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# Potential nitrate pollution of groundwater in Germany: A supraregional differentiated model

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**Abstract** Implemented on behalf of the Federal Ministry for Research and Technology (BMFT), a model is developed to trace the nutrient flow of nitrate in the soil and the groundwater on a supraregional scale. Research work is intended to indicate regionally differentiated hazardous potentials and thereby provide a basis for recommending comprehensive measures to protect groundwater in Germany. The adaption of the model to the hydrogeological and agricultural conditions of other states is possible in principle. This article focuses on the hydrogeological model parts. A high nitrate pollution of groundwater can be expected in all regions with intensive agricultural use of the topsoil. In particular, groundwater in solid rock areas is susceptible to nitrate pollution. There a rapid groundwater turnover and thus a short residence time for the groundwater in the aquifer is typical. Oxidizing aquifer conditions usually prevail in solid rock aquifers, preventing nitrate degradation. In many loose rock areas, in contrast, the groundwater has a low flow velocity and a long residence time in the aquifer. Because of a lack of free oxygen, a complete degradation of nitrate can occur, as long as iron sulfide compounds and/or organic carbon are available in the aquifer. A more detailed presentation of the whole research work is given in Wendland et al. (1993).

**Key words** Nitrate · Groundwater · Modeling · Denitrification · Nitrogen balance

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## Introduction

In addition to oxygen, carbon, and sulfur, nitrogen is one of the most important structural elements for life on earth. It is a component of the proteins, nucleic acids, and other important cell content materials of living organisms. The nitrogen compounds which can be taken up by plants are ammonium and nitrate. These nitrogen compounds are applied in agriculture in the form of mineral fertilizers and/or fertilizers produced on farms, e.g., liquid manure or stable manure. In order to ensure maximum yields, crops must be supplied with sufficient quantities of nitrogen at every stage of growth. However, for economic reasons in current agricultural practice, more nitrogen is often added to the soil than can be removed from the soil when harvesting the crops. The excess nitrogen not taken up by plants largely remains in the soil in the form of nitrate. Since nitrate compounds are readily water soluble and do not interact with soil exchange capacity, they can be washed off the root zone very easily and end up in the groundwater together with the percolation water. High concentrations of nitrate in drinking water can endanger human health. If large quantities of nitrate reach the surface waters, then eutrophication phenomena may result, such as increased growth of algae. Urgent measures are required to reduce nitrate contents in groundwater. It is therefore necessary to investigate the fate of nitrate in the soil and groundwater. The present paper provides a contribution to this work.

## Procedure

A large number of detailed but regionally limited studies on nitrate pollution of groundwater are available at present, providing extensive scientific knowledge. However, these results have not yet been used for a comprehensive comparative review covering, if possible, the entire area of a country.

A systems analysis approach was selected to solve this problem since this approach permits large quantities of data to be interlinked for complex, interdisciplinary relations. The aspects relevant to the problem were selected from the abundance of data and characteristics on nitrogen discharges from the soil, the hydrological and geological conditions, as well as the nitrate conversion, degradation, and movement processes in the soil and groundwater, and then combined to form a comprehensive model. This model was transformed into a computer program and coupled to a graphics program system, permitting a clear representation in the form of colored grid charts. The grid charts are designed in the form of a matrix, in which each element represents a geographic unit area of 3 × 3 km. Exact position determinations are thus possible by means of the matrix element indices (220 columns and 290 lines). The flow chart (Fig. 1) shows the structure of the entire model. The result of one submodel (e.g. groundwater recharge level) is an important parameter for a following submodel (e.g. nitrate concentration in recharged groundwater). Mathematical description of submodel is given in the references of the corresponding sections.

The degree of accuracy of the model results corresponds to the scale of the input data. As the input data are mainly derived from general maps (scale 1 : 500,000 to 1 : 2,000,000), the resulting grid charts are not to be used for small-scale investigations. The results of large area models have a bearing on the presentation of generalized interrelations. This information is needed by national institutions like governmental agencies for, e.g., the elaboration of directives for protection areas.

