions, 8.0% (23) are in anoxic groundwater conditions, and 11.9% (34) are in mixed groundwater conditions.

The potential areas of anaerobic conditions are only in the area of confined aquifers or their peripheries. In these aquifers, groundwater is not well oxidized due to the presence of reducing species, with high geogenic contents of iron, manganese, ammonium, and arsenic being characteristic, in the absence of oxygen and nitrate. The rest of Slovenia consists of karst aquifers, alluvial aquifers of sedimentary rocks - carbonate and non-carbonate (sand, gravel), where groundwater was found to be well oxidized and where oxidation conditions prevail.

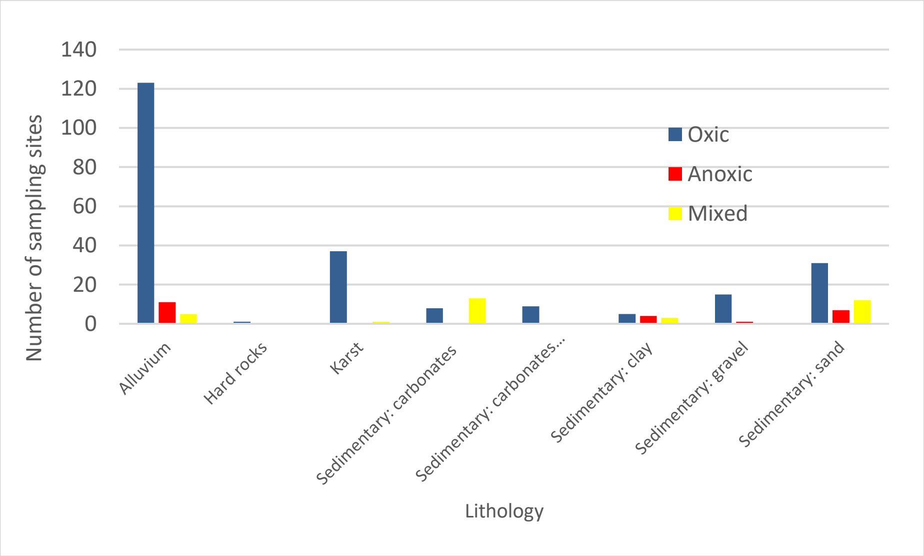

Figure 7: Distribution of sampling sites by category and lithology in Slovenian groundwater

