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Assessment of complex subsurface redox structures for
sustainable development of agriculture and the environment

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Abstract

Cost-efficient targeted nitrogen (N) regulation of agriculture with low impact on the environment is the new N regulation paradigm. It requires detailed knowledge on the geological and geochemical conditions of the subsurface that is crucial for assessing the nitrate flowpaths and reduction processes. An integral part of this is analysis of the subsurface redox structures to determine the locations of nitrate reduction. This knowledge has so far not been easy to access because of lacking technology. Here we present a new concept consisting of integration and interpretation of data from the geophysical towed transient electromagnetic method, borehole information on lithology, sediment colour descriptions, geochemistry and groundwater chemistry. The concept is demonstrated in three small first-order hydrological catchments. National GIS screening analyses show that the new concept is highly needed in large parts of Denmark where the redox structures are complicated e.g. in marine landscape types and in glacial moraine landscapes but less needed in areas dominated by homogeneous meltwater plains. Providing subsurface knowledge for locally targeted N regulation of agriculture is paramount in many developed countries with intensive agriculture to lower the environmental impact, and it could also be critical in developing countries to support sustainable economic and environmental development.

1. Introduction

Agricultural food production, management, and nitrogen (N) fertilization creates excess reactive N (Galloway 2003, Galloway *et al* 2008) which is lost to the atmosphere and aquatic environment (Dalgaard *et al* 2014, Hansen *et al* 2019) with environmental and human health consequences (Schullehner *et al* 2018, Ward *et al* 2018, Temkin *et al* 2019). Worldwide, this dilemma is a well-known environmental and economic sustainability challenge. On a national level, the severity, of the excess N in the environment can be assessed by evaluating the relationship between N pollution and economic growth (Chow and Li 2014) known as the environmental Kuznets curve (Grossman and Krueger 1995). Such an analysis shows that many developed countries have experienced a trend

reversal while developing countries are on the rising side of the curve with increasing N pollution (Zhang *et al* 2015, Hansen *et al* 2017).

In many European countries, the N mitigation measures imposed on a national one-size-fits-all level such as N-application-quotas for specific crops, procedures for handling of manure, maximum livestock density have successfully lowered the level of N pollution of the aquatic environment (Grizzetti *et al* 2011, Dalgaard *et al* 2014). However, the goals of both national and EU environmental legislations have not yet been reached in many areas (European Commission 2018).

1.1. Definition of targeted N regulation

Cost-efficient targeted N regulation of agriculture has been suggested as a way forward to reduce the impact

on groundwater, surface and marine waters (Jacobsen and Hansen 2016). The idea is that the local N regulation of a field is adjusted to the natural denitrification potential of the subsurface, which depends on the water pathways and the N reduction rates and capacities of the subsurface media below the field. The capacities are determined by the amounts of the reactive reduced compounds. The nitrate reduction rates are determined by the reactivity of minerals and chemical compounds in the geologic layers (e.g. pyrite or organic matter) that reduces nitrate to inactive N_2 gas mediated by microorganisms.

The targeted N regulation aims to delineate robust fields which can have a higher N-application rate with higher yields and more vulnerable fields, which should have a low N-application rate. In this way targeted N regulation aims at obtaining both high agricultural production and low environmental impact on groundwater and surface waters.

1.2. Definition of redox structures

In the simplest case with only downward infiltration of water in a homogenous geologic layer, three redox zones related to nitrate can be found: (a) an upper oxic zone with no active nitrate reduction, (b) a lower anoxic zone with active nitrate reduction, and (c) a deeper reduced zone with no active nitrate reduction but a potentially high preserved nitrate reduction capacity (Appelo and Postma 2010, Hansen *et al* 2016).

However, in heterogeneous geological layers much more complex redox structures are found due to complicated water pathways and varying mineral content and reactivity of reductants in the geological layers. Such conditions are for example typically seen in formerly glaciated landscapes as found in Denmark (Hansen and Thorling 2008, Kim *et al* 2019) and other countries in e.g. North America (Rodvang and Simpkins 2001, Best *et al* 2015).

1.3. Redox structures and scale

Regional or national scale studies attempt to predict the redox zones or interfaces using statistical methods as seen in the US (Tesoriero *et al* 2017) and New Zealand (Close *et al* 2016, Friedel *et al* 2020, Wilson *et al* 2020). In Denmark, a national first redox interface (FRI) has been assessed by expert knowledge from e.g. borehole sediment colours (Ernstsen and von Platen 2015), and recently by machine learning (Koch *et al* 2019). At a catchment scale of about 100 km², a concept for modelling the depth to the FRI was based on simulations of water recharge, historical oxidation of the subsurface, and calibration based on measured input and output data (Hansen *et al* 2014).

Field scale studies typically show much more complex redox structures than the larger regional scale studies (Jacobsen *et al* 2019, Petersen *et al* 2020). At a catchment scale of approximately 10 km², multiple point statistics with redox training images

relying on field scale studies has been used to simulate complex redox structures in the subsurface (Madsen *et al* 2020).

In areas with heterogeneous hydrogeology and geochemistry of the subsurface, we hypothesize that multiple redox zones below the FRI may play a significant role for the flux of reactive N to the stream and coastal waters. Here, we propose that assessment of subsurface redox structures in 3D should be based on integration of geophysical, geological, and geochemical data. This integration of knowledge is crucial as input to catchment modelling and assessment of natural denitrification of the subsurface to be used in targeted N regulation of agriculture.

The aims of this study are: (a) to present a concept for integration of geophysical, geological and geochemical data for assessment of local subsurface redox structures, and (b) to demonstrate the importance of the concept on a Danish national level for future sustainable development of agriculture.