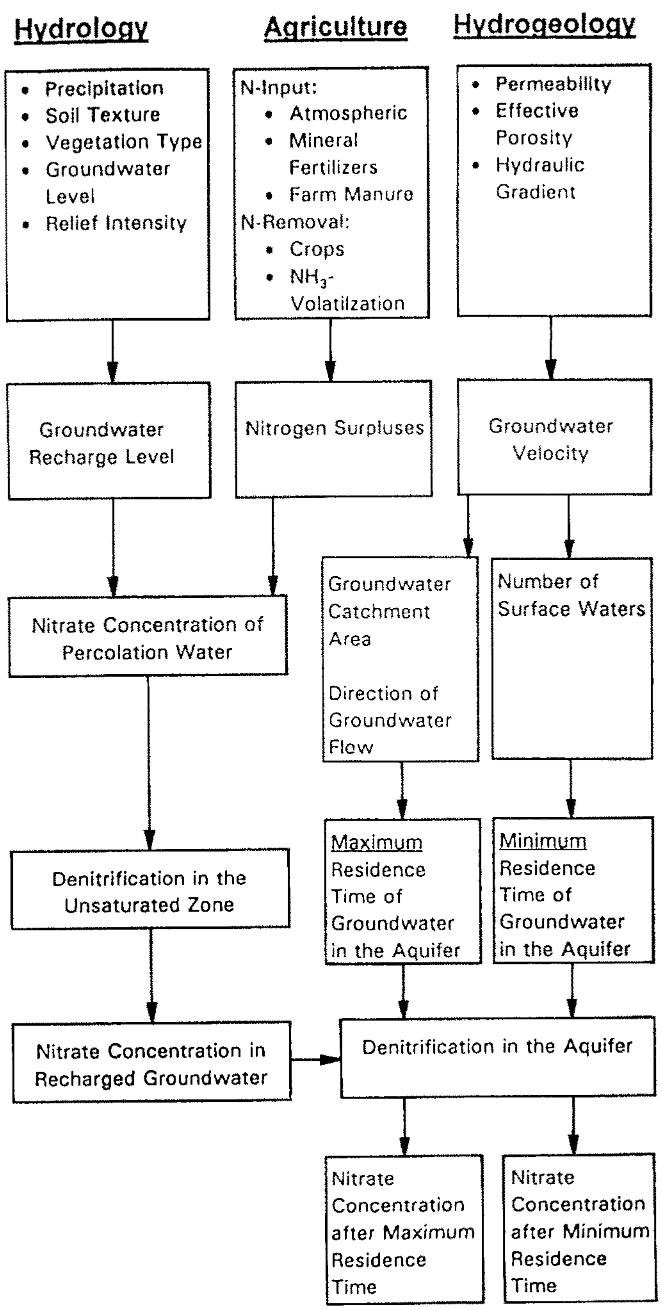


**Fig. 1** Flow chart showing connection of input data to form a coherent model

## Groundwater recharge level

The basic data for average annual precipitation, soil type category, crop area, depth of groundwater table, and relief energy serve to determine the components of the water cycle (evaporation level, surface runoff level and groundwater recharge level) according to Dörhöfer and Josopait (1980). Relatively small area variations in groundwater recharge levels between 50 and 400 mm/yr are found for wide parts of Germany. In addition to nitrogen surpluses, the groundwater recharge level is the decisive parameter for calculating the nitrate concentration in recharged groundwater.