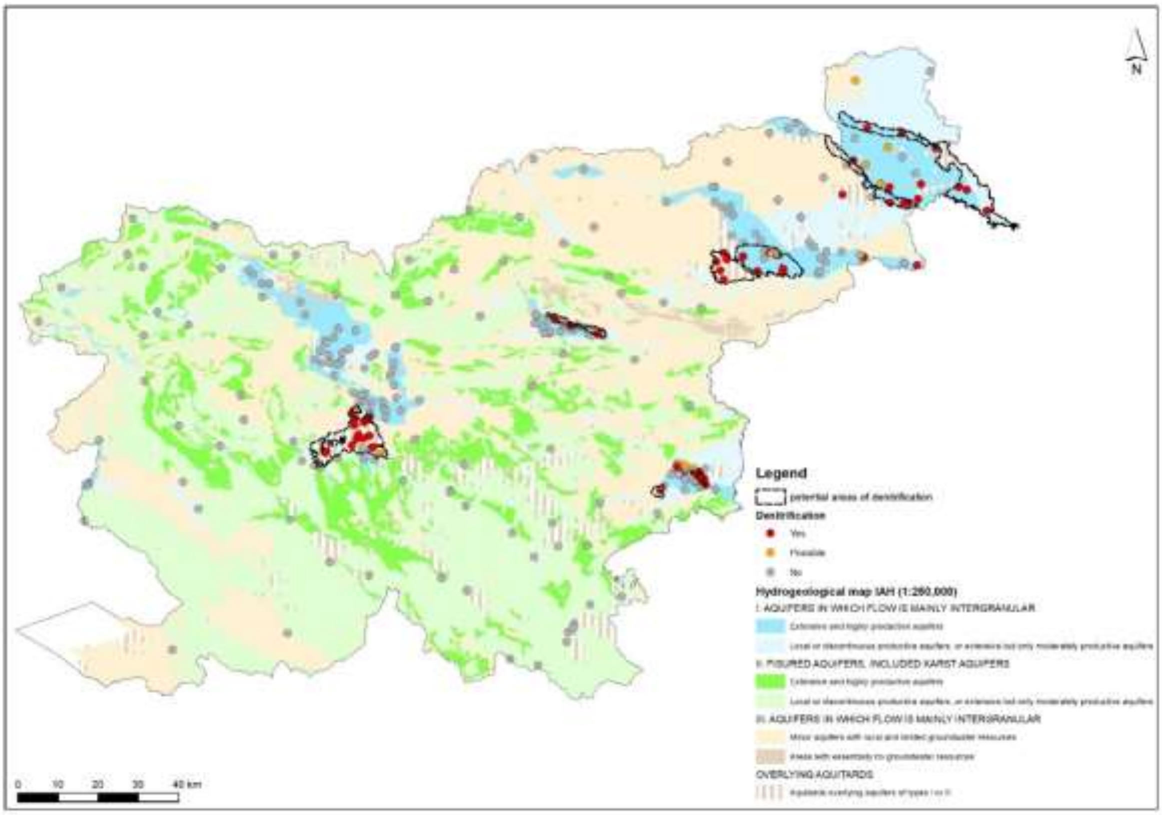

Figure 8: Potential areas with anaerobic groundwater conditions in Slovenia.

3.6 Latvia

In Latvia, data were collected on 154 monitoring points for the period 1994-2019. Monitoring points are distributed over 18 GWBs throughout the country. According to the common method, data were collected from monitoring points with a depth of less than 100 m, where mainly alluvial, carbonate (dolomite) and sandstone sediments are distributed. Steps 1 and 2a from the proposed classification tree were applied to determine the redox conditions. According to the performed analysis, in most monitoring points anoxic conditions dominates - 86%, followed by 9% oxic and 5% mixed. A summary of the analysis results is shown in the *Table 5*.

Table 5 - Synthesis of the results per lithological units for Latvia

Lithology	**Number of points**	**Number of oxic/%**	**Number of anoxic/%**	**Number of mixed/%**
Alluvial	66	10/15	53/80	3/5
Sedimentary-Carbonated	50	4/8	45/90	1/2
Sedimentary-Sandstone	38	-	35/92	3/8
Total:	154	14/9	133/86	7/5

Anaerobic conditions in aquifer sediments ensure the accumulation of dissolved iron in groundwater and in most cases in Latvia iron concentration exceeds 0.3 mg/l. Also, there is naturally small concentration of nitrates, under anaerobic conditions they are reduced (denitrification process). For these reasons, test results in the case of Latvia, mostly indicate anaerobic conditions.

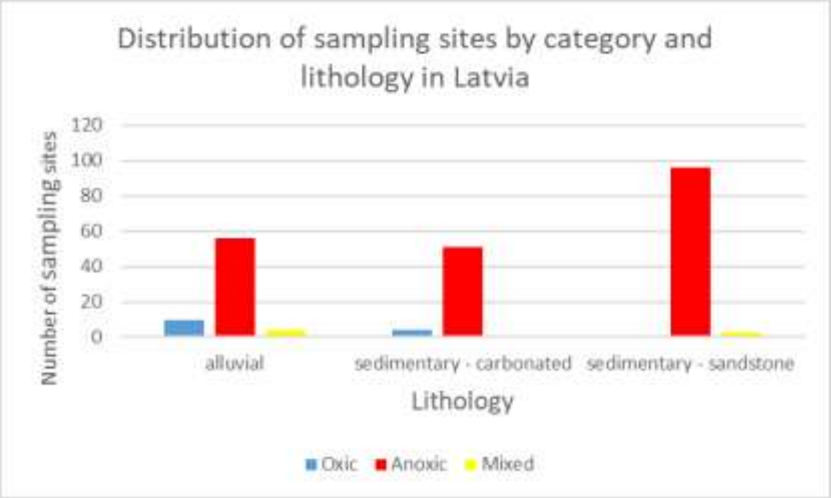

Figure 9 – Distribution of points by category and lithology in Latvia

3.7 France

For France we used 19238 points with a depth of less than 100m. These points correspond to the first aquifer level encountered and are distributed over 491 groundwater bodies. The classification tree was applied to all points and the best results were given using step 1 and step 2b (oxygen concentration). Dissolved oxygen is more often measured and of higher accuracy than ammonia. The results were synthesised in *Table 6* and *Figure 10*.

Table 6: Results of the classification test for France

Category	Number of points	percentage
Anoxic	4260	22.1 %
Mixed	2344	12.2 %
Oxic	12634	65.7 %
total	19238	100 %

