

Review and assessment of nitrate reduction in groundwater in the Baltic Sea Basin



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ABSTRACT

Study region: Six countries within the Baltic Sea Basin: Denmark, Sweden, Finland, Lithuania, Poland and Germany

Study focus: During transport from the field to the sea nitrogen undergoes natural reduction, but with large spatial variations. Mapping this variation would allow more optimal regulation strategies, by imposing most restrictions in areas with low natural reduction. In the present study, a map for spatially variable nitrate reduction in groundwater is developed covering six countries in the Baltic Sea Basin. In contrary to previous studies within the Baltic Sea Basin, the present study provides an independent estimate of the nitrogen reduction in groundwater, based on review of national data and studies. Depending on availability, different approaches were used for the countries ranging from national modelling to expert judgement. Through a joint workshop the assessments were, to the extent possible, harmonised.

New hydrological insights for the region: The review revealed large variations in the hydro-geochemical conditions important for transport and degradation of nitrogen in groundwater. This includes the hydrogeology, the reducing conditions of the subsurface, and the fraction of water transported by drainage systems bypassing the reducing subsurface environments. Significant variations in groundwater reduction between the countries and within most of the countries were thus found, indicating that strategies for nitrogen regulation and mitigation measures may be optimised, if variation in the natural reduction of nitrate is considered.

1. Introduction

Nutrient load, primarily by waterborne riverine transport, has changed the environmental conditions for the Baltic Sea from oligotrophic to eutrophic conditions in most parts (Larsson et al., 1985). To revert the conditions, the Baltic Sea Action Plan (BSAP) was adopted in 2007 (HELCOM, 2007) and revised in 2013 (HELCOM, 2013). In the updated fifth Baltic Sea pollution load compilation (PLC5.5) it is estimated that nitrogen loads has been reduced by 9% from the reference period (1997–2003) to 2013, but

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it is also found that a further abatement of 14% is required (HELCOM, 2015). Analysing trends in monitoring data from 1970 to 2000, Saaltink et al. (2014) found that the reduced loads in nitrogen is not evenly distributed but display large spatial variation and are related to the socio-economic developments within the Baltic Sea Basin. The estimated required abatement similarly varies significantly with a required reduction of up to 26% in the Baltic Proper (HELCOM, 2015). Furthermore, specific estuaries and coastal waters may require even higher specific abatements in order to protect coastal and transitional water ecosystems and comply with the good status objectives of the Water Framework Directive (e.g. Hinsby et al., 2012).

A significant part of the nutrient reduction to the Baltic Sea can be attributed to major developments in the wastewater treatment, due to technological developments and more people being connected to municipal wastewater treatment plants. In combination with the improvement of fish farms, direct nitrogen input from point sources to the Baltic Sea has been lowered by 43% in the period 1994–2010 and contributes with approximately 4% to the total waterborne nitrogen input (HELCOM, 2015). Although some further decrease in the nutrient load to the Baltic Sea may be realised by improved wastewater treatment, the fifth Baltic Sea pollution load compilation (PLC-5) (HELCOM, 2011) estimates that the diffuse sources with a share of approximately 45% constitutes the largest anthropogenic contribution of riverine nitrogen of which 70–90% is estimated to originate from agriculture.

During transport from the root zone to the discharge into the sea, nitrogen may be removed in either the groundwater or the surface water system. Removal occurs by different natural biogeochemical processes or sedimentation, often referred to as retention or reduction and expressed as a percentage removal. The magnitude of the retention/reduction depends on the actual hydro-biogeochemical conditions and may vary significantly. Applying the statistical model MESAW to the 117 catchments in the Baltic Sea, Stålnacke et al. (2015) estimated a total nitrogen retention of approximately 40% in surface water. As noted by the authors, this estimate is substantially higher than the estimate by Mörth et al. (2007), reporting a mean in-stream nitrogen retention of 15% in the Baltic Sea rivers. Combining a statistical nitrogen leaching model with a fully distributed groundwater/surface water hydrological model and statistical surface water retention models, Højberg et al. (2015) developed a national nitrogen model for Denmark. They estimated mean retentions of 63% and 25% for groundwater and surface water, respectively, but with large spatial variations.

Natural removal of nitrogen is, however, generally not sufficient to reduce the diffuse nitrogen loads to the required levels. Implementing various mitigation measures has successfully lowered the diffuse loads from several of the member countries of the Baltic Marine Environment Protection Commission (HELCOM); Denmark, Estonia, the European Union, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. These measures have typically been implemented in response to a general and uniform regulation, i.e. a regulation imposing the same restriction in all areas without considering the variation in the natural reduction of nitrogen. Reaching a further abatement in nitrogen load calls for new and innovative measures and regulation strategies, where measures are targeted towards areas, where the natural reduction is low and the measures thus most cost-effective (Jacobsen and Hansen, 2016). A wide range of different mitigation measures may be employed to combat the nitrogen load from diffuse sources. These may be located on the agricultural fields, e.g. catch crops, at the edge of the fields, such as constructed wetland (MST, 2015) or in the surface water system upstream the outlet to the Baltic Sea. Efficiency of the mitigation measures varies according to the type of measure and where in the hydrological regime they are located. Studies devoted the estimation of optimal location of measures have primarily studied on-field measures, based on the estimation of nitrogen leaching from the root zone and possible protection areas (Hirt et al., 2012; Andersen et al., 2016; Hiscock et al., 2007; Kunkel et al., 2008; Rode et al., 2009). Most studies only consider either the groundwater or surface water system, but fail to include the entire hydrological system and are thereby not able to evaluate whether the optimal location of measures are on-field or in-stream.

Studies at the Baltic Sea scale (Stålnacke et al., 2015) and for Finnish catchments discharging to the Baltic Sea (Lepistö et al., 2006; Huttunen et al., 2016) found a generic relationship between nitrogen retention and the areal fraction of lakes in the different catchments, indicating that retention in lakes is dominating, when the percentage of the area covered by lakes is high. Groundwater is, however, the linkage between the root zone and the surface water system, and nitrate removal was found to be dominated by subsurface processes in other studies within the Baltic Sea Basin, with a small percentage of lakes (Hansen et al., 2009; Hesse et al., 2013; Windolf et al., 2011). Although reduction in groundwater is an important process, it is most commonly only included in a lumped approach in nutrient modelling studies. In a review of the current state of distributed catchment nutrient water quality modelling Wellen et al. (2015) found that most modelling concepts are based on empirical descriptions of groundwater at sub-catchment level, and of the 275 scientific studies included in the review they reported only one study that includes directly simulations of groundwater flow. Some recent studies emphasizes the need to include the groundwater nitrate transport more explicitly in the models (Hesser et al., 2010; Rode et al., 2010), but such studies have primarily been restricted to detailed small scale studies, with few exceptions such as the Danish national nitrogen model (Højberg et al., 2015).

Knowledge on how much and where nitrogen is degraded in the groundwater is a prerequisite for designing optimal cost-effective mitigation measures utilising the natural nitrogen reduction in the subsurface. Spatially variable nitrate reduction in groundwater has, however, only been considered by few studies, either by detailed geochemical modelling (Wriedt and Rode, 2006; Hesser et al., 2010), or by the estimation of travel times and the association of different first-order decay rates for different geological formations (Kunkel et al., 2008; Wendland et al., 2004; Tetzlaff et al., 2013). Assuming the subsurface to be divided into an upper oxic part with no nitrate transformation and a lower reduced part with instantaneous removal of nitrate, Hansen et al. (2014b) studied the impact of a spatially heterogeneous redox interface on the reduction of nitrate in the groundwater. No previous study has focused on the spatial heterogeneity at the Baltic Sea scale. The objectives of the present study are thus to:

- Provide a review of studies addressing nitrate reduction in groundwater in the Baltic Sea Basin
- Develop a map of nitrate reduction in groundwater in the Baltic Sea Basin with best possible spatial resolution, based on a compilation of existing knowledge

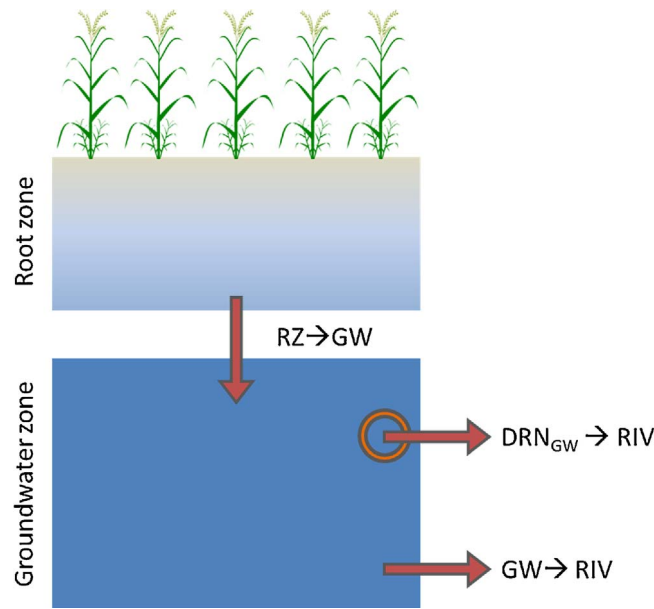


Fig. 1. Concept figure for nitrate transport in the root zone and the groundwater zone. RZ → GW: N-leaching from the root zone to the groundwater zone; DRN_{GW} → RIV: transport from groundwater to river by drainage; GW → RIV: transport from groundwater to surface water.

