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Groundwater-borne nitrate intakes into surface waters in Germany

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Abstract The nitrogen loads entering the surface waters in Germany via the groundwater path were quantified. For this purpose, the results of a nitrogen balance model (Bach *et al.*, 2000), which considers the most important N-inputs to the soil (manure, inorganic fertiliser, atmospheric deposition) and N-removals from the soil through crop harvest, were combined with the groundwater residence time/denitrification model WEKU (Kunkel and Wendland, 1997; Wendland *et al.*, 2001). The modelled groundwater-borne nitrogen inputs into surface waters were validated using results from the MONERIS model (Behrendt *et al.*, 2000) concerning riverine nitrogen retention, nitrogen inputs from point sources as well as nitrogen inputs through direct run-off (drainage etc.). In the vicinity of surface waters and in solid rock areas, the groundwater borne nitrogen inputs into surface waters are considerably high compared to the inputs into the aquifer due to predominantly unfavourable de-nitrification conditions and short residence times of groundwater. In the North German lowlands, however, the groundwater-borne nitrate inputs into surface waters are considerably low compared to the inputs into the aquifer. There, the residence time of groundwater in the aquifer is high and the groundwater is predominantly oxygen free and contains pyrite and/or organic carbon compounds, allowing a halving of the nitrate loads in the groundwater within a period of 1 to 4 years (see Wendland and Kunkel, 1999).

Keywords Denitrification; groundwater; modelling; nitrate leaching; nitrogen balance

Introduction

All major processes involved in the turnover of nitrogen in soil and water have been thoroughly investigated by numerous scientists. Nevertheless, it has proved to be difficult to model large-scale phenomena, such as the delivery of nitrogen to rivers via groundwater. Both environmental managers and scientists must admit that the inertia of the systems that control the nutrient delivery was underestimated when the goal of a 50% reduction of the input of nutrients to the Baltic Sea and the North Sea was adopted. Several major European rivers have exhibited a remarkable lack of response to the decrease in the use of commercial fertilizers that started in the late 1980s. In the present paper, we present the results of a model analysis that is based on input data and mechanisms that are particularly relevant for the turnover of nitrogen at a spatial scale of river basins or regions and a temporal scale of years to decades.

Method

The approach used for the analysis of groundwater-borne nitrate inputs into surface waters is designed for area-differentiated modelling on a supraregional scale. According to the model's applicability to the entire Federal Republic of Germany, the hydrological, pedological and hydrogeological input parameters needed for modelling were taken from thematic maps. The scale of these maps, ranging from 1:500,000 to 1:200,000, determine the degree of detail of the model input values and define in connection with the suitable model approaches the validity range of the model results. The nitrogen inputs into groundwater are calculated from the nitrogen surpluses reduced by the denitrification losses in the soil related to the groundwater recharge/total runoff ratio. These inputs are transported with the groundwater to the surface waters. On its way nitrate degradation may occur. Thus, a calculation of the groundwater-borne nitrate inputs into surface waters requires knowledge of the groundwater flow paths, the total residence time of the nitrate and the denitrification kinetics in the upper aquifer. These processes were considered by different models.