## Potential excess nitrogen

Diffuse areal input sources account for the largest portion of groundwater nitrate pollution, i.e., atmospheric nitrogen input mineral fertilizers, and farm manure. Bach (1993) calculated the average annual excess nitrogen from statistical data for the period 1987–1991 for the crop area in West Germany and for the period 1986–1989 for eastern Germany. Estimating the excess nitrogen of the noncultivated subareas per grid, the results of Bach were converted to obtain a weighted nitrogen surplus for the entire grid. High nitrogen surpluses are found in all regions with intensive farming (e.g., fertile plains, regions with intensive animal husbandry). Low nitrogen surpluses are found in regions with extensive grassland and forage farming (e.g., highland farming).

As a rule a certain part of the excess nitrogen is reduced by denitrification in the unsaturated zone. In the course of research presented here, denitrification rates were estimated (50 percent of the excess nitrogen). In this way, a first-order kinetics is initated, i.e., denitrification losses in the unsaturated zone rise with increasing nitrogen surpluses.

### Potential nitrate concentrations in recharged groundwater

The nitrogen surplus in the grids reduced by the denitrification losses in the soil is used to calculate the potential average annual nitrate concentration in recharged groundwater (Fig. 2).

Generally large area land-use patterns and the corresponding nitrogen fertilization nitrogen surpluses and potential nitrate input in the aquifers often reveal the pedological, hydrological, and geological structures of a region.

Very high potential nitrate concentrations in recharged ground water ($> 150$ mg $NO_3$/l) have been calculated for large areas of the eastern states. The decisive factor for this is not only the amount of the nitrogen surplus but also the low groundwater recharge level ($< 100$ mm/yr). In the western states groundwater recharge level is higher, causing an more intensive dilution of the nitrogen surpluses. There, groundwater in regions with intensive farming and/or intensive animal husbundry are susceptible to nitrate pollution. Low potential nitrate concentrations in recharged groundwater are calculated for hill country, where extensive farming predominates.

The majority of the groundwater of significance for the drinking water supply in Germany is found in regions of intensive agriculture and potentially high nitrate concentrations in recharged groundwater. This demonstrates the high responsibility that has to be borne by the agricultural cultivation of the soil for the quality of the drinking water.

### Residence time of groundwater in aquifers

The residence time of the groundwater in the aquifer is calculated from hydrogeological data (permeability, effective porosity, direction of groundwater flow, hydraulic gradient, system of rivers and streams) according to Wendland (1992). The residence time of groundwater means the period the groundwater requires from percolating into the water-bearing formation until transfer to surface waters (river, ocean, lake). The residence time represents an important parameter for calculating time-dependent denitrification rates in the aquifer. In regions with long underground residence times for the groundwater, denitrification may lead to a considerable reduction of the nitrate concentration in groundwater.

The transfer of groundwater to surface waters may take place at a considerable distance into a major river (main receiving water) or into the ocean—in this case the residence time is long; on the other hand, the groundwater may be transferred into a small stream or drinking water well close to the point of its input—the residence time is then short. Figure 3 gives a diagrammatic representation of the different flow distances of the groundwater. It has been possible to calculate the residence time for about 60 percent of the area of Germany. These regions are largely identical to those provinces from which a high potential nitrate pollution of recharged groundwater can be expected. For the other regions, insufficient hydrogeological data are available to do further model calculations. These areas are therefore shown in white in the following charts. Due to the low risk to the groundwater arising from the low nitrate inputs in these regions, it is not decisive for the results of this work.

In order to demonstrate the entire range of possible residence times, two extreme cases are distinguished for the model calculation. In the first case, the maximum residence time of the groundwater is calculated; this is valid for that part of the groundwater which flows towards and is fed into the main receiving water (cf. Fig. 3, $l_{max}$).

As can be seen from Fig. 4, the calculated maximum residence times in the aquifer display great regional differences. They vary from approx. 1 year in the karst aquifers to more than 1000 years in some loose rock aquifers of the North German Plain. In regions without any significant nitrate degradation capacities in the groundwater, a discharge of nitrate into the surface waters may possibly only be expected after a very long time. This represents an ecological time bomb.