2. Materials and methodology

2.1. Approach

Nitrate reduction in groundwater has been assessed to various degrees by the countries in the Baltic Sea Basin. While laboratory and plot to small catchment scale studies have been undertaken in most of the countries, few have assessed it at regional or national scale and evaluated the importance for the total nitrogen load to the Baltic Sea. In Denmark, Sweden and Germany regional to national scale models have been developed, which have been used to quantify the nitrate reduction in groundwater and its spatial variation. For the other countries there is no reporting in the international literature on nitrate reduction at national scale, and information was thus insufficient for the construction of a groundwater nitrate reduction map for the entire Baltic Sea Basin.

As part of the BONUS project Soils2Sea (www.soils2sea.eu) a workshop with national experts from Finland, Lithuania, Poland, Sweden and Denmark, was therefore arranged with aim of 1) providing an updated overview of national studies on nitrate reduction in groundwater at various scales, and 2) develop an approach to quantify nitrate reduction in groundwater based on existing studies in the countries and available data at national scale. In addition to the participating countries, groundwater reduction for the part of Germany discharging to the Baltic Sea was included in the final map, based on detailed studies on nitrate reduction in groundwater reported in the literature.

2.2. Definitions

Nitrate reduction is in the present study defined as the difference between the nitrogen lost from the root zone and found in the surface water system. Using the notation in Fig. 1, reduction in the groundwater (Nred_{GW}) is given by:

$$Nred_{GW} = \left(1 - \frac{DRN_{GW} \rightarrow RIV + GW \rightarrow RIV}{RZ \rightarrow GW} \right) \times 100\% \quad (1)$$

Where RZ → GW is N-leaching from the root zone to the groundwater zone, DRN_{GW} → RIV is transport from the groundwater to the surface water system by drainage and GW → RIV is transport from groundwater to the surface water system.

2.3. Nitrate reduction processes in groundwater

2.3.1. Redox conditions

Nitrate can be transformed naturally by reduction where nitrate acts as the electron acceptor. The reduction process have several intermediate stages (NO₂[−], NO and N₂O), but N₂ is the predominant reaction product. Reduction of oxygen has the highest energy yield and is thermodynamically preferred and nitrate reduction therefore only occurs under anaerobic conditions. Furthermore, an electron donor must be present for nitrate reduction to occur. In Quaternary glacial sediments the most important electron donors in the reduction of nitrate are organic carbon, pyrite (FeS₂) and structural Fe⁺² in some minerals (Pedersen et al., 1991; Postma et al., 1991; Korom, 1992; Rodvang and Simpkins, 2001; Appelo and Postma, 2005). Dissimilatory nitrate reduction to ammonium (DNRA)

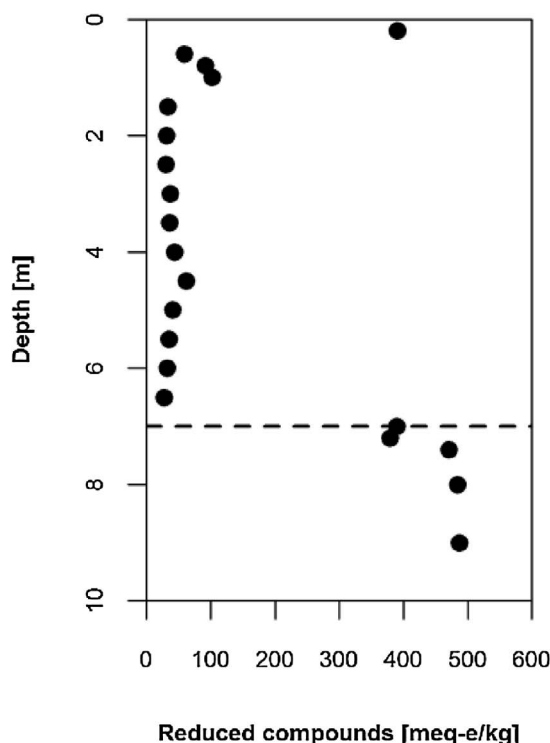


Fig. 2. Amount of reduced compounds (meq e⁻/kg) at different depths in a till sediment (left), figure from Hansen et al. (2014a), and (right) colour change in till sediment from brown to grey indicating the location of the redox interface, picture from Ernstsén (2013).

has recently been shown to occur under certain conditions (Behrendt et al., 2013; Necpalova et al., 2012).

Nitrate reduction by organic carbon is referred to as denitrification and is a well-documented process in the saturated zone (Bradley et al., 1992; Starr and Gillham, 1993; Klimas, 1996). Oxidation of organic carbon is catalysed by microorganisms (Korom, 1992) and the reactivity of the organic matter is often controlling the reaction rate (Appelo and Postma, 2005). Nitrate reduction by pyrite has also been reported in several studies (Kolle et al., 1983; Pedersen et al., 1991; Postma et al., 1991; Robertson et al., 1996; Jorgensen et al., 2009) and is also mediated by microorganisms (Appelo and Postma, 2005; Jorgensen et al., 2009). Nitrate reduction by organic carbon is thermodynamically favoured over pyrite (Korom, 1992). However, the sequence of these two reactions is also determined by reaction kinetics. Studies have shown that the reaction with pyrite can be more important than organic carbon in cases where the reactivity of the organic matter is low e.g. if the organic matter is old or has a high molecular weight (Kolle et al., 1983; Postma et al., 1991; Wriedt and Rode, 2006). Finally, the reaction with structural Fe⁺² in minerals (clay minerals and some silicate minerals) has been reported as both a microbial (Ernstsén et al., 1998b; Weber et al., 2001) and chemical process (Postma, 1990; Ernstsén, 1996; Ernstsén et al., 1998a).

The total reduction potential available in a sediment for reducing nitrate (or oxygen) can be expressed by the term redox capacity, which is the total amount of reduced compounds (organic carbon, pyrite, Fe⁺²) in the sediment and can be estimated as a lumped measure not discriminating between the individual reduced species. The content of reduced compounds is lower in sandy materials than clayey materials (Ernstsén et al., 2001; Ernstsén, 2013; Postma et al., 1991). Hansen et al. (2014a) measured the amounts of reduced compounds at different depths in a borehole located in the clayey till Lillebæk catchment in Denmark, Fig. 2. The transition from low to high amounts of reduced compounds at approximately 7 m depth corresponds to the redox interface.

The redox condition of the sediment and location of the redox interface can be estimated directly in the field from the sediment colours (Ernstsén and Morup, 1992; Ernstsén, 1996; Hansen et al., 2008; Pedersen et al., 1991; Robertson et al., 1996). Oxidized sediments have red, yellow and brown colours, whereas reduced sediment have grey and black colours. The change from oxidized to reduced conditions at the redox interface can therefore be observed as a change in the sediment colour, as found by Ernstsén (2013), Fig. 2. The redox potential can also be measured by the voltage difference between an inert and a standard hydrogen electrode. In aerated soils the applicability of redox potential has been criticized (Bartlett and James, 1995), but under reduced conditions redox potential is found to give results that are comparable to values obtained in the laboratory (e.g. Connell and Patrick 1968; Pan et al., 2014) and in fields (Patrick et al., 1996; Mansfeldt 2004), especially when iron and/or sulphur are present in abundance.

2.3.2. Spatial and temporal variations

In areas where the stratigraphy is more or less uniform a well-defined redox interface can be found. A well-defined upper oxic zone above an anoxic zone was e.g. found by Postma et al. (1991) in the sandy Rabis Creek, Denmark, and in Finnish acid sulphate soils by Palko (1994). In areas where the stratigraphy is more complex multiple redox interfaces can exist (Robertson et al., 1996;

Ernstsen, 2013), and anaerobic micro-environments can be found above the redox interface (Fujikawa and Hendry, 1991; Pedersen et al., 1991; Ernstsen et al., 1998b).

The spatial variability of depths to the redox interface can locally be large. Several studies have reported that the location of the redox interface in tills can vary several meters over short horizontal distances (Fujikawa and Hendry, 1991; Ernstsen, 1996; Hansen et al., 2008). Spatial heterogeneity of the redox interface have been addressed by Hansen et al. (2008) and Hansen et al. (2014a) by means of variogram analysis. Using borehole data with a spacing of 200 m Hansen et al. (2008) found no correlation in observed redox depths in a clayey till area on the island of Funen in Denmark. Using a finer spacing between cores Hansen et al. (2014a) found a correlation length of 289 m for a clayey till area in the eastern part of Jutland in Denmark.