2. Materials

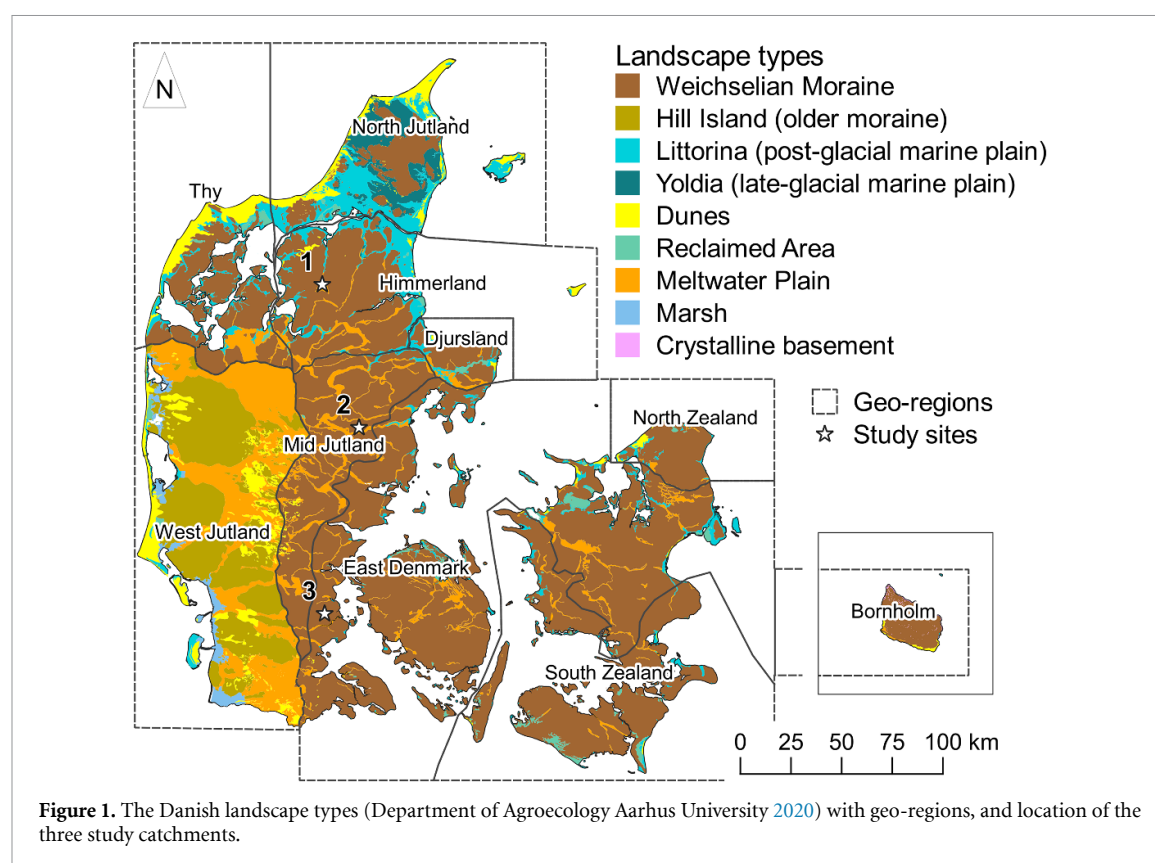
2.1. Description of study sites

Denmark is a Scandinavian country in Northern Europe with a total area of about 43 000 km², and a population of more than 5.8 million. It is the country in Europe with the largest proportion of agricultural landuse (Christiansen *et al* 2020) of about 61%. The climate is coastal temperate, and the precipitation varies from 600 to 1000 mm yr⁻¹. The land surface has a modest topography with the highest point 170 m above sea level, and the landscape is dominated by moraines and meltwater plains from the Weichsel glaciation (figure 1). Thus, the geological conditions in the upper geologic layers are 50–200 m thick Quaternary deposits which are underlain by Palaeogene and Neogene deposits or Cretaceous limestone and chalk. The groundwater aquifers consist of either unconsolidated sands and gravels or fractured limestone and chalk.

This study includes both analyses for three selected small Danish first-order hydrological catchments, and analyses on the national level for the whole of Denmark. Catchment 1 called Odderbæk or LOOP2, is in the geo-region Himmerland and part of the National Environmental Monitoring Programme. Catchment 2 is Javngyde, in the geo-region Mid Jutland and catchment 3 is Sillerup in the geo-region East Denmark in southern Jutland. All catchments are placed in the Weichselian Moraine landscape type dominated by Quaternary deposits, and a high percentage (>80% of the land) of agricultural fields (figure 1).

2.2. Data used for the three catchments

Three types of data are used for assessment of redox structures at a local scale: geophysical, geological and geochemical data. The geophysical data come from



recently conducted surveys while the geological and geochemical data both come from historical data that are publicly available in the Danish national geo-database Jupiter (www.geus.dk) and newly collected data from wells. The new wells were placed at central sites with lacking knowledge on redox conditions.

2.2.1. Geophysical data

Geophysical data consist of continuously measured transient electromagnetic (TEM) soundings using the newly invented towed TEM (tTEM) system. The system consists of a transmitter and a receiver coil that is towed by an all-terrain vehicle. The fields were densely mapped with 20–30 m space between the survey lines. The tTEM surveys were performed on all available fields in the three catchments. Resulting resistivity models from tTEM surveys usually have 2–5 m vertical resolution, and an investigation depth of 40–60 m depending on the geology. These resistivity models provide the spatial information about the geological structures of the subsurface. More details about the method can be found in Auken *et al* (2019).

2.2.2. Geological data

The data on geology consisted of:

- Lithology descriptions from wells registered in the national geo-database Jupiter and new conducted wells
- Digital elevation models (Danish Agency for Data-supply and Efficiency 2020)

- Surface geological maps (Jakobsen *et al* 2011)
- Previous geological studies (e.g. Sandersen and Jørgensen 2017).

2.2.3. Geochemical data

Different types of geochemical data were collected:

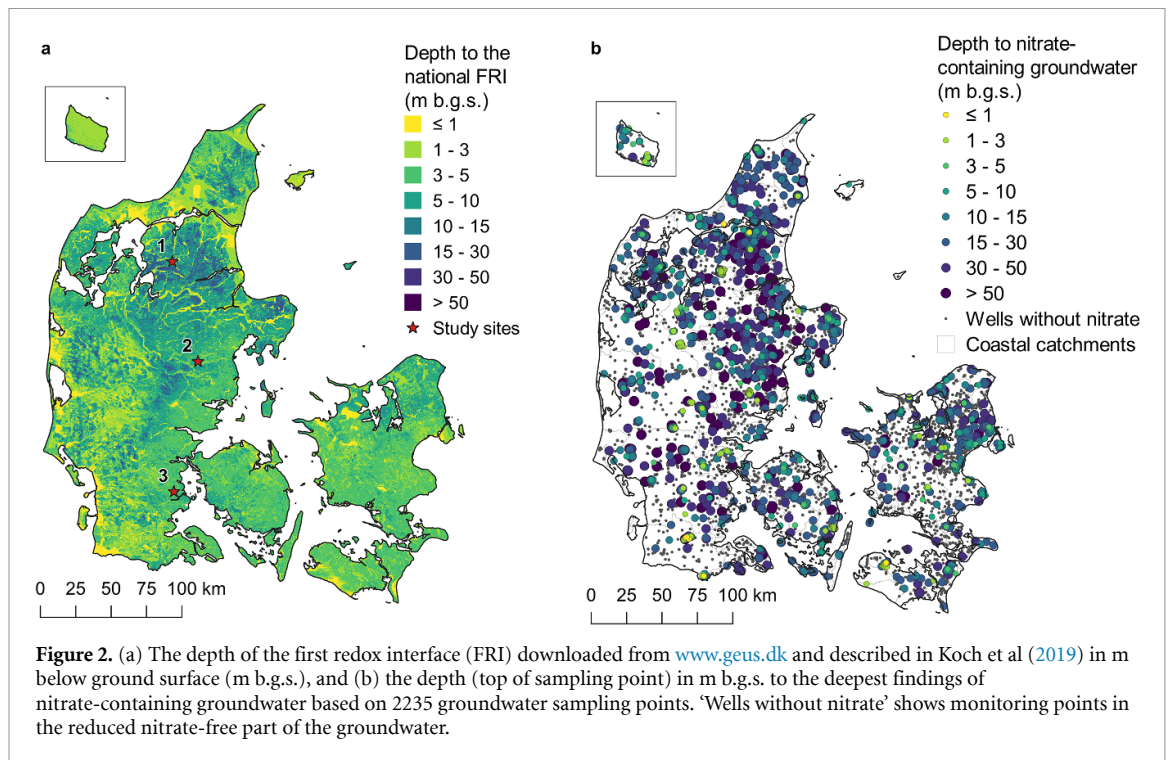
- Colour descriptions of sediment in wells
- The Fe(II) fraction of the formic acid extractable Fe phase ($\text{Fe(II)/Fe}_{\text{tot}}$) of the sediment (Sø *et al* 2018)
- The concentrations of redox sensitive parameters in groundwater such as oxygen, nitrate, iron, and sulphate.