- Diffuse nitrogen surpluses are quantified with a nitrogen balance model (Bach *et al.*, 2000). Agricultural statistics with data on crop yields, livestock farming, land use, etc. served to balance the actual nitrogen supplies and extractions for the agricultural acreages. The long-term nitrogen balance averaged over several vegetation periods is calculated considering the organic nitrogen fertilization, the mineral nitrogen fertilization, the symbiotic N fixation, the atmospheric N inputs and the N extractions with the crop substance. As a rule, the sum of nitrogen supplies, primarily by mineral fertilizers and farm manure, and nitrogen extractions, primarily by field crops, leads to a positive balance.
- The GROWA98 model (Kunkel and Wendland, 2002) was used to carry out an area differentiated water balance analysis for the hydrological period 1961–1990. The mean long-term total runoff was modelled as a function of the regional interaction of the climate, soil, geology, topography and land use conditions. The total runoff was separated into the direct runoff (interflow and surface runoff) and groundwater runoff (groundwater recharge) using base-flow indices, depending on area characteristics (e.g. geology, depth for groundwater). The total runoff/groundwater recharge ratio was taken as a measure for the extent that diffuse nitrogen surpluses are displaced from soil to groundwater.
- Nitrate degradation in soils was calculated according to Michaelis–Menten kinetics using the approach of Köhne and Wendland (1992). Denitrification losses occur mainly in the effective root zone of the soils, and can be described as a function of the nitrogen surpluses, the average field capacity and the site-specific denitrification conditions.
- Reactive nitrate transport in groundwater is modelled with the WEKU-model (Kunkel *et al.*, 1999). In the first step groundwater velocities are calculated according to Darcy's law from hydraulic conductivity, effective yield of pore space of the aquifer and the slope of groundwater surface (hydraulic gradient). The calculation of the residence times of the groundwater runoff is performed in a second step. Based on groundwater contour maps, a digital relief model of the groundwater surface is generated. This is analysed paying attention to information on the water network as well as the groundwater discharge or transfer areas with respect to lateral flow dynamics and groundwater-effective recipients. The residence times of the groundwater runoff are then obtained for each initial grid by summation over the individual residence times in the grids resulting from the groundwater velocities and individual flow distances along the flow path until they enter a surface water.
- The WEKU model was extended by a model for the quantification of nitrate degradation in groundwater. According to extensive field studies by Böttcher *et al.* (1989) in a catchment area in the North German Lowlands and van Beek (1987) for a site in The Netherlands a first order denitrification kinetics has been assumed with a reaction constant in the range of 0.17 to 0.56 a^{-1}. This corresponds to a halving of the nitrogen leached to the groundwater after a residence time between 1.2 and 4 years. Rather simple indicators, such as the presence of Fe (II), Mn (II) and the absence of O_2 and NO_3 can be used to decide whether a groundwater province has hydrogeochemical conditions in which denitrification is possible or such transformation of nitrogen can be neglected (Wendland and Kunkel, 1999).

- The validation of the groundwater-borne nitrate inputs into rivers was done based on results of the MONERIS model (Behrendt *et al.*, 2000). The model distinguishes between point source emissions from waste water treatment plants and direct industrial discharges and six diffuse pathways, including the inputs via groundwater. According to Behrendt *et al.* (2000) it was assumed that the observed nitrogen concentrations in rivers under base flow conditions correspond to groundwater borne nitrate inputs. Thus the modelled nitrogen inputs into surface waters from groundwater were compared to the corresponding values given by the MONERIS model. In the case that the overall agreement between the values given by the MONERIS model and the calculated values given by the WEKU model are satisfied we conclude that the chosen procedure gives reliable estimations for the groundwater-borne nitrate input into the aquifers.

Results and discussion

Nitrogen surpluses (1990–1995)

The actual nitrogen surpluses as a result of balancing the inputs by mineral fertilizers and farm manure, and nitrogen extractions, primarily by field crops, are shown in Figure 1. On average for Germany, about 85 kg nitrogen per hectare and year are applied in excess of extraction to the agriculturally used land (Bach *et al.*, 2000). Especially in regions with area-independent animal processing (intensive animal production) large annual nitrogen surpluses up to more than 200 kg N/ha result from the animal excretions. This form of land use management is not very site-specific, which may also contribute to the fact that it predominates in regions, where infertile sandy soils are limiting the yield of crops, e.g. in Emsland and Northern Munster land. In addition, all regions with commercial and specialty crops predominantly cultivated on mostly fertile loamy soils and favourable climatic conditions display large nitrogen surpluses. This includes, for example, the fertile loessian plains north of the midlands, such as the Lower Rhine Embayment, but also the Upper