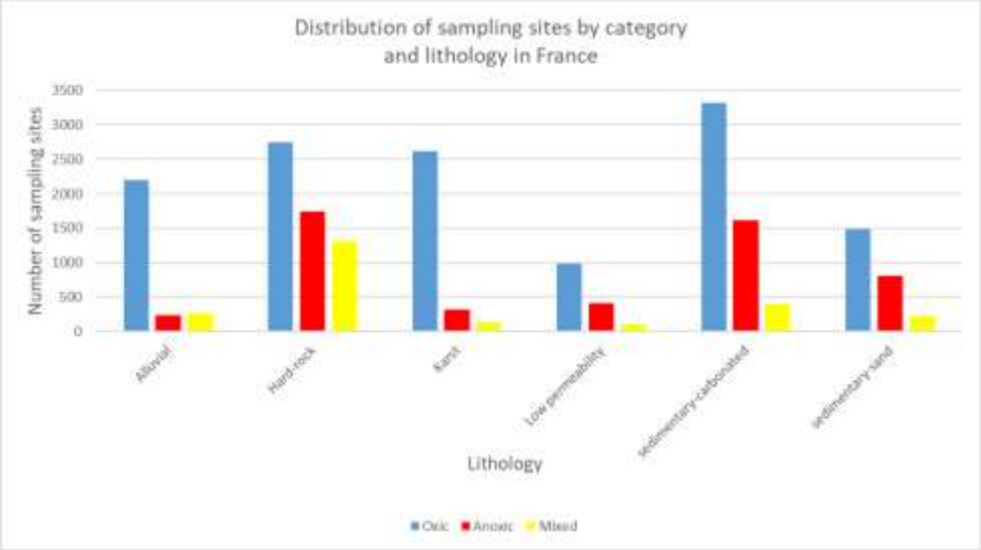

Figure 10 – Distribution of points by category and lithology in France

The results obtained using a quite simple method are, at national level, comparable to other national-scale studies (such as pressure-impact project[1]) of denitrification. For the first horizon of groundwater bodies oxic conditions are dominating in all type of aquifers. Hard-rocks areas such as Armorican Massif presents the highest number of monitoring points presenting anoxic conditions and therefore denitrification potential. Autotrophic denitrification is usually dominating in this context (Aquilina et al., 2018; Roques et al., 2018).

3.8 Ireland

The assessment of the spatial extent and importance of denitrification in Ireland was carried out based on the following criteria:

- the median value for the required parameters
- period time: free (as indicated in the file)
- lithological unit: Hover and Bridge lithology

The 244 monitoring points (MPs) from the Irish EPA's national groundwater monitoring network were assessed using Step 1 and 2b. The majority of the monitoring points are oxic (188 of 244, 77%) with 46 MPs anoxic and 10 MPs mixed water (*Table 7* and *Figure 10*).

Table 7: Results of the Redox classification exercise in Ireland

Category	Number of points	Percentage
Anoxic	46	19
Mixed	10	4
Oxic	188	77
Total	244	

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[1] Pinson et al. (2016) – Description de la méthode appliquée à l'échelle nationale pour l'étude pression-impact du nitrate sur les eaux souterraines. http://infoterre.brgm.fr/rapports/RP-67428-FR.pdf

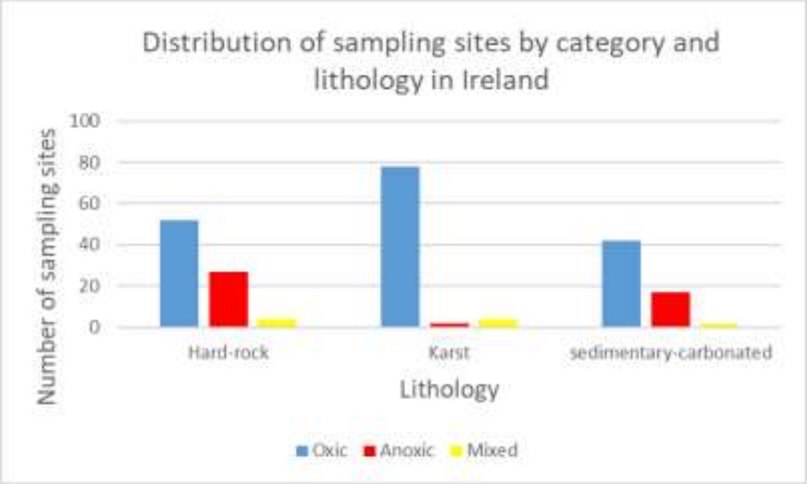

Figure 11 – Distribution of points by category and lithology in Ireland

Ireland is underlain by heterogeneous bedrock strata, which is overlain by extensive and spatially variable, subsoil (Quaternary) deposit. The groundwater flow within the Irish bedrock aquifer is through secondary porosity and is dominated by the fracture flow.

As such, anoxic/reduced groundwater conditions in Ireland are either confined by:

- low permeability subsoil (usually clayey/silty till or sometimes lake clays are overlaid by peat), or
- lithology (e.g. low permeability shales or muddy limestones). However, they are not as common in Ireland as in certain other European countries.