2.3. National data

On a Danish national level, different types of data are used to investigate the importance of assessment of complex redox structures at catchments in different regions.

2.3.1. The national first redox interface (FRI)

On a national level, the depth to the FRI was obtained from the simulations by Koch *et al* (2019) defined as the first interface between oxic and reduced layers (figure 2(a)). The interface was modelled with the machine learning method ‘Random Forest’ using data from 13 000 observations of sediment colour shifts in wells and explanatory variables such as clay content in the soil and topography (Koch *et al* 2019). The national map of the FRI has a spatial grid resolution of 100 m and is available for download at



the homepage of Geological Survey of Denmark and Greenland (www.geus.dk).

2.3.2. National groundwater data

On a national level, information on the nitrate content in groundwater was obtained from groundwater quality data downloaded from the Jupiter database in May 2020 (figure 2(b)). These data originate from (a) the Danish national environmental monitoring programmes, GRUMO (Jørgensen and Stockmarr 2009) and LOOP (Rasmussen 1996), and (b) the mandatory testing of the groundwater quality in drinking water abstraction wells. All nitrate analyses, as well as sampling date, sampling depths, borehole IDs and geographic coordinates are in the extracted data totalling 117 613 nitrate analyses from 9302 monitoring points belonging to 8242 wells, covering the period 1988–2019. Sampling and analyses are conducted by certified laboratories following the Danish technical standards.

2.3.3. The coastal catchments

The complexity of the redox structures in the subsurface is investigated in different coastal catchment areas. Denmark has 88 hydrological coastal catchments. Currently these coastal catchments are used for N regulation of Danish agriculture, and for reporting to the EU Water Framework Directive regarding surface water quality (EU 2000).

2.3.4. The geo-regions

The complexity of the redox structures is also explored at a regional level (figure 1) using the ten

Danish geo-regions (Kronvang *et al* 2008). The geo-regions are delineated according to landscape elements and geological settings with a varying degree of agricultural N impact (Hansen *et al* 2012).

2.3.5. The landscape types

The complexity of the redox structures is furthermore explored at a landscape type level (figure 1) using different landscape types defined by Aarhus University (2020) based on different available geological and soil type maps.

3. Methods

3.1. Geological interpretation in the study sites

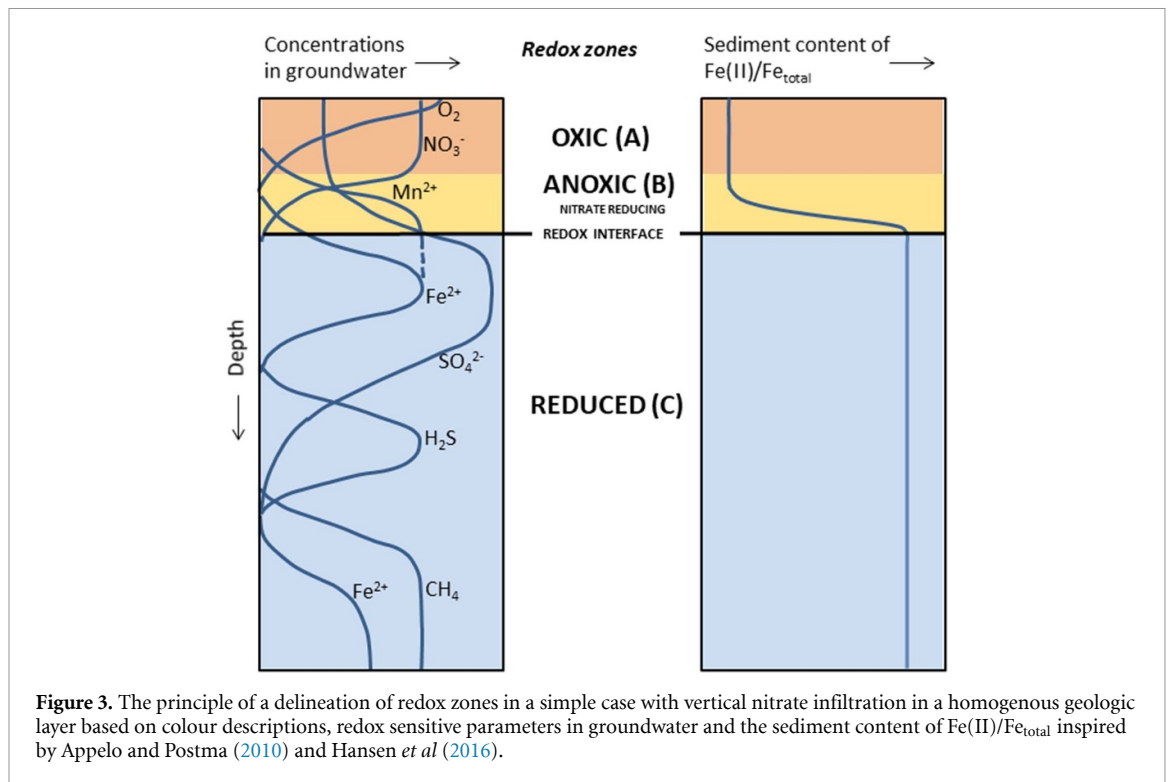
In the three hydrological catchments, a geological interpretation of the subsurface was performed by integrating the tTEM resistivity models obtained from processing and inversion of tTEM data (Auken *et al* 2019), with lithology data from wells, topography, surface geological maps and earlier geological investigations.

3.2. Assessment of redox zones in the study sites

The different redox zones were assessed by using the following geochemical data as indicators (figure 3):

Oxic zone (A):

- Red, yellow, and brown colours of the sediment
- Consistently high nitrate concentrations and low sulphate concentrations in groundwater
- Close to zero and stable Fe(II)/Fe total of the sediment (≈ 0).



Anoxic nitrate reducing zone (B):

- Grey, green and olive colours of the sediment
- Low and/or decreasing nitrate concentrations over depth at times supported by increasing sulphate concentrations
- Increasing $\text{Fe(II)/Fe}_{\text{total}}$ content of the sediment approaching 1 (≈ 1).

Reduced zone (C):

- Grey, green and olive colours of the sediment
 - Stable nitrate concentrations below $1\text{--}3\text{ mg l}^{-1}$
 - High and stable $\text{Fe(II)/Fe}_{\text{total}}$ of the sediment (≈ 1).

3.3. Complex redox structures on a national level

The complexity of the redox structures on a national level was evaluated by comparing the depth of nitrate-containing groundwater with the depth of the FRI simulated by Koch *et al* (2019). Here the presence of complex redox structures is defined as infiltration of nitrate to levels below the location of the national FRI.

Nitrate-containing groundwater was defined as groundwater with $>3\text{ mg l}^{-1}$ nitrate in order not to include any nitrate that could come from ammonium oxidation during sampling. The most recent result of nitrate analysis from each sampling point is used in this study. The depth to the nitrate-containing groundwater was set as the depth to the top of the screen to avoid exaggerating the depth of nitrate infiltration. In wells with multiple monitoring points the depth to the top of the deepest one is selected for further analyses. Based on these pre-selection

criteria, there were 2235 wells with nitrate-containing groundwater and known depth to the top of the well intake (figure 2(b)).

3.4. National GIS and statistical analyses

The nationwide comparison between the FRI and the depth of the nitrate-containing groundwater was done on different aggregation levels: (a) well (point scale), coastal catchment (from 2.8 to 3561 km²), geo-region (from 588 to 11 216 km²), and also for different landscape types.