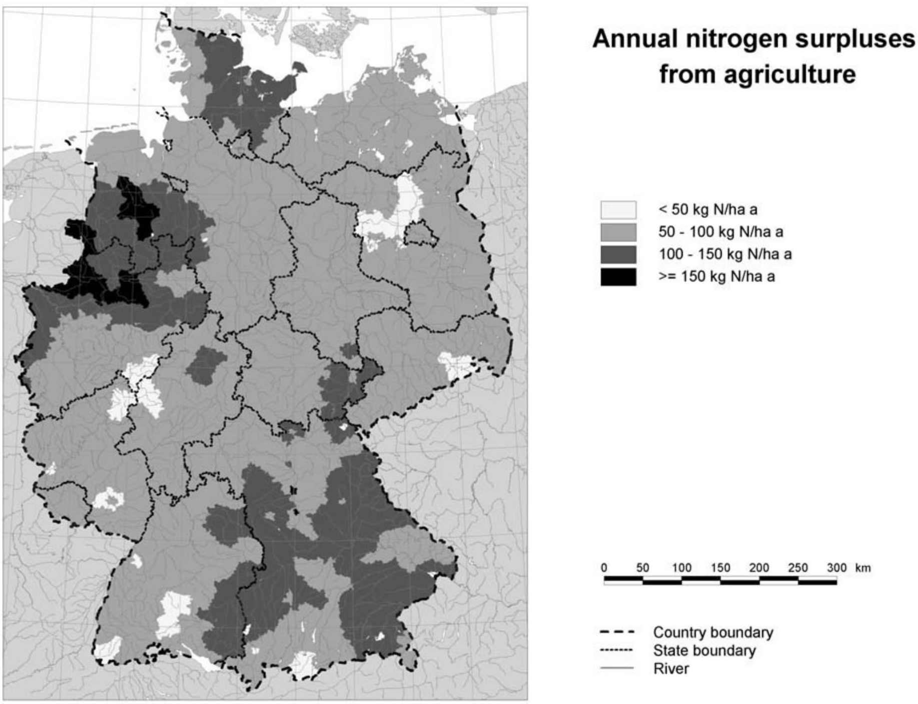

Figure 1 Annual nitrogen surpluses from agriculture

Hessian Sink, Wetterau and the Thuringian Basin. Low nitrogen surpluses are calculated for regions with mostly forage crops production. In the western Danubian Lowland this is due to the large N-extractions with harvest, whereas in the less fertile regions in the midlands this is due to the more extensive agriculture.

Ratio of groundwater recharge to total runoff

The ratio of groundwater recharge to total runoff is determined on the basis of annual average precipitation levels from 1961 to 1990 using the GROWA model (Kunkel and Wendland, 2002). This long-term annual rate is used to determine from the nitrogen surpluses the part of nitrate leached to the groundwater. In some areas groundwater runoff is not more than 20 to 40% of the total runoff. This situation is typical for regions close to the water table, e.g. in the marshy regions in the north western area. The same situation applies for areas where groundwater runoff is bound in Palaeozoic and crystalline rocks, mainly in the south-western part of Germany. Hence, in these regions direct runoff is the main runoff component. As a consequence, the intake of excess fertilizers from and to surface waters takes place a short time after fertilizer application.

Therefore, all these areas can be classified as areas with a high actual pollution risk of surface waters. On the other hand it can be expected for these areas, that measures to reduce nutrient inputs into rivers will show impact on water quality after a short time.

In areas where unconsolidated rocks predominate and which show deep groundwater tables, groundwater runoff is to a large extent equal to the total runoff. Consequently in these regions aquifer systems are the main pathway for nitrate into rivers. Because of the low flow velocity of groundwater in aquifer systems, the unconsolidated rock areas show a long term pollution risk. Actual displacement of nitrate from soil to groundwater may be detectable in surface waters only after decades. Consequently, remediation measures will be effective in the same time range. For a classification with respect to a nitrate emission risk assessment however, it has urgently to be taken into account that in a number of aquifers in especially unconsolidated rock areas hydrogeochemical conditions occur, which may enhance natural nitrate degradation.

Nitrate inputs into the aquifers

The summarized N-balance results in nitrogen surpluses in a range between ca. 30 kg N/ha a and 120 kg N/ha a. However, the nitrogen surplus is in general not equal to the nitrogen leached from the root zone to the groundwater systems. With the help of the model approach developed by Köhne and Wendland (1992) denitrification in the root zone is quantified as a function of soil properties and crop types. Additionally it has to be taken into account, that a certain fraction of the nitrogen leached from the root zone is coupled to the direct runoff components. Whereas in most regions groundwater runoff is dominant, some sub-regions, i.e. along the river valleys, reveal high direct runoff fractions. In order to separate the fraction of nitrogen leached to groundwater from the total nitrogen leached from the root zone, the total nitrogen leaching from the root zone is weighted by the base flow ratio calculated according to the GROWA model for the whole area of Germany. The results are shown in Figure 2. High to very high nitrogen leaching to the groundwater of more than 100 kg N/ha a was calculated for all regions with a high groundwater runoff fraction and an intensive agricultural use on fertile luvisol soils. Regions with relatively low nitrogen intakes to the groundwater are obtained for areas where either less fertile soils and/or high direct runoff fractions predominate. On the remaining areas nitrogen leaching from the root zone is quantified to be about 60 kg N/ha a.