In the second case, assuming that part of the groundwater does not flow into its main receiving water but, after a short underground passage, into the nearest receiving water, the minimum residence time is calculated (cf. Fig. 3, $l_{min}$. It becomes apparent that the minimum residence times generally amount to less than 10 years. Agricultural measures to reduce the input of nitrate may thus, in many regions, contribute to an improvement in the groundwater after a relatively short period.

### Denitrification in the aquifer

During residence in the aquifer, nitrate may be degraded in certain groundwater provinces to gaseous nitrogen, which does not represent a danger to health or the ecology. This nitrate degradation (denitrification) occurs in the presence of organic carbon compounds and/or reduced iron sulfide compounds. Denitrification is carried out by microorganisms, which, in view of a low concentration of free oxygen, supply their oxygen needs from the oxygen bound in the nitrate. It is known that the less free oxygen the groundwater contains, the more effectively nitrate is degraded, and also that the longer the residence time in the aquifer lasts, the greater the degradation is. Therefore, the large time differences between maximum and minimum residence times in most groundwater provinces have far-reaching consequences for the nitrate degradation process in the aquifer.

Denitrification in the aquifer can be determined in good approximation by a decrease in concentration as a func-

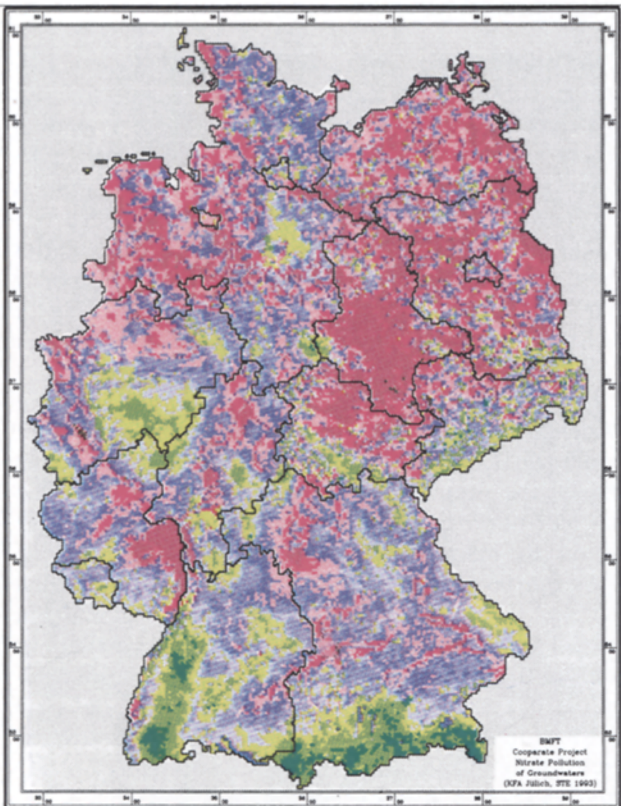


Fig. 2
Potential Nitrate Concentration in Recharged Groundwater with Regard to Denitrification in the Unsaturated Zone

1 : 4 602 000
0 50 100 km

- less than 25 mg/l
- 25 up to 50 mg/l
- 50 up to 75 mg/l
- 75 up to 100 mg/l
- 100 up to 150 mg/l
- 150 up to 200 mg/l
- 200 up to 300 mg/l
- 300 up to 500 mg/l
- 500 mg/l and more
- mining region
- state-borders
- waters
- surroundings