3.9 United Kingdom

The results of the common redox classification for the United Kingdom

This is only for boreholes which have depth attributed and are <100 m deep, and only for boreholes in the groundwater bodies where they are at outcrop. Nationally this produces the following split: 1732 points, 17% anoxic, 74% oxic, 9% mix. Some other points to consider:

- The boreholes in the database used consist of a range of strategic monitoring boreholes and pumped abstraction boreholes. In addition to the boreholes used there are many more but they do not have depth attributes. There is also very limited information on screen length or pumping regime.
- There is a generally a sampling bias towards boreholes in unconfined, well oxygenated aquifers (as these are most exploited for public supply in England) and hence limited denitrification.
- This sampling bias is exacerbated by just looking at boreholes in aquifers where at outcrop and with depths < 100 m. This doesn't show the full picture regarding denitrification in England. Looking at boreholes in confined aquifers (i.e. not in outcrop GWBs) and at any depth, c. 40% of these are classed as anoxic, 30% oxic, 30% mix.
- There is significant denitrification in the confined zones of the Chalk, Lincs Limestone and Sherwood Sandstone but these are (by definition of the method only including outcrop GWBodies) not shown. Only a part of East Anglia comes out of the method proposed here – this is because the aquifer mapped at outcrop but there is overlying quaternary.

The data was produced as a shapefile with the following information for each groundwater body :

- In the attribute table, columns anoxic, oxic and mix give the number of points in each GWB under each class.
- p_anoxic, p_oxic and p_mix give the percentage of points under each class.
- n points gives the total number of points in each GWB.

3.10 Country balance sheet

Table 8 – Final results of the Redox classification exercise

Countries	**Number of points**				**Number of GWB with points**
	Anoxic	**Mixed**	**oxic**	**total**	
Spain	23	54	1006	1083	199
Croatia	1	11	20	32	4
Slovenia	12	11	181	204	21
France	4260	2344	12634	19238	491
Denmark	633	70	625	1333	160
Latvia	203	8	14	225	18
Ireland	42	30	172	244	128
The Netherland	949	89	152	1190	2
United Kingdom					203
Cyprus	3	11	115	129	15

4 DESCRIPTION OF THE CONSTRUCTION OF THE REDOX POTENTIAL MAP

4.1 The background map

The European hydrogeological map at the 1,500,000th (IHME1500, BGR & UNESCO (eds.)2019) is the base map of the map of denitrification potential. The International Hydrogeological Map of Europe, scale 1:1,500,000 (IHME1500) is a series of general hydrogeological maps comprising 30 map sheets, partly with explanatory notes, covering nearly the whole European continent and parts of the Near East. The national contributions to this map series were compiled by hydrogeologists and national experts in related sciences under the auspices of the International Association of Hydrogeologists (IAH). The project is supported by the Commission for the Geological Map of the World (CGMW)

The polygon features (IHME1500 mapping units) of the area theme comprise attribute information on general material specifications (lithology) and typological information on productivity and general nature of potential up-permost aquifer assemblages across Europe. Additionally, information on seawater intrusions is available.

In order to have a map easily readable at large scale and containing information that can be linked to the Redox potential, lithologies of the IHME1500 maps were simplified.

Overall, the lithology information of IHME1500 print maps and draft extensions contains 1220 individual lithological class descriptions. These descriptions comprise petrographic, genetic, stratigraphic and local terminologies that demands generalization to produce harmonized synoptic map information on different aquifer materials. A subsequent semantic harmonization and grouping of the lithological descriptions following a general lithological taxonomic scheme as described in Duscher et al. (2015) results in five hierarchical aggregation levels (Level 1 to Level 5, Table 9).

The IHME1500 hydrogeological map has been simplified by reinterpreting the lithology (level 3) according to the following categories:

- low permeability,
- sandstone, conglomerates, sands, silts and marlstones
- gravel, sands and alluvial,
- chalkstones and karsts,
- limestones
- volcanic rocks
- hard rocks,
- Inland water,
- snow field / ice field

Table 9: Level 3 of the IHME1500 hydrogeological map and the simplified reinterpreted lithology

LEVEL3	interpretation
Clays	low permeability
Claystones and clays	low permeability
Conglomerates	sandstone, conglomerates, sands, silts and marlstones
Conglomerates and clays	sandstone, conglomerates, sands, silts and marlstones
Conglomerates and sands	sandstone, conglomerates, sands, silts and marlstones
Gneisses	hard rocks
Gravels	Gravels, sands and alluvial
Inland water	inland water
Limestones	karsts and chalkstones
Limestones and clays	Limestones
Limestones and marls	Limestones
Limestones and sands	Limestones
Marbles	hard rocks
Marls	low permeability
Marlstones	low permeability
Marlstones and clays	low permeability
Marlstones and marls	low permeability
Marlstones and sands	sandstone, conglomerates, sands, silts and marlstones
Phyllites	hard rocks
Plutonic rocks	hard rocks
Quartzites	hard rocks
Sands	sandstone, conglomerates, sands, silts and marlstones
Sandstones	sandstone, conglomerates, sands, silts and marlstones
Sandstones and clays	sandstone, conglomerates, sands, silts and marlstones
Sandstones and marls	sandstone, conglomerates, sands, silts and marlstones
Sandstones and sands	sandstone, conglomerates, sands, silts and marlstones
Schists	hard rocks
Shales	low permeability
Silts	sandstone, conglomerates, sands, silts and marlstones
Snow field / ice field	Snow field / ice field
Volcanic rocks	volcanic rocks