All GIS analyses were performed in QGIS 3.10.9 (QGIS Development Team 2020), and data analyses and statistical treatment were performed in R 4.0.2 (R Core Team 2020). The national FRI raster was sampled to determine the depth to the FRI at each of the selected wells with nitrate-containing groundwater. An agreement matrix was used for comparison at point level (well). The wells were joined with the polygons of the 88 coastal catchments, the 10 geo-regions, and the 9 landscape types. The proportion of wells with nitrate-containing groundwater $>5\text{ m}$ deeper than the FRI was calculated for each polygon.

A system of scores for the polygons was developed based on the proportion (%) of wells with nitrate-containing water below the national FRI: score 1, if $<20\%$; score 2, if $20\text{--}40\%$; 3, score if $40\text{--}60\%$; score 4, if $60\text{--}80\%$; score 5, if $80\text{--}100\%$. Then, the scores were accumulated (summed) where the polygons of the coastal catchments, geo-regions, and the landscape types intersected each other. The resulting map with accumulated scores indicates the complexity of the redox conditions in a relative way: the higher the score, the more complex.

4. Results

4.1. Detailed redox structures at local scales

At the local first-order catchment scale the complexity of the detailed redox structures at local scales were assessed in line with the geological interpretations in order to integrate the hydrogeology and possible flowpaths with the interpreted redox structures. Assessment of the redox structures and redox zones was done both along a representative profile and in one central investigation well in each catchment (figures 4–6). Indications of the complexity of the redox structures are investigated by comparing the detailed assessment of the complex redox structures with the national FRI.

Both the catchment 1 (Odderbæk) in northern Jutland and the catchment 2 (Javngyde) in central Jutland are located in hilly moraine landscapes (figures 1, 4 and 5), and catchment 1 also has an outwash plain dominating the south-eastern part. Catchment 3 (Sillerup) in southern Jutland is also a moraine landscape (figures 1 and 6) but with less topography and only a small glacial hill at the southern border (figure 6(a)).

Catchment 1 has the most sampling points with chemical analyses (83), compared to catchment 2 and 3 with only 17 and 16 sampling points (figures 4–6(a)). In the catchments, the amount of sampling points with nitrate-containing water above the FRI are 66, 0 and 0 and below the FRI the numbers are 15, 3 and 0 for catchment 1, 2 and 3, respectively. It means that most of the sampling points in catchment 2 and 3 are in reduced nitrate-free ($<3 \text{ mg l}^{-1}$) groundwater.

In the investigation well from each catchment (location shown figures 4–6(c)) with depths of 14–24 m below the surface, the complexity of the redox conditions at point scales was revealed by the lithology, sediment colours, the sediment content of $\text{Fe(II)}/\text{Fe}_{\text{total}}$ and the groundwater content of nitrate (figures 4–6(b)). The sampling for each parameter varies in each well due to varying geological conditions for sampling. The redox zones (A, B and C), defined in figure 3, were delineated according to the criteria in section 3.2. Several shifts between the redox zones in the wells are seen in the sand dominated sediments of catchment 1 and in the clay dominated sediments of catchment 3 (figures 4 and 6(b)). On the other hand, a more classical redox profile is seen in the thrust sandy layers in catchment 2 (figure 5(b)) as the theoretical one in figure 3. In the hilly glaciated landscape, the comparison of the national FRI (figures 4 and 5(a)) and the detailed mapped redox structures in the investigation wells shows that the largest differences are found in catchment 1 (FRI = 3.2 m below ground surface (m b.g.s.) and depth of deepest redox interface $>15 \text{ m b.g.s.}$) and catchment 2 (FRI = 6.8 m b.g.s. and depth of deepest redox interface = 19 m b.g.s.). In the well in catchment 3 there is an overall agreement between

the national FRI (5 m b.g.s.) and the deepest detailed mapped redox interface (6 m b.g.s.) as shown in figure 6(a).

Knowledge about the sandy subsurface layers and thus the potential flowpaths are used to determine and extrapolate the locations of redox structures in areas with no information from investigation wells. This knowledge is obtained from the tTEM profiles (figures 4–6(c)) showing high-resistive layers (red; sandy sediments) and low-resistive layers (blue; clayey sediments). The conceptual geological interpretations along the profiles are sketched underneath the tTEM profiles in figures 4–6(d). Beneath the glacial hills in all of the three catchments there are different degrees of textural and structural heterogeneity, reflecting differences in the glacial environment and in the succession of geological events (figures 4–6(d)). In catchment 1, the sediments are low to moderately deformed compared to catchment 2, where the sediments are strongly deformed by glaciotectionic thrusting. In catchment 3, glaciotectionically deformed layers are only found to the south where they form a single sandy window in a succession that differs from the otherwise homogenous clayey layers to the north. The outwash plain in catchment 1 (figures 4–6(d)) forms a near-surface sandy and gravelly layer with patchy occurrences of organic rich sediments. In catchment 1, the clay till in the glacial hills are very sandy and typically unsaturated resulting in high resistivities in the tTEM data.

The complexity of the redox structures and zones is high in catchment 1 and 2 with relatively large differences between the national FRI and the deepest redox interface due to heterogeneous sandy layers and flowpaths found in this detailed study (figures 4 and 5(d)). In catchment 1, the north-western Quaternary sandy layer in the glacial hill is oxic and underlain by a large sandy anoxic nitrate reducing zone, whereas in the southern part, the nitrate reducing zone is found below near-surface, reduced organic rich layers. In catchment 2, the redox zonation aligns with the glaciotectionic thrust sandy and clayey layers which is not revealed in the national FRI. In catchment 3, there is only a minor difference in the redox boundary related to the geologic window, between the redox zonation from this detailed study and the national FRI.

4.2. National analyses of complex redox structures

On a national level, the complexity of the redox structures is analysed by comparing the depth to nitrate-containing water and depth of the national FRI (figure 2). Figure 2 shows the depth to the FRI (a) and depth to nitrate-containing groundwater (b) and figure 7 shows the comparison between the two. Figure 7 also shows the depth-distribution of nitrate-containing groundwater in Denmark. The highest number of wells with nitrate-containing water are in the depth-classes 15–30 m (28%) and 30–50 m (21%).