The redox capacity in a sediment is being depleted when nitrate and also oxygen is reduced. Due to the continuous supply of oxygen and nitrate with recharging water the redox interface is therefore not static but moving downwards with time (Bohlke et al., 2002; Postma et al., 1991; Robertson et al., 1996; Wriedt and Rode, 2006). The depth to the redox interface is thus dependent not only on the redox capacity, but also the age of the sediment, the downward water flux and land use, i.e. whether nitrogen has been applied on the surface or not (Ernstsen et al., 2001; Virtanen et al., 2016). Today both oxygen and nitrate act as oxidants, but nitrate input has only been high for the last 60–70 years. For pre-anthropogenic conditions, with only input of oxygen, Robertson et al. (1996) reported a vertical migration rate of the redox interface of 0.04 cm/yr in till sediments of Wisconsinian age. In sandy aquifer materials, Bohlke et al. (2002) reported a vertical rate of 0.26 cm/yr and Postma et al. (1991) reported a vertical rate of 0.34 cm/yr. The present high input of nitrate has accelerated the migration rate of the redox interface. For input of both oxygen and nitrate Robertson et al. (1996) reported a vertical rate of 0.1 cm/yr, Bohlke et al. (2002) a vertical rate of 2.2 cm/yr and Postma et al. (1991) 1.8 cm/yr. Assuming a low pyrite concentration Wriedt and Rode (2006) simulated a significantly higher vertical rate of 10 cm/yr for input of both oxygen and nitrate in a till of Saalian age. The variations in migration rates are caused by differences in amount of redox capacity of the sediments, concentration of oxygen and nitrate and the vertical flux. Mass balance calculations indicate that the reserve of reduced compounds in young tills (Weichselian and Wisconsinian age) under natural groundwater flow conditions, i.e. not forced groundwater flow due to abstraction or similar, is large enough to reduce nitrate for at least 100 years (Rodvang and Simpkins, 2001; Hansen et al., 2014b).

3. State-of-the-art in the Baltic Sea Basin

3.1. Site description

The total area discharging to the Baltic Sea comprises 1,720,270 km², which is just above four times larger than the area of the Baltic Sea itself. The Basin spans large climatic variations with annual mean temperatures and precipitation ranging from 0 °C and 400 mm in north to 10 °C and 1000 mm in south. Agriculture takes up 60–70% of the land in the southern countries Denmark, Germany and Poland. Forestry becomes more important towards the north, and agriculture only accounts for approximately 10% in Finland and Sweden, while Latvia, Estonia and Lithuania are in the middle range with 30–50% agricultural land (HELCOM, 2004). The most intensive agriculture in terms of nutrient application is found in Denmark, Germany and southern part of Sweden, and the least intensive countries are Latvia, Estonia and Lithuania (HELCOM, 2015).

3.2. Studies in the Baltic Sea

For some countries estimates of nitrate reduction could be obtained from large-scale or national scale modelling. Where such studies did not exist, estimates were based on national subsurface maps and knowledge obtained from national monitoring programmes. Different approaches have thus been utilised by the different countries. To homogenize the assessment an initial analysis were carried out for Denmark, where groundwater reduction had been estimated from national modelling. Based on the model results and national data, it was analysed how soil types and drainage percentage could be used to estimate a reduction category (low, mean and high), which were used as guidance in situations, where no more detailed data were available.

A summary of the approaches and information used in the different countries are provided in Table 1, while a detailed description is provided in the sections below.

3.2.1. Denmark

The part of Denmark discharging to the Baltic Sea is dominated by young till sediments from the Weichsel glaciation. The clayey till sediments have a high content of reduced compounds dividing the subsurface into an upper predominantly oxidized and lower reduced part. Due to the relatively short exposure time of the sediments (compared to sediments of Saalian age or older) the redox interface are found at shallow depths within 1–5 m from the ground surface in most of the area, Ernstsen et al. (2006). The shallow redox interface together with a groundwater dominated hydrology leads to a large N-reduction in groundwater in Denmark (Hansen et al., 2009; Windolf et al., 2011; Højberg et al., 2015).

3.2.1.1. Local scale studies. Several local studies exist from Denmark of which the best known is the Rabis Creek study by Postma et al. (1991). The studies have found high nitrate concentrations in the oxidized zone and very low concentration or concentrations below the detection limit in the reduced zone below the redox interface (Ernstsen and Morup, 1992; Ernstsen, 1996; Ernstsen et al., 1998a; Hansen et al., 2008; Pedersen et al., 1991; Postma et al., 1991). The studies by Ernstsen (1996) and Ernstsen and Morup (1992) included age dating of the groundwater by tritium, which showed that the groundwater was infiltrated after intensification of

Table 1

Summary of method and data/tools used to produce the map for nitrate reduction in groundwater in the countries included in the study.

Country	Method	Data/tools	Resolution	Reference
Denmark	National modelling	Combination of process based, fully distributed modelling of transport in groundwater and drains, and statistical models for N-leaching from the root zone and N-retention in the surface water system	Catchments with mean size of 15 km ²	Højberg et al. (2015)
Sweden	National modelling	Two versions of the process based and semi distributed HYPE model: S-HYPE and SMED-HYPE	Catchments with mean size of 14 km ² all with unique distributions of HRUs of variable size	Strömqvist et al. (2012)
Finland	Modelling of observed catchments and extrapolation of model results to the rest of the country	MESAW, a statistical model for source apportionment and retention of riverine loads of pollutants	Catchment scale 360–5000 km ²	Rankinen et al. (2016)
Lithuania	Combining information on geology and recharge. It is assumed that the nitrate reduction capacity is highest in clay and lowest in sand and that N-reduction is lower where the recharge is high	National maps of 1. Quaternary geology 2. Shallow gw recharge	1:200 000	Guobytė (1998), P & tys (2013)
Poland	Combining information on: 1) major hydrogeological units: fissured aquifers with no or very limited N-reduction and Quaternary porous aquifers where N-reduction can take place; 2) dominating lithology with varying N-reduction capacity (Table 2), and 3) artificial drainage, where the N-reduction potential decrease with increasing drainage intensity	National maps of 1. Hydrological Provinces 2. Dominating lithologies 3. Fraction of drained areas	First order catchments with mean size of 12 km ²	Witczak (2011)
Germany	Mean estimate from modelling for the federal state of Mecklenburg-Vorpommern and transferring this estimate to the federal state of Schleswig-Holstein	A model complex consisting of a nutrient and a water balance model, and reactive transport models for N-transport in soils and groundwater	Model calculation in 100 m grids, but averaged for the federal states	Wendland et al. (2004)

agriculture. Nitrate free groundwater below the redox interface was thus not caused by nitrate free water at the time of infiltration, but must be ascribed to denitrification. Not many of the Danish studies have quantitatively assessed the denitrification rate. Jørgensen et al. (2009) conducted a lab experiment with sandy aquifer sediment from an agricultural site at Fladerne Creek and found a denitrification rate of 2–3 $\mu\text{mol NO}_3^- \text{ kg}^{-1} \text{ day}^{-1}$. Column experiment in the lab on clayey till columns from an agricultural site in Grundfør Jørgensen et al. (2004) found denitrification half-lives ($T_{1/2}$) of 0.11 days (1.7–2.2 m depth) and 0.8 days (2.4–2.9 m depth).

3.2.1.2. Catchment scale studies. At catchment scale the amount of nitrate reduction in groundwater has been estimated using distributed hydrological models for Karup catchment (Styczen and Storm, 1993a,b; Refsgaard et al., 1999; Thorsen et al., 2001), Odense catchment (Refsgaard et al., 1999; Hansen et al., 2009; Hoang et al., 2014), Horsens Fjord catchment (Hinsby et al., 2012) and Norsminde Fjord catchment (Hansen et al., 2014a,b).

The most detailed catchment scale studies on N-reduction in groundwater in Denmark are carried out by Hansen et al. (2014a, b) for Norsminde Fjord catchment. In these studies, maps of groundwater N-reduction were produced on 100 m scale using particle tracking and assuming instantaneous N-reduction below the redox interface. A spatially distributed redox interface was estimated based on the recharge flux and the redox capacity of the sediments (Hansen et al., 2014a), and the uncertainty on the nitrate reduction map due to geological uncertainty was estimated using stochastically generated geological models (Hansen et al., 2014b). Within a 37 km² study area groundwater reduction varied from 0 to 100% and the standard deviation between the geological models was up to 40%. The studies showed that N-reduction in groundwater may be both highly variable and uncertainty at local scale.

3.2.1.3. National scale studies. National estimates of total N-reduction have been assessed in national projects, with the latest being the study by Højberg et al. (2015). They developed a national nitrogen model consisting of a statistical N-leaching model (NLES), a coupled surface water groundwater hydrological model setup in MIKE SHE on 500 m grid (Højberg et al., 2013) and statistical models describing N-retention in surface waters. Groundwater reduction was simulated by particle tracking and assuming instantaneous and complete reduction below the redox interface. The model was calibrated to stream data on N-transport for a 21-year long period, and used to estimate surface water and groundwater reduction of nitrogen with a spatial resolution of approximately 15 km², as shown in Fig. 3 for groundwater reduction. The redox interface used in the model was developed from approximately 13,000 borehole data and manual interpretation based on soil types, landscape morphology and auxiliary geological data (Ernstsen et al., 2006) (Fig. S1).