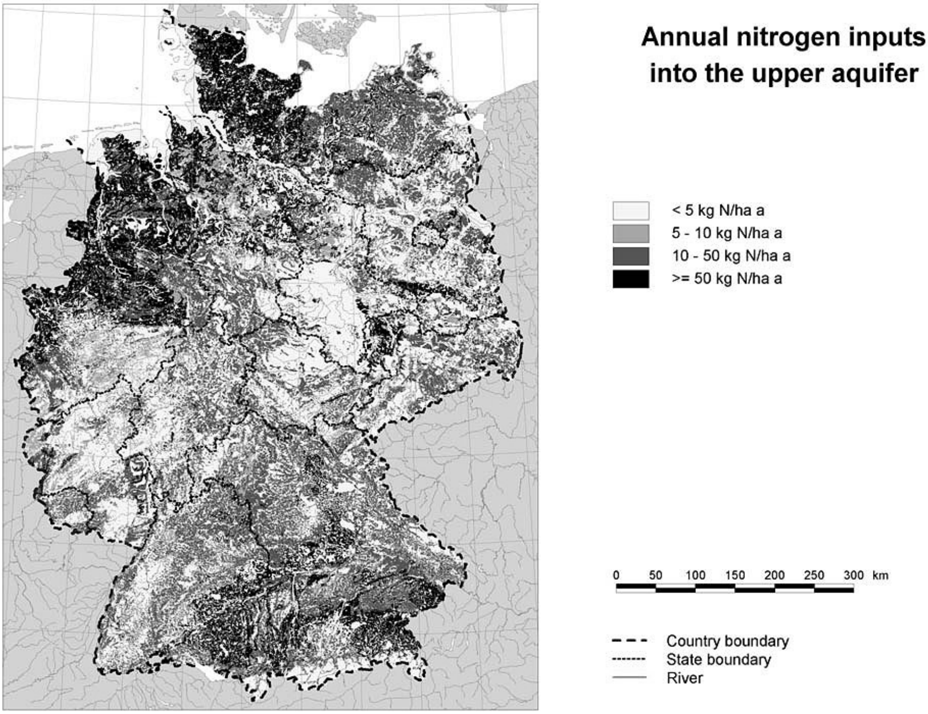

Figure 2 Annual nitrogen inputs into the aquifer

Groundwater residence times in the upper aquifer

Denitrification in the upper aquifer depends on the groundwater residence times (Böttcher *et al.*, 1989). Thus, considering groundwater residence times in the upper aquifer enables the calculation of nitrate concentrations in the aquifer at the outflow into a surface water. Moreover, groundwater residence times specify the time scales, until nitrate reduction strategies to remediate polluted groundwater resources may lead to a substantial groundwater quality improvement.

The mean values of the calculated groundwater residence times for Germany vary between less than 1 year and more than 150 years. Long residence times may result both from small groundwater velocities as well as from long flow paths up to the recipient, pointing to long time periods, after which nitrate inputs into the aquifer can contribute to the pollution of surface waters in some regions. Short residence times generally result for areas in the vicinity of rivers and/or regions with high groundwater velocities.

Denitrification conditions in the aquifer

The analysis of the denitrification conditions in the groundwater was done separately for the different groundwater bearing formations occurring in Germany. In total about 16,000 groundwater samples were evaluated and classified with respect to their nitrate-degrading capacity primarily on the basis of groundwater quality data on Iron(II), Manganese(II), Oxygen and Nitrate.

In case more than 75% of the sampling points in the hydrogeological units display oxygen concentrations below 2 mg O_2/l, the hydrogeological lithologic units were classified as belonging to the predominantly reduced aquifers, in which denitrification may occur. It also came out, that iron(II) concentrations above 0.2 mg Fe(II)/l and Manganese(II) concentrations above 0.05 mg Mn(II)/l occurred for roughly 90% of the sampling points. This is a further indication that the aquifers display predominantly reduced groundwater and have a significant nitrate degradation capacity. At least, more than 80% of the observed nitrate concentrations in the groundwater was below 1 mg NO_3/l. In connection with the high iron(II) and manganese(II) and low oxygen contents, this is an indication that nitrate compounds leached out of the soil can be degraded in the groundwater systems. The groundwater bearing formations of the North German lowlands (glaciofluviatile sands, moraine deposits) were classified as nitrate degrading aquifers. In most areas, where aquifers are composed of consolidated rocks (e.g. sandstones, schists, limestone), usually non-nitrate degrading conditions occur. Groundwater bearing formations which could not be uniformly classified as nitrate degrading or non-nitrate-degrading were attached to an intermediate denitrification type, e.g. the groundwater bearing formations "glacial outwashes" and "greywackes".