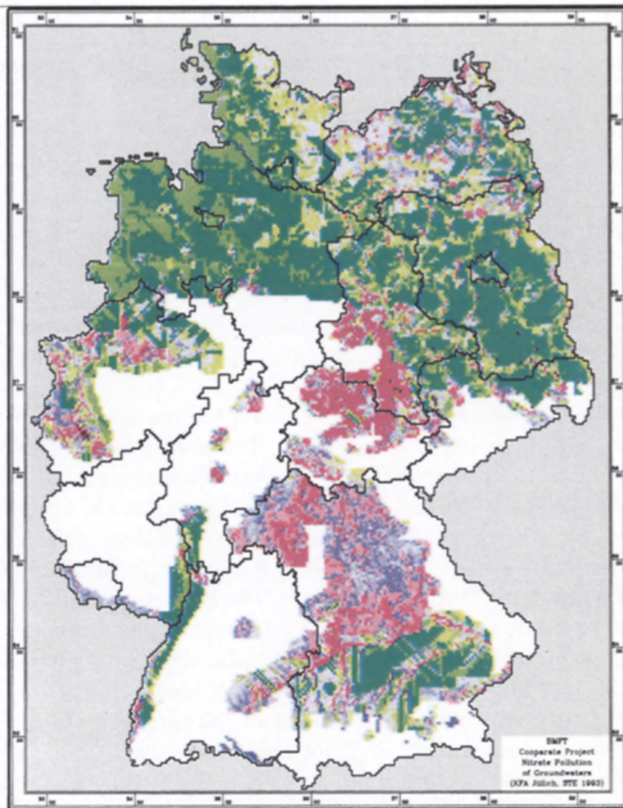


Fig. 5
Potential Nitrate Concentration after Maximal Residence Time
e.g. when entering the receiving stream
– shown in the initial grid –

1 : 4 602 000
0 50 100 km

- less than 2 mg/l
- 2 up to 10 mg/l
- 10 up to 25 mg/l
- 25 up to 50 mg/l
- 50 up to 75 mg/l
- 75 up to 100 mg/l
- 100 up to 150 mg/l
- 150 up to 200 mg/l
- 200 mg/l and more
- mining region
- no calculation possible
- state-borders
- waters
- surroundings

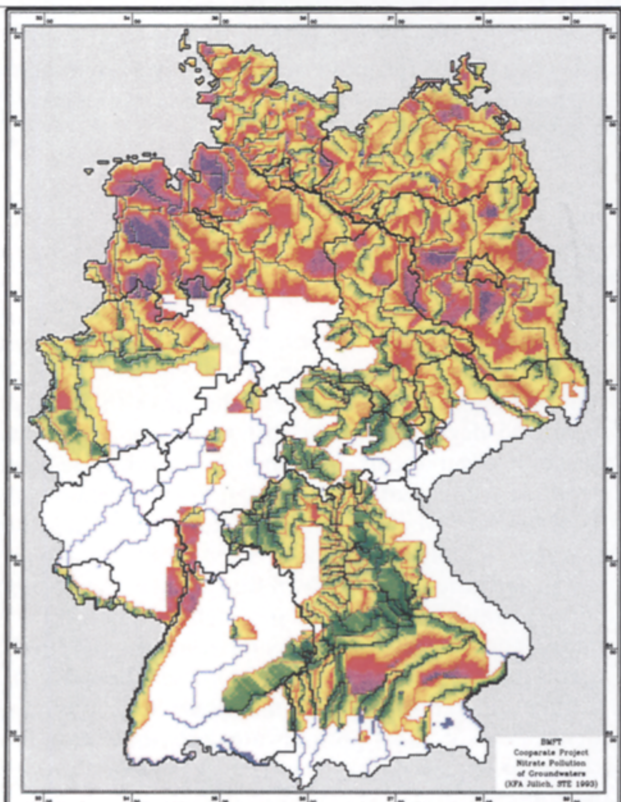


Fig. 4
Maximal Residence Time of Groundwater in the Aquifer
Residence time for the part of the ground-water discharge which feeds the effective receiving stream

1 : 4 602 000
0 50 100 km

- less than 1 a
- 1 up to 5 a
- 5 up to 10 a
- 10 up to 30 a
- 30 up to 60 a
- 60 up to 100 a
- 100 up to 150 a
- 150 up to 200 a
- 200 up to 400 a
- 400 up to 600 a
- 600 up to 1000 a
- 1000 a and more
- no calculation possible
- state-borders
- rivers
- catchment areas
- waters
- surroundings