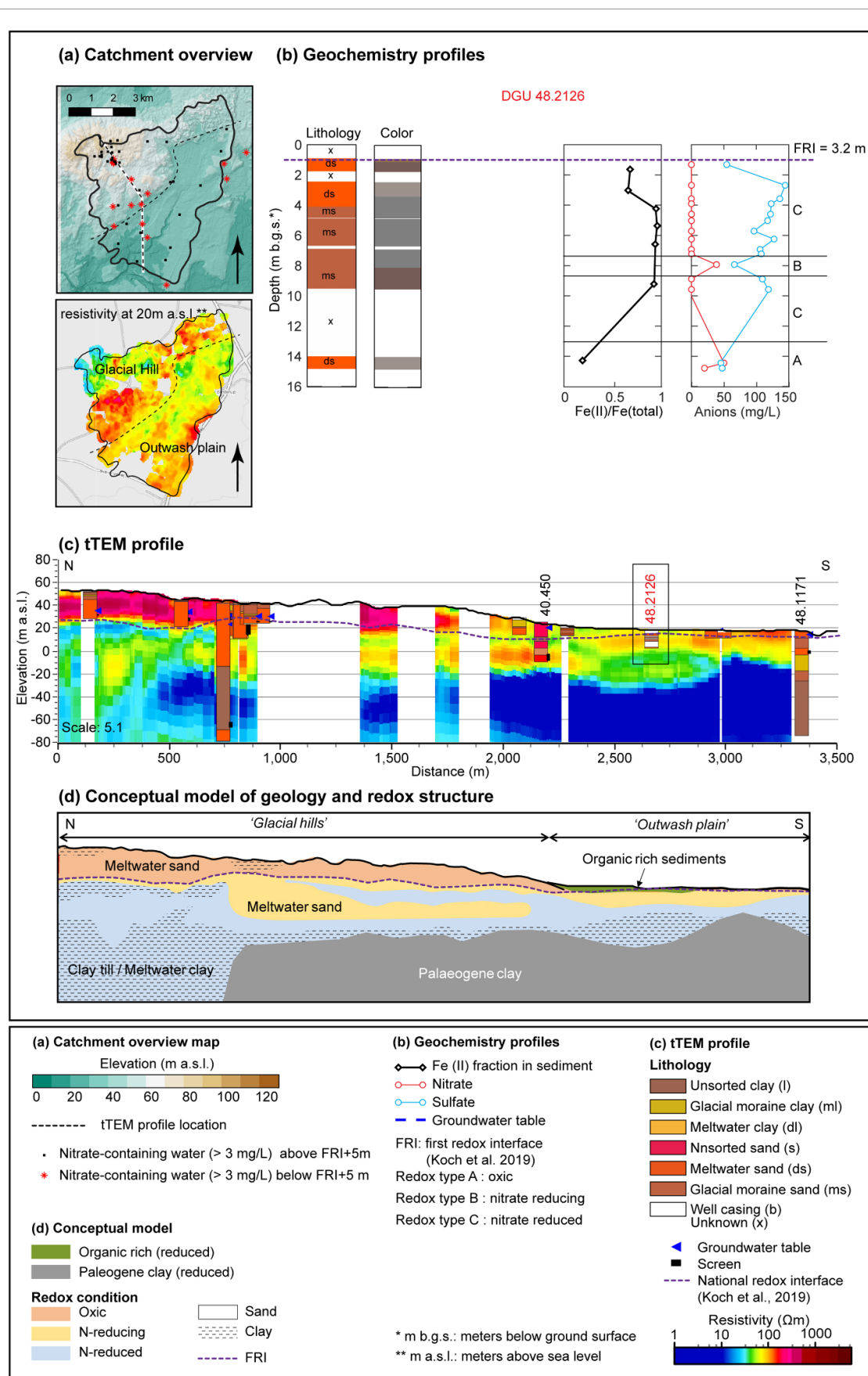


Figure 4. Catchment 1 (Oddebæk): (a) topographic maps with location of profiles and selected wells with complex redox structure, and a tTEM map at a specific elevation above sea level, (b) geochemical parameters and redox zones in a selected well, (c) profile with tTEM resistivity data and wells, and (d) conceptual profile with geological structures and redox zones. Data and interpretations are compared to the first redox interface (FRI) seen in figure 2(a) simulated by Koch *et al* (2019).

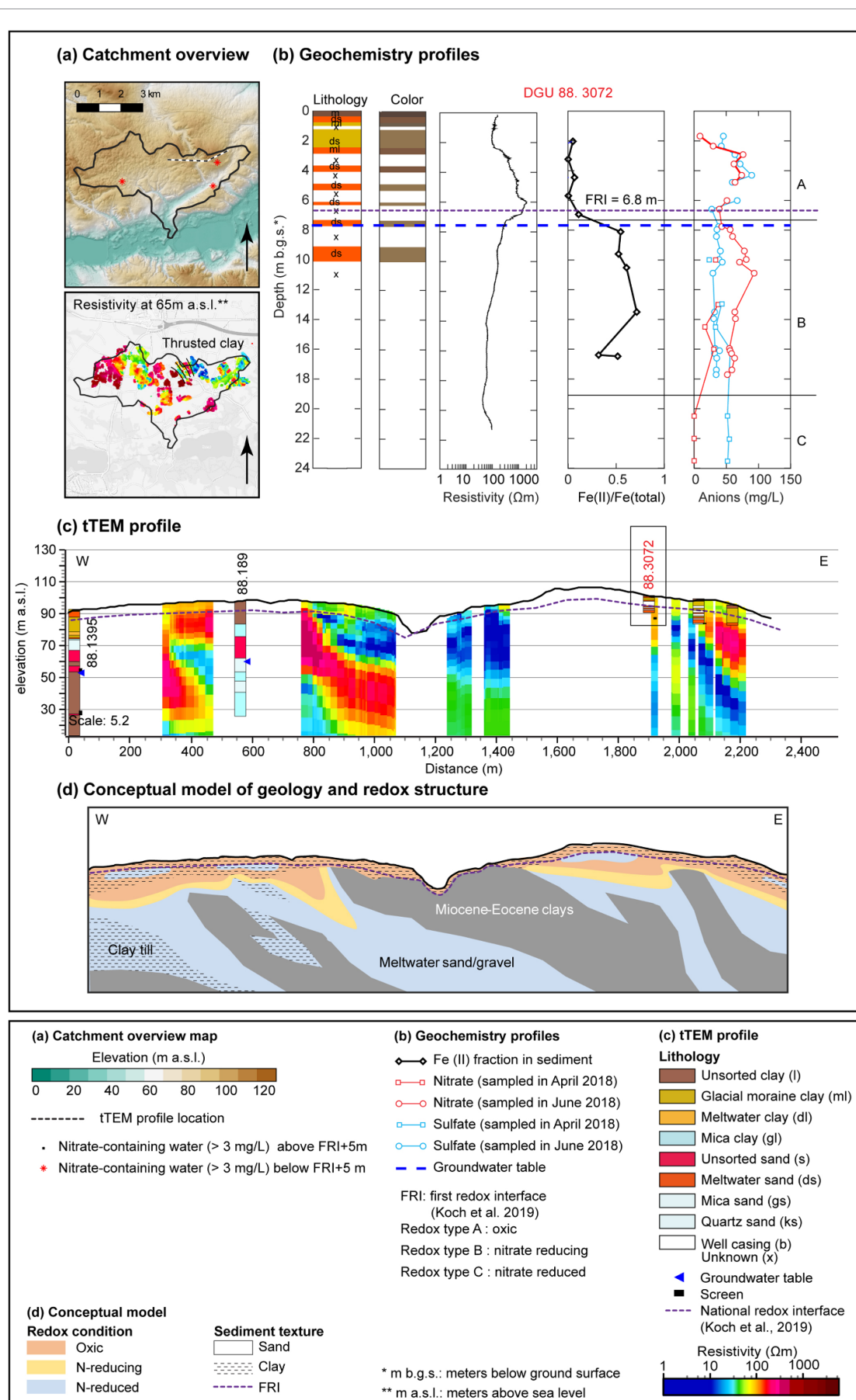


Figure 5. Catchment 2 (Javngyde): (a) topographic maps with location of profiles and selected wells with complex redox structure, and a tTEM map at a specific elevation above sea level, (b) geochemical parameters and redox zones in a selected well, (c) profile with tTEM resistivity data and wells, and (d) conceptual profile with geological structures and redox zones. Data and interpretations are compared to the first redox interface (FRI) seen in figure 2(a) simulated by Koch *et al* (2019).