3.2.2. Sweden

Sweden is dominated by bedrock and relatively thin till soils from the Weichselian glaciation, with a relatively shallow

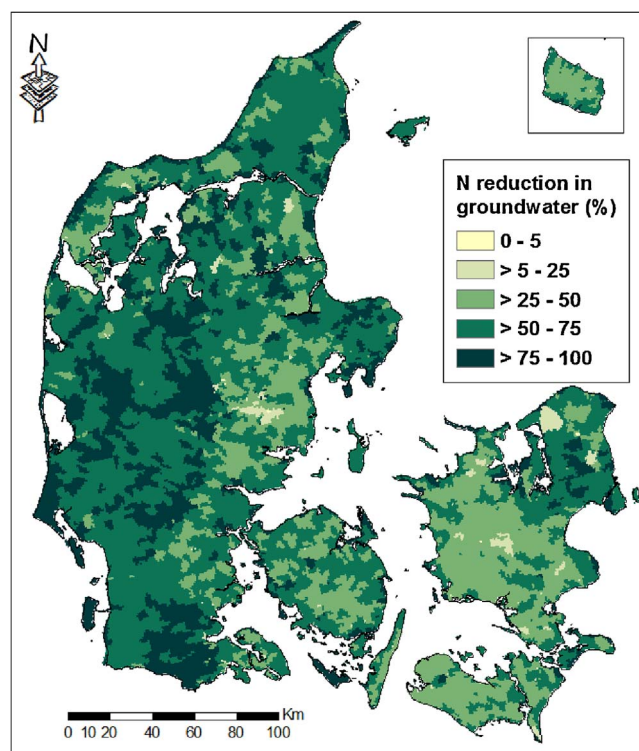


Fig. 3. Groundwater N-reduction map for Denmark, modified from Højberg et al. (2015).

groundwater table. The groundwater resource used for exploitation is primarily associated to porous sediments, while the crystalline rock underlying most of Sweden has smaller water bearing capacity and sedimentary rocks covers a smaller geographical area. Discharge in the till soil landscape is dominated by groundwater, with surface runoff generally only occurring during times of saturation, for example during major snow melt events. Agriculture is mainly concentrated to a few areas in Sweden with post glacial soils. Around half of the arable land is tile drained. Major groundwater aquifers utilised for water abstraction are found in the eskers in the central and southern part of the country. Redox conditions in the subsurface are not examined routinely in Sweden and it is thus difficult to estimate nitrogen reduction capacity of soil layers from national data directly.

3.2.2.1. Local scale studies. Few studies on nitrate reduction in groundwater have been carried out in Sweden. Maxe (2015) made an analysis of nitrate concentrations from sampling of Swedish wells and found correlations with land use, soil characteristics, well type and chemical characteristics of the groundwater. Concentrations of nitrate in the wells were negatively correlated with distance from agricultural fields. Soil clay content on agricultural soils also influenced the nitrate concentration, with a higher likelihood to find high nitrate concentrations in soils with low clay content. The study also looked at correlation with the redox status of the groundwater determined by the concentrations of iron, manganese and sulphate in the samples from the wells. Elevated nitrate concentrations were mainly found in water with high redox potential. Of the samples with low redox potential most were found in wells in the south-west of Skåne, the southern-most county of Sweden. However, this study does not allow for detailed mapping of nitrate reduction in Sweden. Arheimer and Brandt (1998) found in a modelling study that much of the nitrogen retention in southern Sweden takes place in lakes and main rivers in the different catchments, but that locally retention in groundwater and small streams/ditches, contributes significantly in many areas.

3.2.2.2. National scale studies. While N-transport at national scale has been estimated by modelling studies, no studies have assessed the groundwater reduction and its impact on the total N-load to the Baltic Sea. In the present study, the groundwater reduction map for Sweden was developed on the basis of two model systems; the S-HYPE and SMED-HYPE. S-HYPE (Strömqvist et al., 2012) is the national application of the HYPE model for Sweden. HYPE (Lindström et al., 2010) is a process based semi distributed model with integrated calculations of hydrology and nutrients in soils, groundwater and surface waters. In a typical HYPE application the landscape is divided into sub catchments, each with different distributions of hydrological response units (HRUs) comprising unique soil and land use combinations. Each HRU is simulated as a soil profile with up to three layers of which the top two layers constitute the root zone. Simulated runoff and leaching of nutrients from the different soil layers (and tile drains) are routed through the hydrological network of local rivers, main rivers and lakes.

The SMED-HYPE modelling system was developed for periodic reporting of nutrient loads from Sweden to the Baltic Sea for HELCOM. The SMED-HYPE system works in a similar way to the S-HYPE but instead of using the HYPE model's own root zone

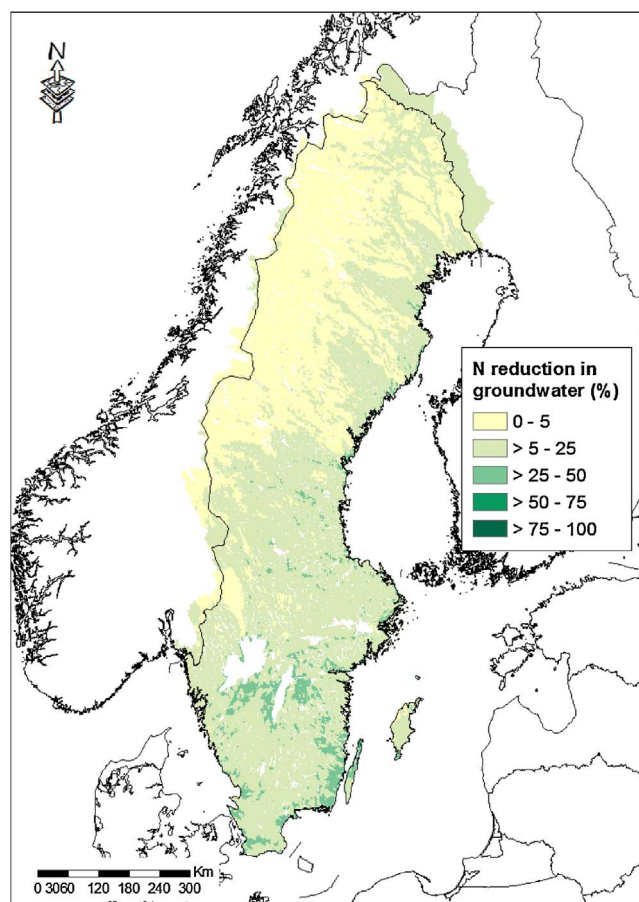


Fig. 4. Groundwater N-reduction map for Sweden.

leaching it uses root zone nitrogen leaching values from the SOIL-N model (Bergström et al., 1991) for agricultural areas and standard leaching values for other land uses. Additionally, N-transport and reduction in the groundwater system and small streams/ditches, i.e. transport and reduction between the root zone and major streams, are described by a lumped process in SMED-HYPE (Tengdelius-Brunell et al., 2016), while the processes are described separately in S-HYPE, Fig. S2.

Due to the different model structures, groundwater reduction was calculated in different ways. For S-HYPE the retention was calculated as the ratio between the reduction of inorganic nitrogen in the ground water zone and the sum of the root zone leaching and losses through direct runoff to the stream network from the upper soil, including tile drain flow. For SMED-HYPE, which does not separate between retention in groundwater and in local streams and ditches, retention was calculated by comparing the gross load from root zone leaching and the load to the main river in each sub catchment. The two modelling systems are assumed to be equally good and the final retention map is hence calculated as the mean of the retention estimated by the two models, Fig. 4.

3.2.3. Finland

The soils in Finland consist mainly of till and sediments from the Weichselian glaciation as well as post-glacial sedimentary soils and peat (Fig. S3). The depth of soils is variable and bedrock can be uncovered or located at 100 m depth, but the mean thickness is only 8.5 m. Major groundwater aquifers utilised for water abstraction are found in the eskers, similarly as in Sweden. The land area in Finland increases continuously due to isostatic land uplift, adding 50,000 km² to the land area since the Litorina stage. Recent studies (Beucher et al., 2015) have estimated that 5–12% of the Litorina soils in Finland may contain acidic sulphate (AS) soils and up to 1300 km² of the AS soils are cultivated. Even though AS soils contain a substantial amount of sulphides (up to 2% w/w) the nitrate leaching is high from these areas.