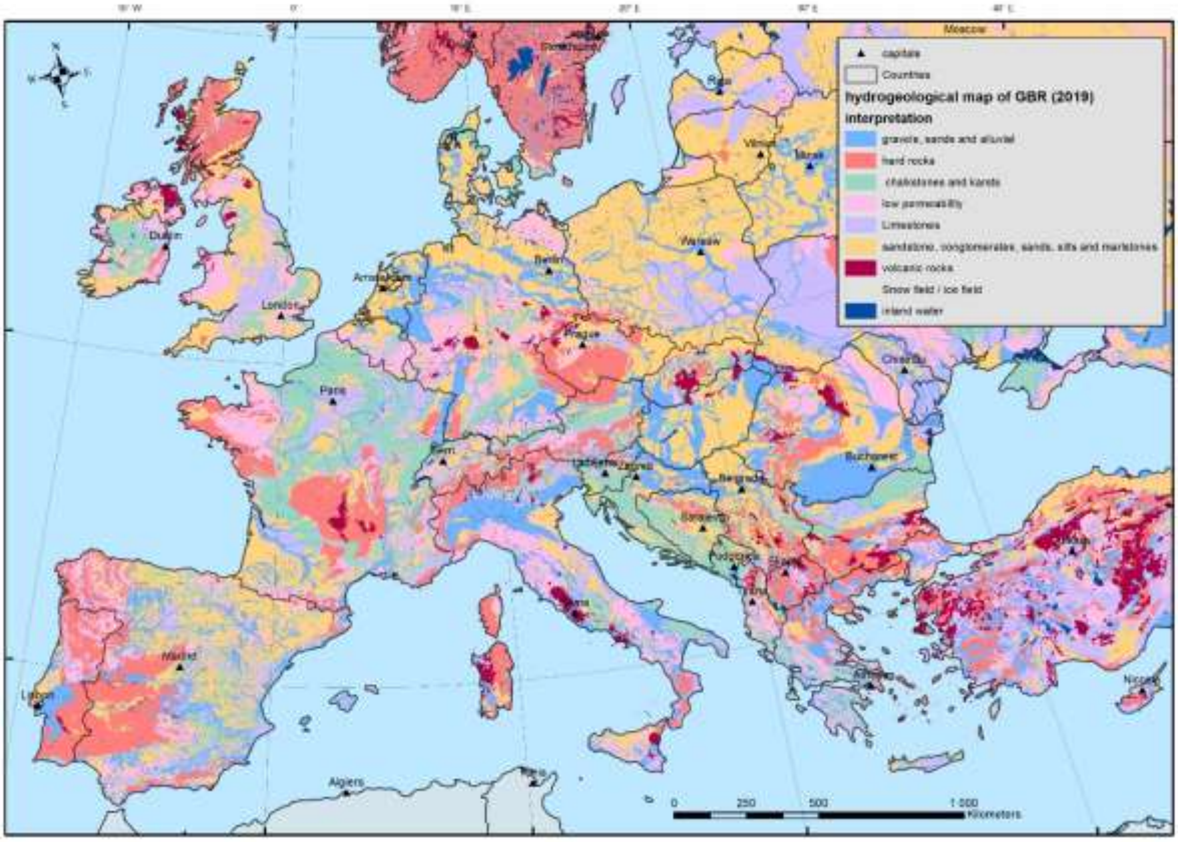

Figure 12 - Simplified lithologies of the IHME1500 map

4.2 The denitrification potential maps

The working group proposed to elaborate two products, one at national/country level (>1/1000000) and one at pilot and smaller sites (beyond 1:750000)

At national scale / 1 million and more
The first GIS layer is based on the statistics made using data for the entire country presented in the various tables of the chapter 8. The results are presented in a pie chart located at the centroids of each country.
The information is available up to a scale of 1 million and more and only for countries having carried out Redox estimation for the whole country (*Figure 13*).

This GIS layer has the following attributes:

- countries,
- the coordinates of the centroids of each country,
- the number of groundwater bodies for which data is available,
- the number of anoxic, mixed and oxic points for each country and,
- the percentage of anoxic, mixed and oxic points for each country.