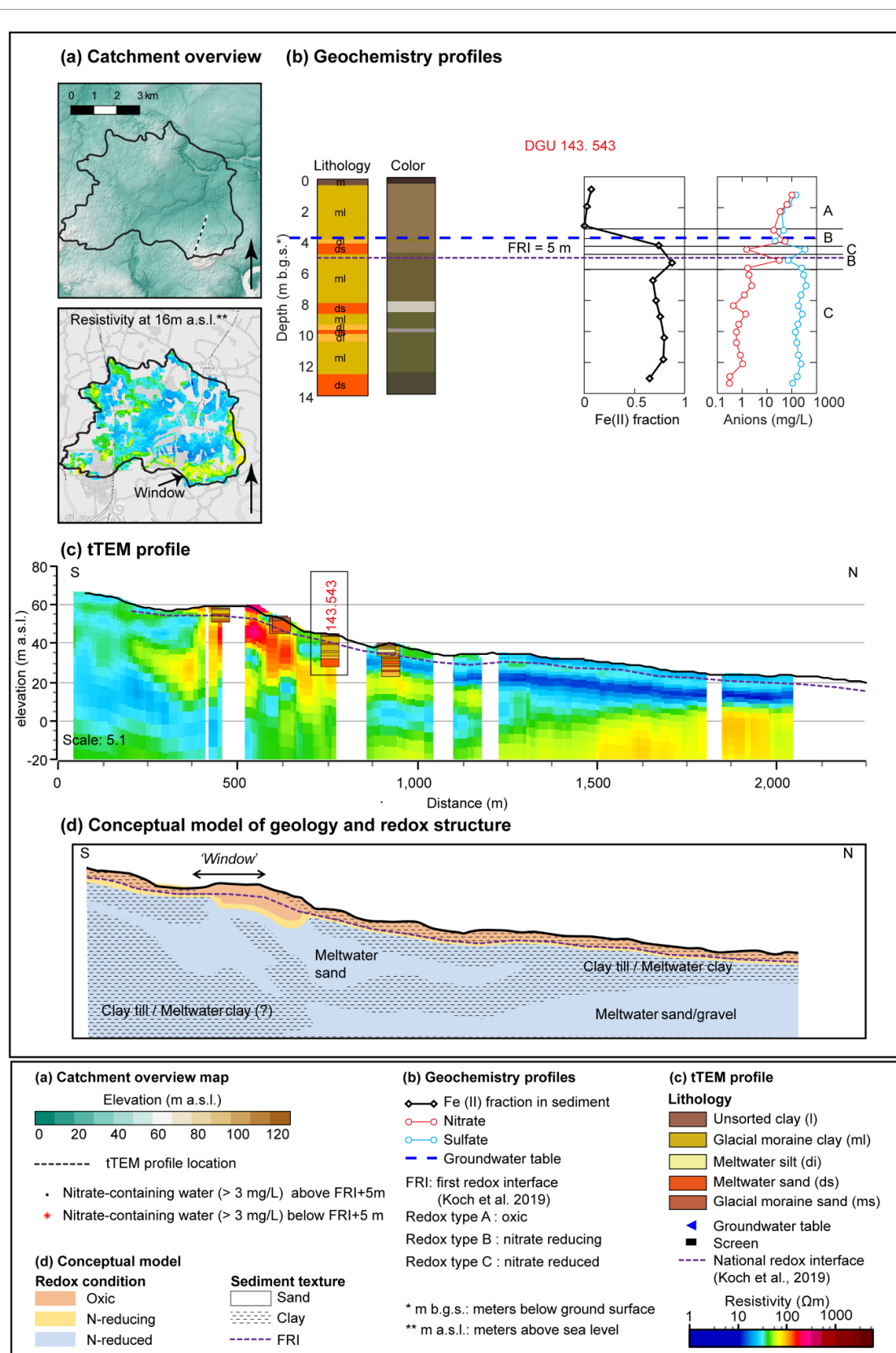
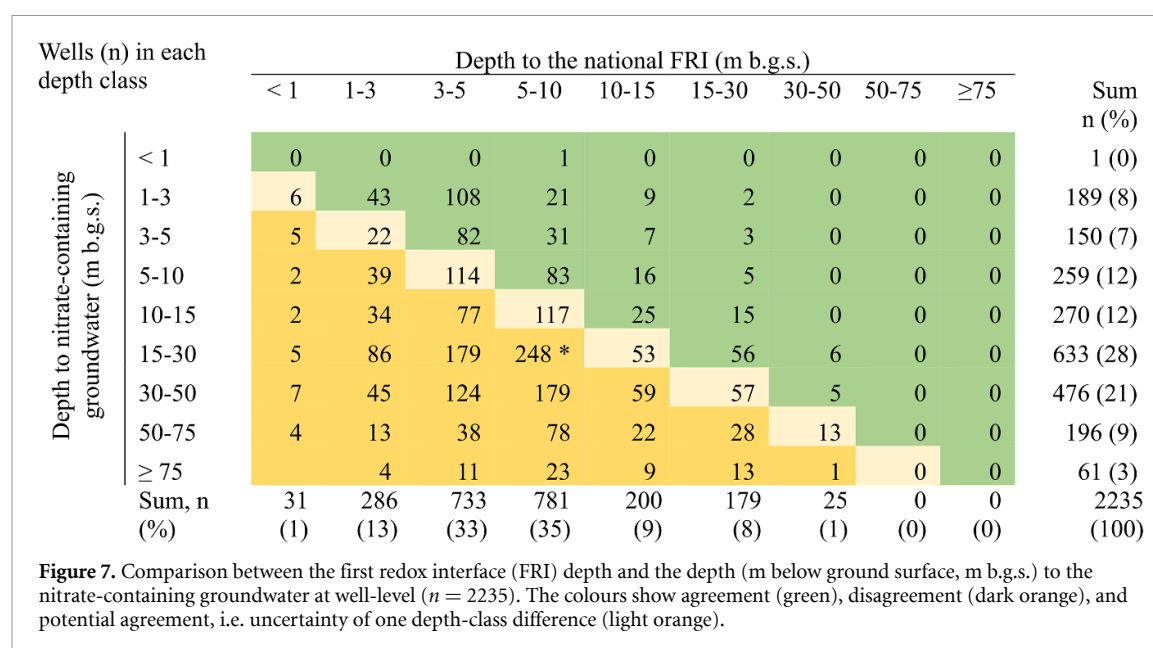


Figure 6. Catchment 3 (Sillerup): (a) topographic maps with location of profiles and selected wells with complex redox structure, and a tTEM map at a specific elevation above sea level, (b) geochemical parameters and redox zones in a selected well, (c) profile with tTEM resistivity data and wells, and (d) conceptual profile with geological structures and redox zones showing the location of a sandy geological 'window'. Data and interpretations are compared to the first redox interface (FRI) seen in figure 2(a) simulated by Koch *et al* (2019).



In contrast, the FRI are mostly in the 3–5 m (33%) and 5–10 m (35%) depth-classes.

The overall agreement between the depth of the national FRI and the depth to nitrate-containing groundwater is app. 40% (900 out of the 2253 sampling points with only one depth-class difference (figures 2 and 7)). These 40% include the wells from the agreement portion of the matrix (518, 23.2%, green part of figure 7) and the one depth-class difference uncertainty (282, 17.1%, light orange part of figure 7). While in approximately 60% of the wells (1335, dark orange part of figure 7), nitrate-containing water was found more than one depth-class below the FRI. This discrepancy could be due to complex geology and a complex redox structure in large parts of the country.