Water saturation of the entire soil profile is common during snow melting in spring or autumn rainfalls but during summer and winter the groundwater drops deeper. Drainage is a prerequisite for cultivation in Finland. Some fields still have open ditch drainage, but 75–88% of the fields are subsurface drained in the southern and south-western parts of Finland, where 50% of the cultivated fields consist of clay soils. In cultivated subsurface drained fields the groundwater may drop up to 2 m below the drains in summer (Äijö et al., 2014; Österholm et al., 2015) exposing subsoils for atmospheric oxygen and converting redox conditions from reduced to oxidized. The mean depth of redox interface in cultivated fields determined by redox potential measurements was found to be 1.5 m (Puustinen et al., 1994), Fig. S4. In AS soils the redox interface was closer to soil surface in clay soils than in coarser soils (Virtanen

et al., 2016) which contain less sulphides than finer-textured AS soils.

3.2.3.1. Local scale studies. Forest and peat land are the dominant land use types in Finland and therefore the largest volume of water discharges from these areas to the Baltic Sea, generally with very low nitrate concentrations. In forests, nitrate loads originate mainly from organic nitrogen and atmospheric deposition, but forestry management practices increase nitrate leaching to surface waters (Piirainen, 2007) and also nitrate concentrations in groundwater (Kubin, 1998).

From agricultural fields, the leaching of nitrogen (mainly in the form of nitrate) have been studied in long-term experiments (e.g. Seuna and Kauppi, 1981; Turtola and Paajanen, 1995; Äijö et al., 2014). Results have been analysed by balance calculation (e.g. Salo and Turtola, 2006; Äijö et al., 2014) as well as by modelling (e.g. Karvonen et al., 1999; Knisel and Turtola, 2000; Rankinen et al., 2007; Salo et al., 2015). Only few modelling studies consider nitrification or denitrification during water flow from soil surface to drain pipes or transport in groundwater separately because the N-load to rivers from groundwater and denitrification in the subsurface have been considered low (Seuna and Kauppi, 1981). However, in an AS soil field, the lack of nitrate below drainage depth was attributed to denitrification or other reducing processes (Simek et al., 2011).

3.2.3.2. Catchment scale studies. In forest catchments, hydrological processes and the major processes controlling the N losses including denitrification have been modelled (e.g. FEMMA model, Laurén et al., 2005), but the denitrification was found to be minuscule. In agricultural areas, catchment scale nitrogen leaching have been estimated using data from a network of small hydrological catchments and national monitoring data from river catchments (e.g. Rekolainen, 1993; Tattari et al., 2015), by nitrogen balance of fields (e.g. Salo and Turtola, 2006) and by modelling (Puustinen et al., 2010; Granlund et al., 2007; Rankinen et al., 2016). However, denitrification in groundwater has not been quantitatively assessed at catchment scale. In a state-of-the-art study Randall et al. (2014) noticed that the lowest measured nitrogen concentrations were below the lowest modelled concentrations, suggesting that some reduction processes may be missing in the model.

3.2.3.3. National scale studies. From mass balance studies, including the majority of catchments in Finland, Rekolainen (1993) estimated that approximately one fourth of the N surplus from agricultural fields is lost to the surface water system and an equal proportion removed by denitrification. Denitrification in groundwater was, however, not separated from denitrification occurring in root and vadose zone in their study. In well-structured heavy soils Paasonen-Kivekäs et al. (1999) found that nitrate concentration in surface water was nearly equal to that in the drain water, while the nitrate concentration in groundwater was only 2% to 16% of the surface water concentration. This implies that drainage is the major transport pathway for nitrate from agricultural fields to surface water at the study site. The low nitrate concentrations in the groundwater indicate that nitrate reduction may occur below the drains but due to the very low hydraulic conductivity of the clayey subsoils, the vertical flux below the drainage system is very limited. Defining groundwater reduction as the difference between the root zone leaching and loads to the surface water, the total groundwater reduction for such well-drained soils is low.

From the past studies (e.g. Seuna and Kauppi 1981; Paasonen-Kivekäs et al., 1999), reduction of N in groundwater appears to be very limited in Finland. This may be related to the fact that the highest N losses occur during autumns and springs in events which are reported to take only a few days. The rapid outflow and low temperature limits microbial activity and thus the denitrification or other N reducing processes. In summer, when temperature is higher, high groundwater levels might result in nitrate reduction by denitrification and decrease nitrogen losses from soil to sea.

Retention for all catchments in Finland has previously been estimated by Lepistö et al. (2006) and Huttunen et al. (2016) as a total catchment scale retention, i.e. with no differentiation between surface water and groundwater. At a more detailed scale Rankinen et al. (2016) have estimated the retention using the MESAW model for 20 catchments. None of the previous studies have, however, assessed the N-reduction in groundwater. In the present study, results from Rankinen et al. (2016) was therefore analysed and the total catchment retention estimated for the 20 catchments was divided into surface water retention and groundwater reduction, respectively. For each catchment a relation between the estimated groundwater reduction and the areal fraction of eskers in the catchment, was established. Like in Sweden, the dominant groundwater aquifers are associated to the eskers, which have thus been used as a proxy for the size of the groundwater aquifers. The relation between the area of the eskers and the groundwater reduction was used to divide the total catchment scale retention by Lepistö et al. (2006) and Huttunen et al. (2016) into surface retention and groundwater reduction for the remaining part of the country not covered by the 20 catchments. The national N-reduction map for Finland is provided in Fig. 5.

3.2.4. Lithuania

Lithuanian is dominated by sandy and clayey Quaternary sedimentary cover of glacial origin, whose thickness varies from 10 to 100–200 m. Pre-Quaternary sandy, clayey and carbonate sediments are found below the Quaternary and the thickness of the active groundwater exchange zone is 200–300 m (Grigelis et al., 1994). The chemical status of groundwater, including nitrogen compounds as well as redox potential, are monitored in all main aquifers as a part of the national groundwater monitoring programme for more than 40 years. Groundwater chemistry is controlled by the petrographical and mineralogical composition of aquifer and aquitard deposits, as well as the connection to surface water and atmosphere (i.e., their confinement degree). One or two aquifers can typically be found in a vertical section through the Quaternary deposits, but in some places up to five or six exists, where intermediate confined groundwater is the transitional type of groundwater between unconfined and deep confined groundwater. They are usually hydraulically interconnected and may have good hydraulic contact with both underlying artesian water and overlying unconfined groundwater. Deep, confined water can be found in deposits of all geological ages and is one of the main sources for large, public

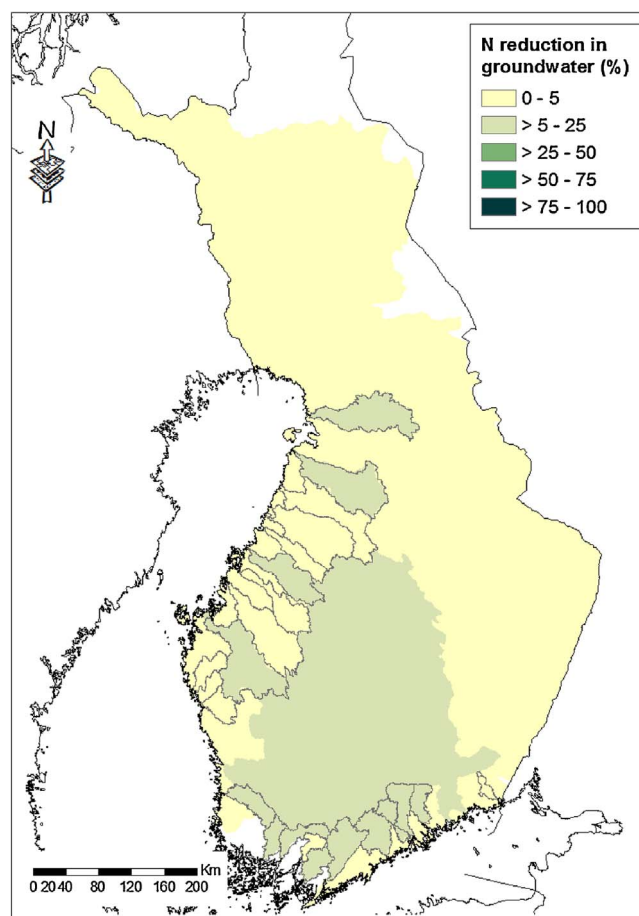


Fig. 5. Groundwater N-reduction map for Finland. Catchments subject to detailed studies by Rankinen et al. (2016) and used to extrapolate groundwater reduction to the entire Finland are indicated by black outline.

water supplies in Lithuania. In recharge areas (topographical highs) deep confined groundwater is recharged from intermediate confined and unconfined groundwater. Reduced environments are found in various depths in the subsurface stimulating removal of nitrate by denitrification.

3.2.4.1. Local scale studies. The lateral and vertical distribution of nitrogen and the distribution of oxidized and reduced nitrogen species in groundwater were studied by Klimas and Paukstys (1993). In aquifers with high oxygen concentrations, nitrogen is mostly found as nitrate, while ammonia concentrations are low. Anoxic conditions often occur in confined aquifers, where the redox potential may be controlled by iron and nitrogen predominantly is found as ammonia. It appears that the low nitrate and elevated ammonium contents typically found in deep confined groundwater are the result of the chemical reduction of nitrate to ammonium in aquitards below unconfined aquifers (Klimas and Paukstys 1993).