Groundwater-borne nitrate input into the rivers

Figure 3 shows the remaining nitrogen outputs to surface waters from groundwater after its residence time in the aquifer. The outputs are shown in the initial cell for which the inputs into the soil have been calculated. As can be seen, nitrogen intakes in the vicinity of surface waters and high nitrogen leaching levels contribute considerably to the groundwater-borne nitrate inputs into the rivers. Even with good conditions for a complete degradation of nitrate in the aquifer, the brief residence times in the aquiferous layers are not sufficient for an adequate degradation of high nitrate inputs. There is, furthermore, a hazard potential in many regions where high nitrate inputs are associated with relatively short residence times of the groundwater, as well as restricted and/or insignificant degradation conditions in the aquifer. These regions include parts of the Thuringian Basin and the Lower Rhine Embayment as well as some solid-rock areas such as Lower Franconia and the Swabian and Franconian Jura. In contrast, even with high nitrate concentrations in the recharged groundwater only very slight nitrate concentrations result for the aquifers of the North German Plain upon entry into the main receiving waters. There, nitrate input via groundwater pathways was quantified to be about 2 kg N/ha a. The comparison of this value with the average

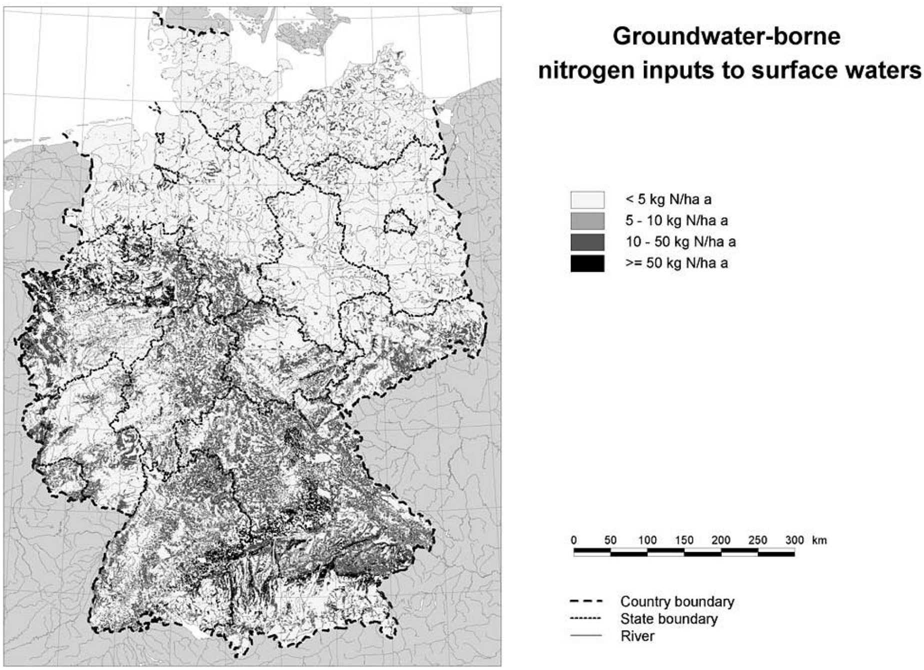

Figure 3 Groundwater-borne nitrogen inputs into surface waters

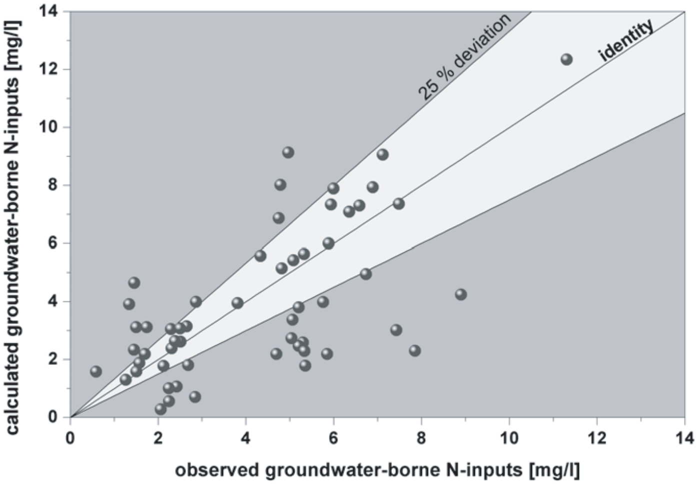

Figure 4 Comparison between measured and calculated groundwater-borne nitrogen inputs into surface waters