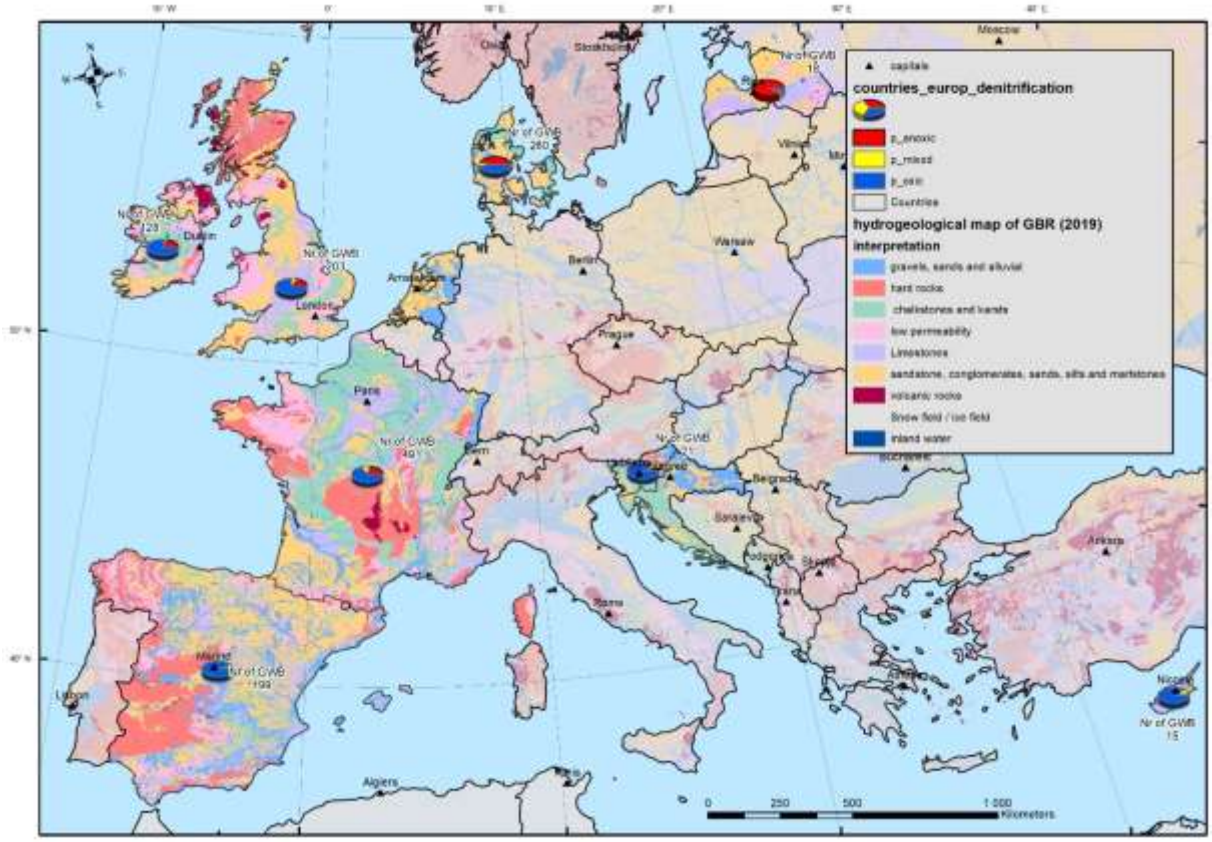

Figure 13 - Map with pie charts showing the percentage of anoxic, mixed and oxic groundwater for each country

At regional/pilot sites scale

The GIS layer represents the results of percentages of anoxic, mixed and oxic calculated at groundwater bodies and the number of monitoring points considered for calculation (*Figure 14*). For this layer, you will not be able to see the pie charts representing the results when zooming out beyond the scale of 750 000.

This GIS layer contains the following attributes:

- countries,
- the European code of the groundwater body,
- the coordinates of the centroids of each groundwater body,
- the name of groundwater body,
- the year in which the groundwater body contours were completed,
- the number of points for each groundwater body,
- the number of anoxic, mixed and oxic points for each groundwater body, and,
- the percentage of anoxic, mixed and oxic points for each groundwater body.