Depth to the redox interface has been studied based on descriptions of change in till sediment colour in more than 1000 wells, where distinction was made between; highlands where the regional recharge is high, river valleys which are predominantly discharge zones; and transit zone between the highlands and river valleys (Klimas, 1996). The results are shown in Table 2, where wells have been divided into three categories depending on the colour changes, where “End of brown/red zone” indicate the transition from oxidized to reduced condition, “Start of grey zone” indicate a more reducing environment; and “start of blackish/greenish zone” the

Table 2

Depth below surface to reducing environment in Lithuania determined from changes in sediment colours (Klimas, 1996).

Hydrogeological zone	Mean depth to change in sediment colour (in m below surface)		
	End brown/red zone	Start gray zone	Start blackish/greenish zone
Recharge	12	36	51
Transit	18	19	34
Discharge	11	12	16

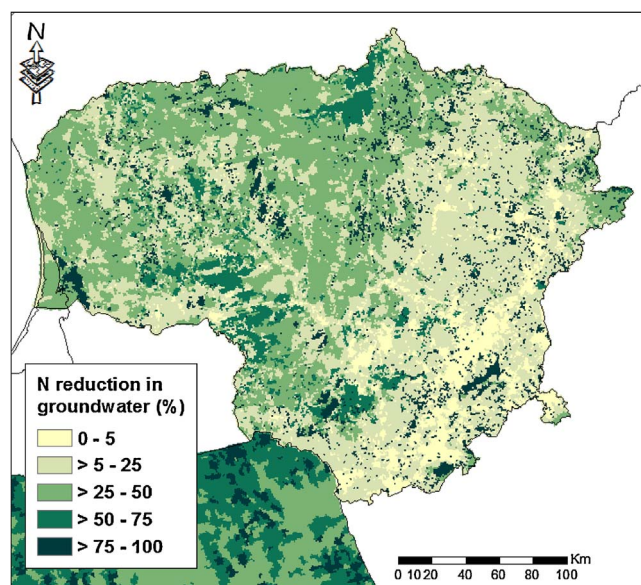


Fig. 6. Groundwater N-reduction map for Lithuania.

most reducing environment. A single or several of the colours may occur within a well. The data confirm the expectations of a deeper redox interface in groundwater recharge areas, where the flux of oxygenated water and nitrate is large, while the interface is found closer to land surface in regional groundwater discharge zones.

An extended study of nitrogen in groundwater (Paukštys, 2011) revealed, that only a small part of nitrogen, applied as fertilisers on land surface, infiltrates to groundwater (1–20%). Highest concentration of nitrates in groundwater is found in catchments, where agricultural activities are most developed (Nevėžis and Šešupė), but the total nitrate loads to surface water bodies are highest in catchments, where recharge to groundwater is highest (Neris, Merkys and Šventoji). Typically, such catchments are located in highlands, dominated by sandy deposits. The nitrate load to rivers in lowlands covered with clayey deposits is far less, which may be attributed to higher reduction potential in clayey deposits.

3.2.4.2. National scale study. A national assessment of N-reduction in groundwater has not been carried out previously for Lithuania. The map developed in the present study is compiled by combining a national map of the Quaternary geology with lithology and genesis of the uppermost deposits, Fig. S5, (Guobytė, 1998) and a map of the shallow groundwater recharge, Fig. S6, (Pūtys, 2013). Based on previous studies (Paukštys, 2011; Klimas, 1996) and groundwater monitoring data it is assumed that sandy deposits with high infiltration rate have a relatively low nitrate reduction potential, clayey deposits with medium and low infiltration rate have medium to high reduction, and peatland is associated with very high nitrate reduction potential. Nitrate reduction has not been the primary focus in previous projects and the present nitrate reduction map for groundwater (Fig. 6), based on existing data and knowledge and a simple index approach, is thus the first attempt.

3.2.5. Poland

99.7% of the Polish area discharges to the Baltic Sea. Northern Poland is dominated by glacial sediments from the Vistulian glaciation with thickness up to more than 300m. The central part is covered by glacial sediments from the Wartanian (Saalian) glaciation with thickness ranging from 10 to 100–200 m, while the southern part is dominated by Mesozoic bedrock covered by Quaternary deposits, mainly loess. Hydrogeological, Poland is divided into two provinces, Fig. S7. The Lowland Hydrogeological Province (LHP) is associated with Quaternary porous aquifers developed mostly in glacial deposits with diverse nitrate reduction potentials. The Mountain-Upland Province (MUHP) prevailing in the south of Poland is associated with fissured, fissured-porous or fissured-karstic aquifers, usually covered with thin Quaternary deposits, inter alia, loess with low denitrification potential (Kleczkowski, 1990; Kleczkowski and Witczak, 1990; Witczak et al., 2010).

In the Polish national monitoring programme, consisting of 1177 observation points, nitrate was found to exceed the quality limit of 50 mg NO₃/L in only 5.1% of the monitoring points for the period 2008–2011 (Rojek et al., 2013). The national monitoring programme is, however, affected by a low density and uneven distribution of monitoring points for shallow groundwater and by the inadequacy of sampling protocols (Alterra, 2007). Consequently, results of the national monitoring network tend to underestimate nitrate levels and many local studies reveal nitrate pollution, especially in shallow groundwater in agricultural areas (e.g. Płochniewski and Macioszczyk, 1983; Błaszyk and Górski, 1989; Żurek, 1991; Mikołajków, 1995; Kaźmierczak-Wijura, 1996; Malina et al., 2007; Ćwiertniewska et al., 2008; Michalczyk et al., 2016).

3.2.5.1. Local to catchment scale studies. Published studies on nitrate reduction in groundwater do not provide a scientific basis for



Fig. 7. Hydrogeological Provinces in Poland: Lowland Hydrogeological Province (LHP) (green colour) and Mountain-Upland Hydrogeological Province (MUHP) (red colour) (after Kleczkowski, 1990). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

relating nitrate reduction potential directly to geological and hydrogeological conditions in different parts of Poland. Nevertheless, groundwater nitrate reduction is generally controlled by hydrogeological conditions, particularly the redox potential, and higher nitrate concentrations are associated with lighter, more permeable soils, while the lowest concentrations occur under clayey soils.

Quaternary aquifers of the LHP, particularly in the valley, ice-marginal valley and intermorenic aquifers, show low redox potentials favouring denitrification (Żurek, 2002), which is often confirmed by high concentrations of iron and manganese (Witczak et al., 2013). In the polluted aquifers, nitrate concentrations distinctly decrease with depth (Dragon et al., 2016). Górski (1989) found a direct relation between the thickness of glacial tills and nitrate concentrations, with 20 m thick till covers providing protection of groundwater from nitrate pollution.

The hydrogeological conditions in the MUHP do not support denitrification in groundwater (Żurek et al., 2010a; Żurek and Mochalski, 2010) as exemplified by observations of high nitrate concentrations in the fissured-karstic (Kryza and Kryza, 2001; Dąbrowska et al., 2005; Malina et al., 2007; Żurek et al., 2010a, 2010b; Śledzik, 2014) and fissured – porous (Żurek, 2007) aquifers.

3.2.5.2. National scale studies. There have been no previous attempts to develop a national map for N-reduction in groundwater for Poland, and in the present study the map was developed by combining existing data at national scale in three steps:

Step 1 – Identification of major hydrogeological units.

Delineation of the two hydrogeological provinces: Lowland Hydrogeological Province (LHP) (represented by green colour in Fig. 7) and Mountain-Upland Province (MUHP) prevailing in the south of Poland (red colour in Fig. 7).

Step 2 – identification of dominating lithology

Nitrate reduction in groundwater is assumed to be proportional to the residence time and the redox potential of the geological formation (lithological type), where the redox potential in till generally is larger in clay compared to sand (Ernstsen, 2013). The classification of lithology from the Groundwater Vulnerability Map of Poland (GVMP) (Witczak et al., 2007; Witczak, 2011) was applied (Table 3, Fig. 8). This classification generally reflects the flow condition in saturated zone and hence the nitrate reduction capacity, with one exception. The semi- and low permeable porous sediments (class 7, Table 3) comprise generally clayey sediments, but also loesses not containing clay particles, which form the protective cover over aquifers in the MUHP. Due to the low hydraulic conductivity in loess, the travel time through the unsaturated zone is high, but the nitrate reduction capacity is low due to oxidizing conditions. The contribution of the semi- and low permeable sediments (class 7) in the unsaturated zone profile that constitute the aquifer cover (C_{lp}) (cf. Fig. 8 and explanations in Table 3) was taken into consideration as a separate layer included in the GVMP (Witczak et al., 2007; Witczak, 2011; Wachniew et al., 2016).

Step 3 – influence of artificial drainage

Assessment of the influence of drainage on nitrate reduction is not straightforward. The density of drainage network is not directly related to the soil conditions but also to the individual farmer's economy and therefore differs significantly between regions ranging from 1% in Lubuskie to 32% in Wielkopolskie (Fig. S8). The installation of the drainage networks occurred mostly before 1990. Since then the density of the functional drains have not increased, but rather decreased due to lack of maintenance. Loadings of nutrients in drainage networks were estimated in several studies (Lipiński, 2002; Fic et al., 2003; Durkowski and Lipiński, 2010).