nitrogen load leached from the root zone (Figure 2) indicates that through denitrification in the groundwater more than 90% of the nitrogen inputs into groundwater are retained in the aquifer systems. The, as a rule, long residence times of the groundwater and good hydrogeochemical conditions cause unrestricted nitrate degradation, with the result that the groundwater of the North German Plain is almost nitrate-free after maximum residence time when it enters the rivers.

The modelled groundwater-borne nitrogen inputs into surface waters have been compared with observed nitrogen concentrations in rivers at low flow conditions and low temperature for about 100 monitoring stations mainly in the Elbe basin. The method for the calculation of these indicators is described in detail by Behrendt *et al*. (2002). The values calculated with the combined SOIL-N/WEKU model only show relatively small differences to the observed values (about 10–20%), as indicated in Figure 4. This can be regarded as a good agreement.

Nevertheless, this fact should not be used as an argument to abandon a general reduction of the nitrate inputs into the groundwater or to delay such measures. Nitrate degradation is associated with the consumption of iron sulphide compounds and/or organic carbon. Once the natural content of these components in an aquifer is exhausted, a rapid increase of the nitrate concentrations of the groundwater results, the so-called nitrate breakthrough. With regard to the idea of a sustainable management of groundwater resources in Germany, natural denitrification capacities have to be protected against avoidable nitrate pollutions.

Conclusions

Studies of groundwater-borne nitrate input into surface waters showed that both the groundwater residence time and the amount of nitrogen that is denitrified can vary strongly with the site in which the nitrogen enters the saturated zone. From the results of this study we conclude for the river basins in the North German Plain, that about 90% of the diffuse nitrogen input into the groundwater is degraded in this way. For river basins in Germany's consolidated rock regions it could be shown that only 30% of the diffuse nitrogen input into the groundwater is degraded. The comparison with observed groundwater-borne riverine nitrogen loads proves the reliability of the modelled values.

With regard to the European perspective of the nitrogen loading of rivers via the groundwater path, we think that it is possible to generalize and transfer the results. E.g. the North

German Plain is part of the supraregional geological structure of the European Pleistocene Lowland, which ranges from The Netherlands in the west and Denmark in the north to the Baltic States and the Ukraine in the east. As could be shown, the key factors controlling the subsurface nitrate retention (residence times, denitrification capacity) are correlated to specific hydrogeological site conditions, occurring in the North German Plain. Parallel studies carried out in the Uecker basin (Germany) and the Gjern basin (Denmark) showed an equal distribution of groundwater residence times as well as the same hydrogeochemical characteristics (Wendland *et al.*, 2001; Grimvall *et al.*, 2001). We would assume on the basis of these results that "long" residence times and "good" denitrification conditions should in general be valid for the entire European Pleistocene Lowland. Due to the results obtained for all regions in Germany, which, from a geological point of view, are dominated by consolidated rocks areas, it becomes obvious that there no significant denitrifying aquifer conditions can be expected. Also it is well known (e.g. Kunkel and Wendland, 1997) that not groundwater runoff, but direct runoff is the dominant runoff component in solid rock areas. Generalizing this observation with regard to the European perspective we would assume that nitrogen retention in groundwater would be of minor significance only in large parts of i.e. Southern Europe and Scandinavia.

Consequently we think that the transfer and application of the chosen procedure to other areas in this supraregional geological structure should be possible without major problems. The advantage of such a broader application of the model concept would lie in the supraregional quantification of the dimension subsurface nitrogen retention may play in Europe. In the same way, it would be possible to evaluate sensitive regions, i.e. areas with high nitrogen surpluses and low groundwater residence times and hence incomplete subsurface nitrogen retention. However it has to be taken into account, that this generalization so far is not more than a rough estimate on the basis of the results from our study and on knowledge about the general geological structure in Europe. Statements about the applicability of the combined model for these areas can only be proven in the course of further selective studies.

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