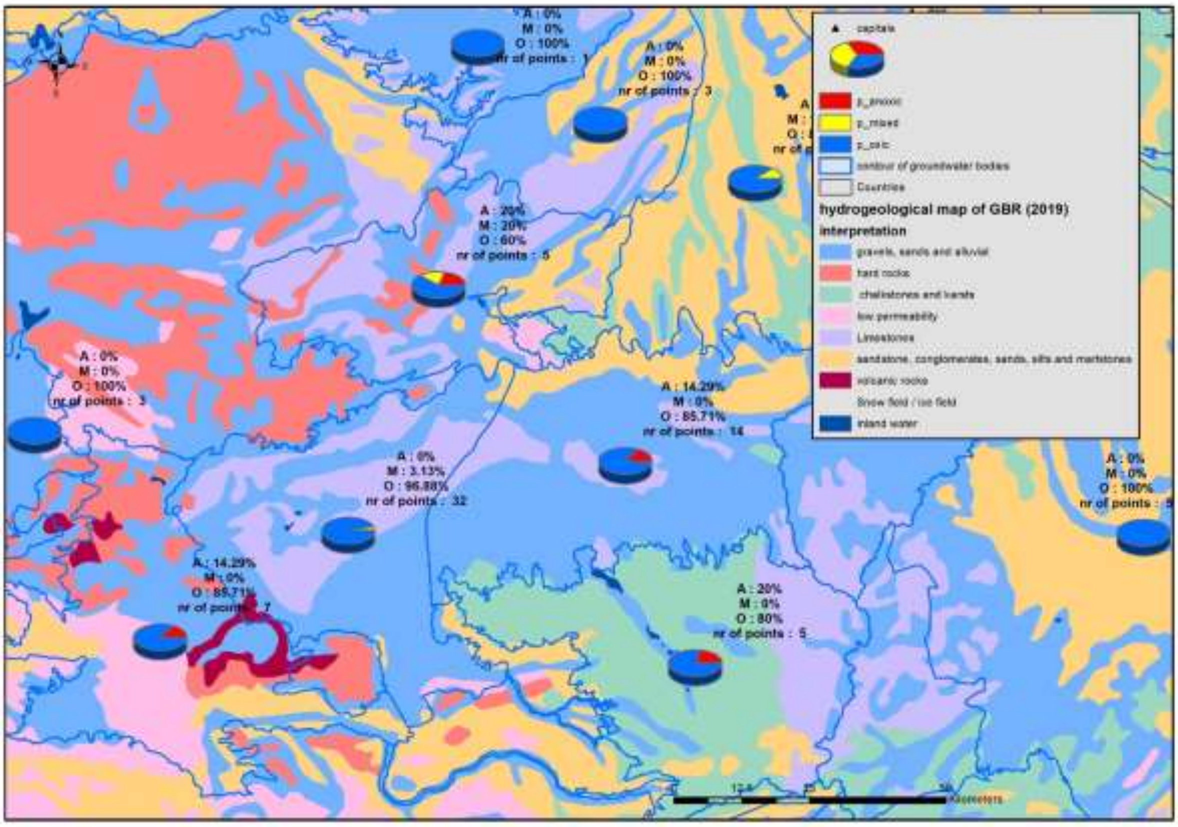

Figure 14 - Map of an area in Spain with groundwater body contours and information on denitrification

The layer of groundwater bodies delineation can be seen only beyond the scale of 750 000. This GIS layer comes from the 2016 European water body reference and, for some countries, have been updated by the project participants and remains under their responsibilities.

In sandstone/conglomerate/sand/silt/marlstone dominating areas such as in Denmark or The Netherland anoxic conditions prevail (*Figure 15*).

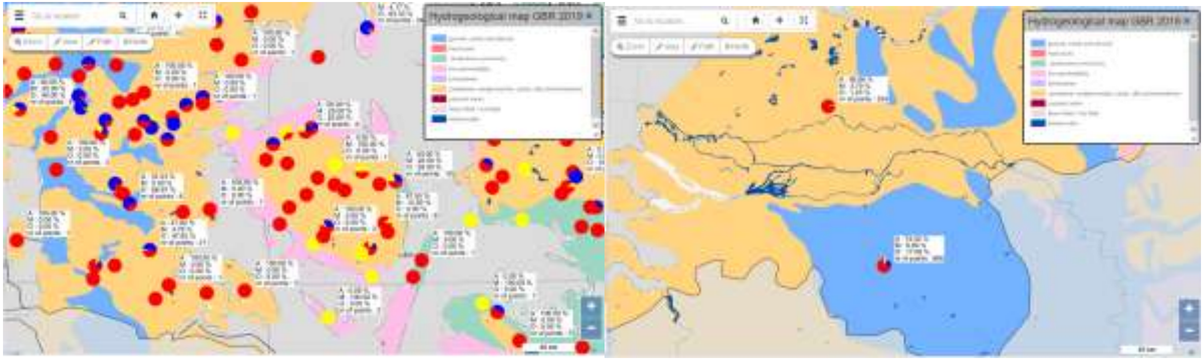

Figure 15: Zoom for some groundwater bodies of Denmark (left) and The Netherland (right)

In the chalkstones and karstic areas (UK or France, *Figure 16*) the oxic conditions are predominant.