4.3. Areas of complex redox structures

The wells with nitrate-containing groundwater more than 5 m below the national FRI are found all over the country (black dots in figure 8). However, is it possible to point out areas in Denmark with a larger tendency for complex redox structures?

Among the 88 coastal catchments only the larger 48 catchments, covering app. 91% of the total area of Denmark, with more than five wells (sampling points) are used in this study (figure 8(a)). Of these catchments the proportion of wells with nitrate-containing groundwater more than 5 m below the national FRI varies from 3% to 100% with the lowest values in southern Denmark and the highest proportions especially in northern Denmark and major Eastern parts of the Country at Funen and Zealand. See more details in table S1 (available online at stacks.iop.org/ERL/16/025007/mmedia).

In general, all geo-regions have wells with nitrate-containing water more than 5 m below the national

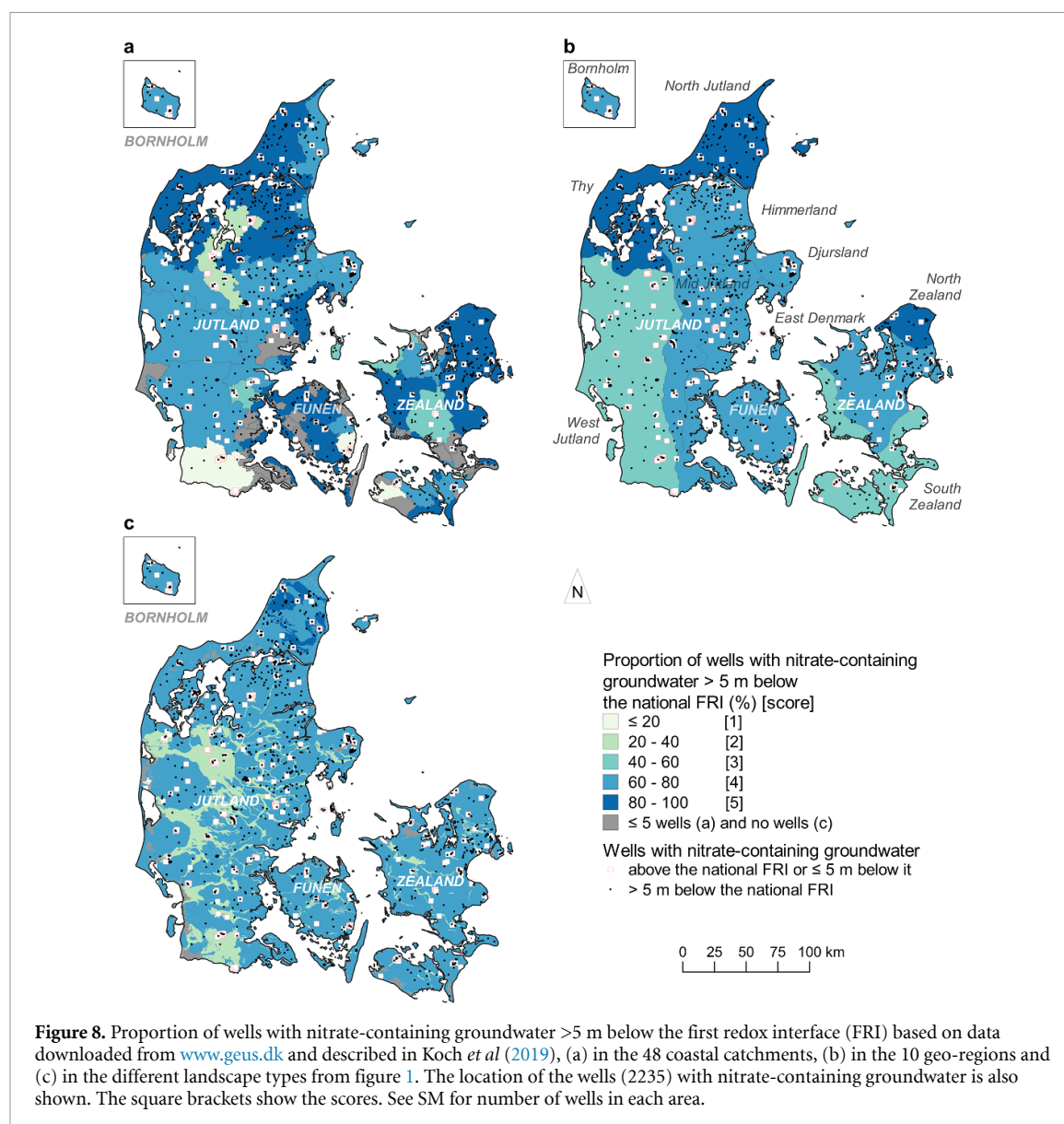
FRI (figure 8(b)). However, the geo-regions in northern Jutland called Thy and North Jutland, and also North Zealand have the highest proportion of wells (83%–86%, 37–225 sampling points) with nitrate-containing groundwater more than 5 m below the national FRI. The lowest proportion is found in West Jutland (43%, 142 sampling points) and South Zealand (55%, 96 sampling points). See more details in table S2.

From a landscape type perspective only the six landscape elements Yoldia (late-glacial marine plain), Weichselian moraine, Littorina (post-glacial marine plain), Hill Island (older moraines), dunes and meltwater plain have data on nitrate-containing groundwater (figure 8(c)). However, these landscape types cover app. 98% of the area of Denmark (figure 1). It means there are no data on nitrate-containing groundwater in reclaimed areas, marsh and crystalline basement shown in figure 1.

A nationally accumulated scoring of the complexity of the redox structures was developed and calculated based on the maps of the coastal catchments, geo-regions, and the landscape types (figure 8) as described in section 3.4. In general, the higher the score, the stronger the indication that the area has a complex redox structure (figure 9).

Overall, the strongest indications of complex redox structures were found in the landscape types with glacial moraine and recent marine deposits, while meltwater plain areas showed the weakest indications.

The results therefore indicate that the most widespread complex redox structures are found in catchments and geo-regions of northern Jutland in the Yoldia late-glacial marine plain, the Littorina post-glacial marine plain, the dunes and the Weichselian moraine landscapes, and also in northern part



of Zealand in the Weichselian moraine landscape types (figures 8 and 9).