Only in two voivodships (provinces), Wielkopolskie and Łódzkie, more than 20% of the agricultural land is drained. In the Wielkopolskie Voivodship 32% of the agricultural land is drained. A similar percent of the area is covered by fine grained soils (clays,

Table 3

Classification of typical lithologies of unsaturated and saturated zone (under the root zone) in Poland (from Witczak et al., 2007; Witczak, 2011) with suggested nitrate reduction.

Class number	Groundwater environment	Typical lithologies	Nitrate reduction [%]
1	Permeable fissured-karst	limestones, dolomites	< 10; 20 ¹ ; 25 ²
2	Permeable fissured	granites, metamorphic rocks	< 10; 20 ³ ; 30 ⁴
3	Permeable fissured-porous	sandstones, flysch rocks	< 10; 15 ⁵
4	Permeable porous-fissured	chalk marls, opokas, chalk	15; 20 ⁶ ; 25 ⁷
5	Permeable porous	gravels and sands	60 ⁸ ; 50 ⁹
6	Permeable porous	silty sands, loamy sands, etc.	70
7	Semi- and low permeable porous ($K < 10^{-6}$ m/s)	loess, glacial till, silt, loam, etc.	80 ¹⁰

Explanations: ¹ – for fissured-karst rocks covered with sediments of class no.5; ² – for fissured-karst rocks covered with sediments of class no.6 and no. 7 (only loess); ³ – for fissured rocks covered with sediments of class: no.5; ⁴ – for fissured rocks covered with sediments of class no.6; ⁵ – for flysch rocks with dominated shales; ⁶ – for porous-fissured rocks covered with sediments of class no.6; ⁷ – for porous-fissured rocks covered with sediments of class no.7 (only loess); ⁸–contribution of semi- and low permeable materials in the cover (C_{ip}) equal or higher 0.4 (Fig. 8 – right panel); ⁹–contribution of semi- and low permeable materials in the cover (C_{ip}) equal or lower 0.3 (Fig. 8 – right panel); ¹⁰–does not apply to loess (see text).

silty clays, clay loams) as identified in one of the information layers of the GVMP (Witczak et al., 2007; Witczak, 2011). This correspondence indicates that in this voivodship all fine grained soils in the area have been drained. No relationship between the area of the drained land and soil types was found for Łódzkie Voivodship. The influence of drainage was considered only for Wielkopolskie and for the other voivodships drainage was assumed to have no significant influence on nitrate routing. Due to its similarity in geology and drainage between Wielkopolskie and the drained clayey soils in Denmark, a nitrate reduction of 40% was adopted from the Danish study. The final map for estimated N-reduction in Poland is shown in Fig. 9

3.2.6. Germany

The two northernmost federal states in Germany; Schleswig-Holstein and Mecklenburg-Vorpommern discharge to the Baltic Sea. This part of Germany was covered by ice during the last glaciation (Weichsel). The recent geological history and depositions is thus comparable to the part of Denmark discharging to the Baltic Sea. The importance of geology on local scale N-reduction in the groundwater is therefore expected to be similar to the observations in Denmark.

3.2.6.1. Catchment and national scale. Nitrogen transport and reduction has been assessed for the federal state of Mecklenburg-Vorpommern by Wendland et al. (2015). They utilised a model complex described by Wendland et al. (2004) consisting of a nutrient balance mode, a water balance model (GROWA), a reactive nitrate transport model in soil (DENUZ) and a reactive nitrate transport model in groundwater (WEKU). In the model complex the nitrate reduction is assumed to occur by first-order decay, where rate constants are estimated from groundwater analyses. High and low decay rates are associated to reduced and oxidized groundwater, respectively, while intermediate rates are used for aquifers that cannot be unambiguously categorized as aerobe or anaerobe. Actual reduction in the groundwater is calculated from the decay rates and resident times. Assuming two-dimensional groundwater flow parallel to the groundwater table, residence times are estimated in a GIS approach from groundwater gradient and expected hydraulic conductivity and porosity. Spatial variation in N-reduction in groundwater is thus determined by a combination of the geochemical conditions (assigned from monitoring data) and estimated residence times.

Similar to the Danish conditions, drainage was found to be an important pathway transporting approximately 35% of the N-

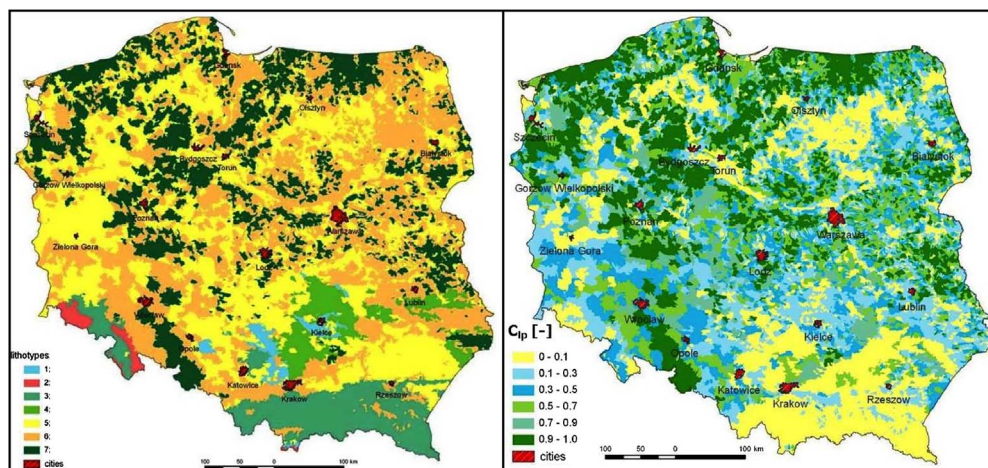


Fig. 8. (left panel) Map of dominating lithologies in Poland with class number as in Table 3 and (right panel) contribution of semi- and low permeable sediments (class 7 of lithologies) in the aquifer cover (C_{ip}) (from Witczak, 2011).

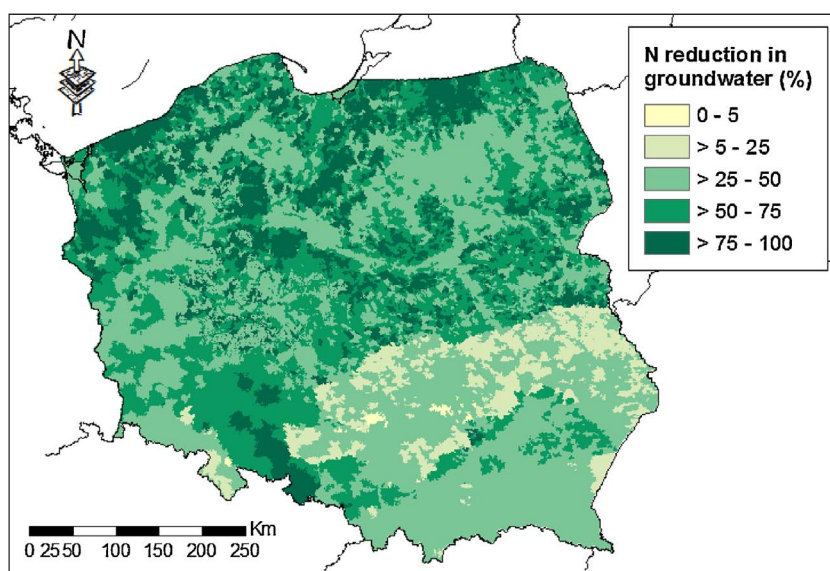


Fig. 9. Groundwater N-reduction map for Poland.

leaching from the fields to the surface water system. For the federal state of Mecklenburg-Vorpommern [Wendland et al. \(2015\)](#) estimated that 54% of the nitrogen leaving the root zone is reduced before it reaches the surface water system. With groundwater reduction being proportional to the residence time, which is determined by the proximity to surface waters, the estimated N-reduction in groundwater is expected to vary at a fine scale. However, since this was not the purposes of the study this variation is not reported and a single N-reduction of 54% is assigned for N-reduction in groundwater for the federal state of Mecklenburg-Vorpommern as well as the federal state of Schleswig-Holstein.

3.2.7. Baltic sea basin scale

The first model study including the entire Baltic Sea Basin in one uniform model setup to study riverine nutrient transport to the Baltic Sea was made by [Mörth et al. \(2007\)](#) using a the lumped hydrological model CSIM. In the model a fixed percentage of nitrogen in manure was assumed retained in the soils, thus no spatial variation was considered, nor was it considered whether retention occurred in the root zone or below.