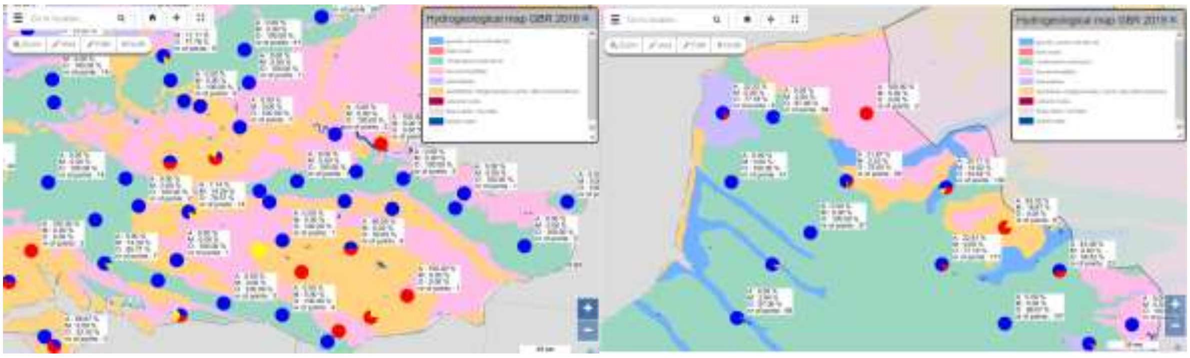

Figure 16: Zoom on some groundwater bodies of United Kingdom (left) and France (right)

It is worth mentioning that the contents and distribution of reductants are seldom known in detail for most aquifers, and that the reduction capacity of the sediments may be used up. Hence, there will be a tendency towards more oxic water types depending on the contents of reductants in the subsurface, especially in areas with intensive agriculture, where high nitrate loadings oxidize the reductants in the aquifers at a higher rate than under natural conditions (Postma et al. 1991). In addition, nitrate reduction result in increased concentrations of other contaminants such as sulphate (Jessen et al., 2017) that further along the flow path will result in additional oxidation of reductants in the aquifers.

This means that the pie diagrams illustrating redox conditions in the maps will become more blue (oxic) in the future as the reduction capacity of the aquifers are used up and that the pie diagram for Denmark will approach the ones for France and the UK with time. This will occur at a variable and unknown rate as the reduction capacity and reaction kinetics are poorly known and vary in Denmark as well as most if not all other European countries. Hence, the presented map is not static and should be updated at regular intervals to follow how the redox boundary and hence nitrate and other pollutants (Hinsby et al. 2007) will migrate through the aquifers in EU member states.

Oxidation of reductants in the subsurface and the advance of modern potentially contaminated groundwater (Hinsby et al., 2001) will constitute an increasing problem if pollution mitigation measures are not sufficient. The contents of reductants and the position of the redox interface have many and potentially severe implications for the migration and potential degradation of pollutants in the subsurface. Postma et al. (1991) estimate that the reduction capacity of a sandy aquifer is reduced by an additional factor of five in a Danish nitrate polluted setting in the late eighties-early nineties because of agricultural nitrate loadings, and that the redox boundary will move downwards at a rate of a couple of centimetres a year. The migration of nitrate and the redox boundary have, however, declined since then because of the implementation of successful mitigation measures at the Rabis Creek site (Jessen et al., 2017) and Denmark in general (Hansen et al. 2019).

Climate change is another important factor that most probably will impact nitrate leakage and hence redox conditions in the subsurface (Ortmeyer et al., 2021), demonstrating the strong need for better description of the location of redox boundaries at national (Koch et al. 2019) and European level, and the distribution of oxic and anoxic aquifers across Europe.

5 CONCLUSIONS

This explanatory notes has two primary objectives: 1) presenting quickly the results at country or pilot-site scale of the implementation of the method described in the report D5.4. and 2) describing the construction of the map representing the results and available on EGDI.

The method was easy and fast to implement in countries of different spatial extension, geology, database of groundwater quality monitoring. This method can be easily used in other countries in order to have an overview of the European groundwater redox conditions. The map established within HOVER could be further developed to cover more of Europe or even allow the elaboration pf t a pan-European map.

The results, at national scale, are consistent with the existing knowledge on Redox condition in groundwater in the pilot countries.

Within the pilot countries we observed quite contrasting Redox conditions, oxic water strongly dominating in Spain, Cyprus and Slovenia, oxic condition prevailing in France, United Kingdom and Ireland, anoxic conditions being more important in Denmark, Latvia and the two GWB of The Netherland. Mixed conditions were most often determined in the transboundary Drava-Mura aquifer in Croatian/Slovenian. Globally, this patterns fit quite well with the simplified lithologies proposed using the IHME map.

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