5. Discussion

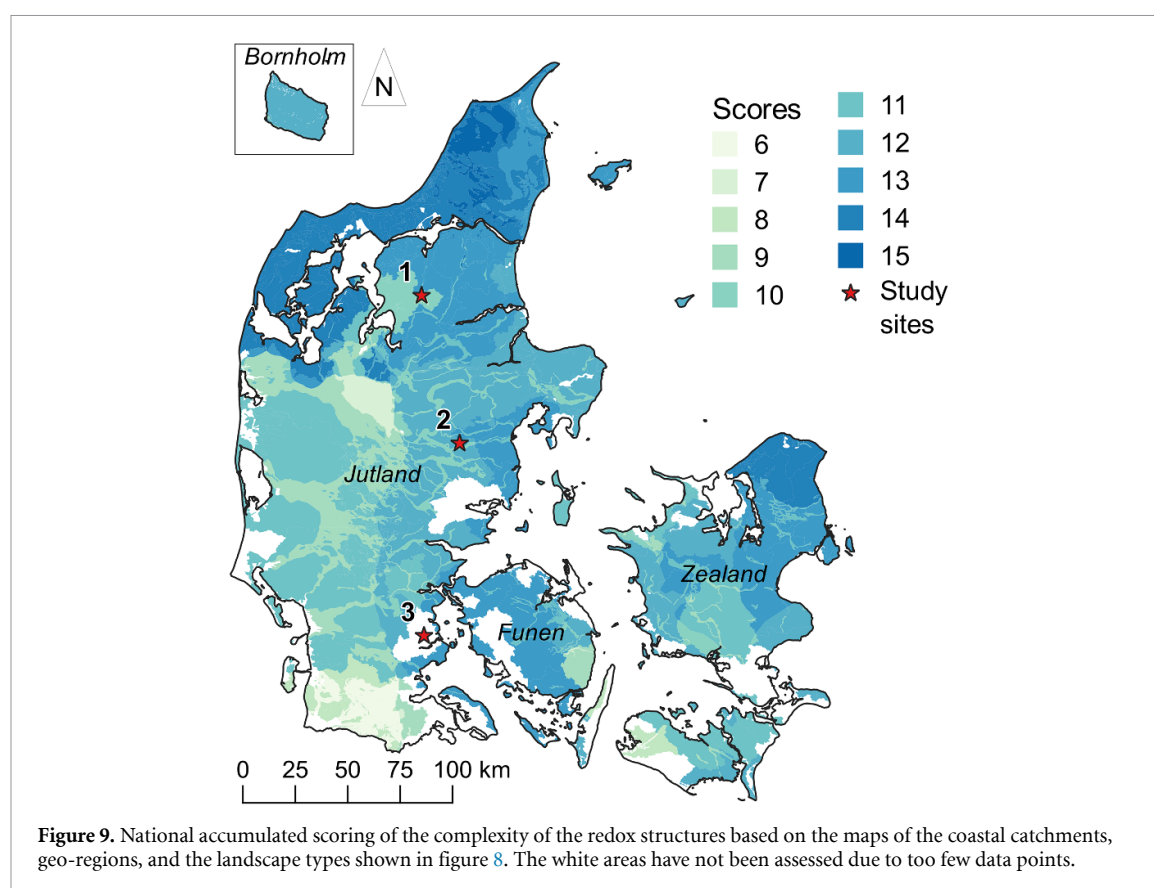
5.1. The need for detailed knowledge in a new sustainable N regulation

In the Western world, stricter national regulations and regionally differentiated mitigation measures have been suggested as a means to further reduce the N impact on the aquatic environment (Sarris *et al* 2019), but implementation is often hampered by social, economic and political factors (Davidson *et al* 2015, 2016, van Grinsven *et al* 2015).

Both scientifically and politically there seems to be consensus in Denmark that locally targeted N regulation is the way forward. Since 2015 (Danish Ministry of Environment and Food 2015), the N regulation of Danish agriculture has slowly been

moving from one-size-fits-all national regulation to also include more locally targeted regulation.

However, a major obstacle has been the lack of sufficiently detailed knowledge about the subsurface conditions which is needed for local field-scale targeted N regulation. Detailed knowledge is crucial for cost-efficient decisions on which mitigation measures to use and where to place them within the landscape of a catchment (Jacobsen *et al* 2017). The idea is that vulnerable fields should have high restrictions on the use of N-fertilizers while less vulnerable fields could have a higher N-application and production level. This is especially needed in countries that have harvested the low-hanging fruits of the one-size-fits-all national regulation. There is also an urgent need to promote more sustainable economic and environmental development of agriculture in developing countries for example by more efficient use of fertilisers in specific areas. Thus, for the developing countries on the rising side of the



Environmental Kuznets Curve with increasing high agricultural nitrogen losses due to low N-use efficiency, there is also a need for more precise fertilizer application to increase yields and lower the environmental impact (Zhang *et al* 2015).

5.2. Key areas for detailed investigations

The presented analysis shows that the complexity of the redox structures is not uniform across Denmark but varies according to geology, landscape, and catchment types. A high degree of redox complexity is seen in the former specific marine and glaciated landscape types while a lower degree of complexity is seen on the sandy meltwater plain landscape types. It is important to stress that this national analysis can only be seen as a screening exercise, and more detailed investigations are needed to understand the redox structures and pattern in local areas especially for the smaller landscape types with a low data density as e.g. the marine landscape types. However, the national analysis indicates that detailed investigations of redox structures are especially needed in similar glaciated landscapes and geologic deposits found in many places of the world such as in Canada, North America, and Europe.

In this study, complex redox structures are defined as a deeper infiltration of nitrate than the location of the national FRI. The complexity of the redox structures can be explained by (a) different structures and textures in the geologic layers creating complex pathways for water, (b) heterogeneity of the mineral content of the geologic layers and microbiological

activity controlling nitrate reduction processes, and (c) near-surface limestone and chalk deposits where the national FRI might underestimate the location of the FRI due to no colour shifts in these type of deposits. In addition, in areas with a high drinking water production the infiltration of nitrate into the aquifers can be accelerated by the abstraction.

Thus, in areas with high complexity of the redox structures as seen in catchment 1 and catchment 2 it is important to obtain detailed geophysical, geological and geochemical data from the specific catchments. This is important because it appears that the current national wide machine learning procedure will underestimate the extent of oxic and anoxic nitrate reducing conditions, and overestimate the reduced conditions. Thereby, the national FRI map potentially underestimates the propagation of nitrate in the groundwater, and furthermore underrates the need for N mitigation measures to protect groundwater and surface waters. Conversely, in a catchment with a more homogenous subsurface, as seen in catchment 3, a more automatic procedure can be justified.

5.3. Scale and uncertainties

A more local targeted N regulation implies a higher need for local knowledge about the subsurface conditions. In other words, the scale of the knowledge on the factors determining nitrate retention needs to match the scale of N regulation of agriculture. At field level, targeted N regulation requires knowledge of the subsurface redox structures below the fields.

By knowing the distribution of these structures, the locations of subsurface natural denitrification can be assessed, and this is the key to the identification of agricultural fields where nitrate leaching will lead to a too high impact on the aquatic environment. Even in an extensively monitored country such as Denmark, there is a need for a higher data density in many parts of the country as can be deduced from figure 8. However, uncertainty on the subsurface redox structures is not the only challenge for locally targeted N regulation. This new paradigm of regulation is also dependent on: effects on land prices, farmers resistance, challenges related to re-allocation of land use between farmers, as well as collaboration of farmers, citizens and authorities (Hansen *et al* 2017).

6. Conclusion

An unmet need for local subsurface knowledge has been identified for new targeted N regulation of agriculture. The essential detailed knowledge of the subsurface redox structures can be obtained by using a new concept for integration of data from the new geophysical tTEM method (Auken *et al* 2019), combined with borehole information on lithology, sediment colours, geochemistry, and groundwater chemistry. On a national level, in the case of Denmark, this detailed knowledge is needed especially in areas with specific marine deposits and moraine landscapes, while outwash plains areas are more homogenous regarding redox structures.

A new targeted N regulation should be adjusted to the local subsurface structures and redox conditions to lower the impact on the aquatic environment. At the same time, there are possibilities for using this new knowledge in precision farming in the management and fertilization of fields in developed countries with areas of highly intensive agriculture as well as in developing countries moving in this direction.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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