[Wulff et al. \(2014\)](#) recognised the importance of considering nitrogen retention in the design of cost-effective mitigation measures, as retention between the source and the outlet will impact the effectiveness of the measures. They defined the catchment-scale retention as the difference between anthropogenic nutrient inputs and observed riverine export, which conceptually can be subdivided into retention in soils, groundwater and surface water. Building on the results of the BONUS project RECOCA, [Wulff et al. \(2014\)](#) presented a multi-model approach to describe nutrient transport and retention between the source and the sea, which can be used to evaluate various management options. Retention in the surface water system was calculated by the statistical model MESAW as reported by [Stålnacke et al. \(2015\)](#). The model simultaneously estimates catchment N-loads, using N-export coefficients for different land uses classes, and surface water retention. Model performance was evaluated for 88 measured rivers in the Baltic Sea Basin and the total surface water retention for rivers discharging to the Baltic Sea was estimated to be approximately 40%, with the largest retention occurring in catchments with a high areal fraction of lakes. Using the soil-vegetation-atmosphere model DAISY and a data resolution of 10×10 km, [Andersen et al. \(2016\)](#) developed a regression model for N-leaching for dominant combinations of climate, soils and agricultural management. The regression model was used to estimate N-leaching from the root-zone for the entire Baltic Sea Basin at a resolution of 10×10 km, i.e. much finer resolution than the catchment scale assessed by [Stålnacke et al. \(2015\)](#), from which N-loss hot-spots areas were identified.

[Andersen et al. \(2016\)](#) constructed a mass balance for riverine N-load at the catchment scale. Utilising average riverine N load for the period 1994–2006 from the HELCOM pollution compilation PLC-5, together with the estimated N-leaching from their regression model and surface water retention calculated by [Stålnacke et al. \(2015\)](#), the only unknown in the mass balance was N-reduction in groundwater. Hence, the N-reduction in groundwater was not estimated by an independent approach, but as the residual in the mass balance where N-leaching, surface water retention and long-term riverine N-load is known.

4. Results and discussion

The national maps for N-reduction in groundwater developed in the present study are compiled to a single map in [Fig. 10](#), which for comparison also includes the map by [Andersen et al. \(2016\)](#). For Finland the estimates in the present study is similarly based on MESAW at the same scale. In the remaining countries included in the present study, the reduction is estimated at a finer scale. For Denmark, Sweden and Germany (Mecklenburg-Vorpommern) the estimates are based on the use of models that are conceptually very

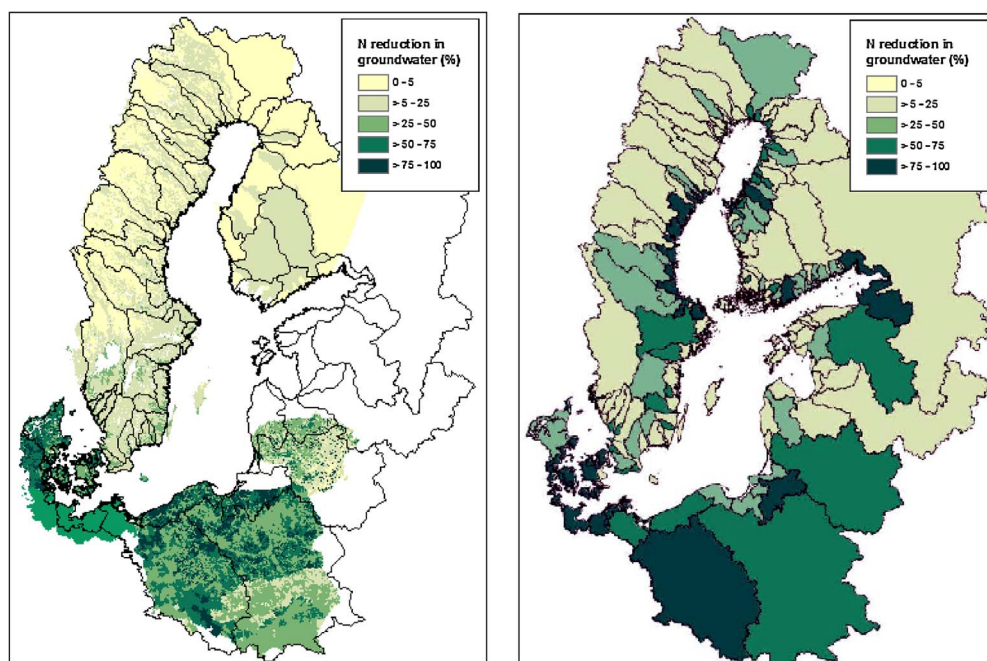


Fig. 10. Nitrate reduction in groundwater as estimated in the present study (left) and by Andersen et al. (2016) (right). Note that the interval 0–5 was not included in the assessment by Andersen et al. (2016).

different but all includes a spatially description to resolve heterogeneity in land use, soil properties and, except for Sweden, subsurface geology at sub-catchment scale. The estimates for Germany were not accessible at the fine resolution and hence only the aggregated value is included in the final map. The estimates for Poland and Lithuania are based on overlay of relevant geological and hydrological maps, and the final resolution in these countries reflects the resolution of the maps used.

Comparing the two maps in Fig. 10 reveals obvious differences with respect to both the magnitude of groundwater reduction and the pattern of high/low values. For Finland the two studies utilises the same model (MESAW) to estimate surface retention at identical catchment scale. However, the estimated groundwater reduction in the coastal catchments is very different, with the estimate of the present study being much lower, which appears to be in better agreement with the local and catchment studies in the country, indicating that although nitrate may potentially be degraded in the groundwater, transport under agricultural fields are dominated by drainage with little N-reduction. Based on the different hydrogeological settings in Poland, and supported by monitoring data and local studies, a distinct difference was found from south to north in the present study, while the result by Andersen et al. (2016) show an east-west division, which cannot be attributed hydrogeological conditions. The details in the maps for Sweden and Lithuania could not be resolve by Andersen et al. (2016) and it is difficult to evaluate how different the estimates are with respect to the total reduction at the catchment scale. The present estimate does, however, tend to estimate lower N-reduction in groundwater for several of the Swedish catchments.

For the two federal states in Germany and the eastern part of Denmark, the estimates by Andersen et al. (2016) indicate high N-reduction, while the present study estimates moderate to low reduction, which is related to the high drainage percentages in these areas. In the work by Højberg et al. (2015), a consistent approach was used to estimate N-reduction for all of Denmark utilising a three dimensional hydrogeological model to describe groundwater flow (Højberg et al., 2013) and data from approximately 340 discharge stations. This study is thus better constrained to data than the approach by Andersen et al. (2016) including only few catchments and only surface water data for Denmark.

In all assessments based on a modelling approach, observed riverine N-loads have been utilised to constrain and evaluate model performance. Hence, the estimated input and retention/reduction in the catchments equals the observations, within a certain model performance. However, N-input (dominated by root zone leaching), retention and riverine N-loads are interlinked. If leaching is estimated too high it must be compensated for by a too high retention. Differences in magnitudes, and to some extent also the pattern, between the two maps may thus partly be ascribed the different approaches used to estimate the N-leaching in the different studies. Retention in surface water and groundwater is similarly interlinked, as the total catchment scale retention is the combination of the two. An overestimation of the surface water retention has to be counteracted by a groundwater reduction that is too low. This was observed by Højberg et al. (2015), who noticed that the model used to describe retention in lakes might overestimate the retention, where multiple lakes are connected, which would result in an underestimation of the groundwater reduction. A similar situation may occur in Andersen et al. (2016), where groundwater reduction is computed as the residual in the catchment scale mass balance for riverine N-load, given that the other variables are known. Finally, the residence time in the subsurface may be significant and must be taken into consideration, as input and output to the groundwater system cannot be balanced directly. Residence times are accounted for differently in the approaches engaging modelling, which may similar contribute to the differences observed in Fig. 10.

In Poland and Lithuania the groundwater retention is estimated based on geological and hydrogeological data combined with monitoring data and knowledge from previous national studies. Since no model study was involved, it is, however, not possible to test the magnitude of the estimated N-reduction by combining estimated leaching, reduction and observed riverine loads.

The two groundwater reduction maps represent two independent estimates. It is not possible to measure the N reduction in the groundwater directly, and it is thus not possible to validate either of the maps directly and provide evidence on which of the maps is most correct. Utilising more detailed data and drawing on local and regional studies we consider the map developed in the present study, in general, to be an improvement compared to the estimate by Andersen et al. (2016).

The groundwater N-reduction map developed in the present study indicates that the spatial variation in nitrate reduction in groundwater can be significant in most countries. This signifies that in many areas there is a potential for utilising the natural N-reduction in future regulations, by focusing the mitigation measures to areas, where the reduction is low. While the map of N-reduction in groundwater is a prerequisite for optimizing N-regulation it is not sufficient. An optimal regulation requires the consideration of both spatial variation in N-leaching, and the variation in N-reduction in both the groundwater and surface water systems. For a groundwater dominated area, Hansen et al. (2017) illustrate how N-regulation can be optimised from N-leaching and N-reduction in groundwater. Such assessments are, however, outside the scope of the present study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ejrh.2017.04.001>.

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