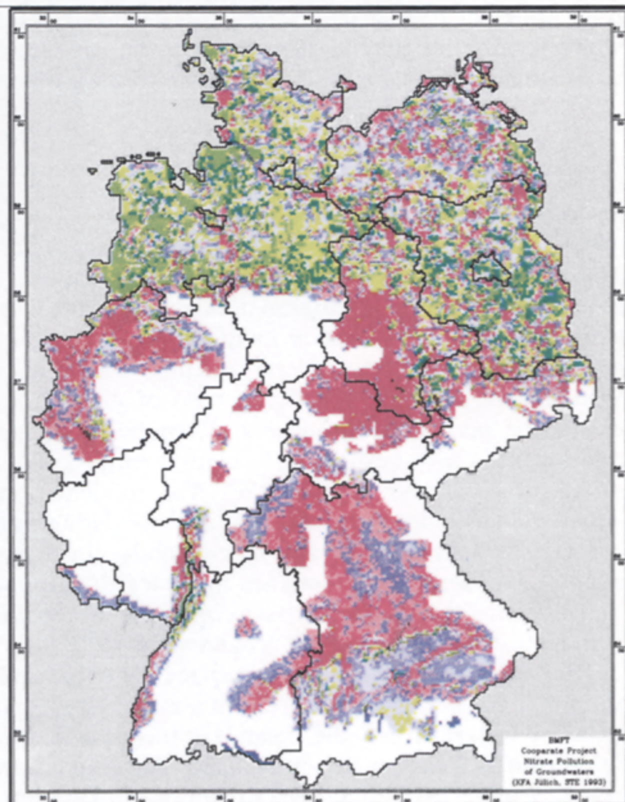


Fig. 6
Potential Nitrate Concentration after Minimal Residence Time
e.g. when entering the receiving stream
– shown in the initial grid –

1 : 4 602 000
0 50 100 km

- less than 2 mg/l
- 2 up to 10 mg/l
- 10 up to 25 mg/l
- 25 up to 50 mg/l
- 50 up to 75 mg/l
- 75 up to 100 mg/l
- 100 up to 150 mg/l
- 150 up to 200 mg/l
- 200 mg/l and more
- mining region
- no calculation possible
- state-borders
- waters
- surroundings

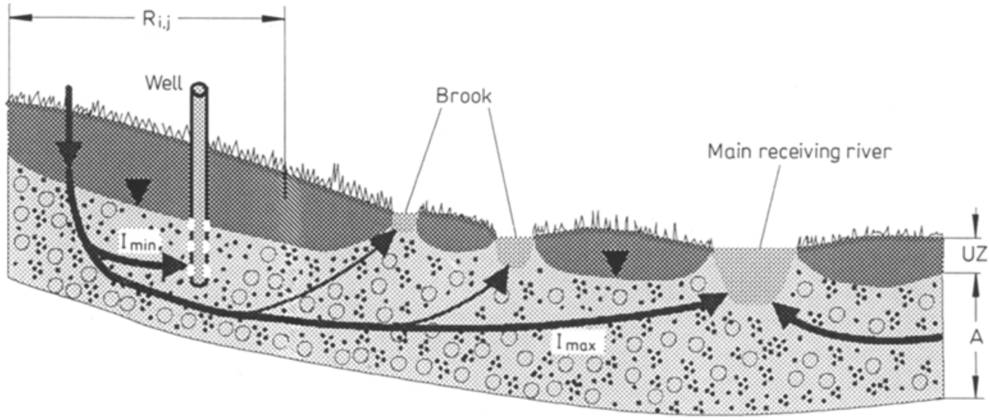


**Fig. 3** Diagrammatic representation of flow distances for ground water in the aquifer. $R_{i,j}$ width of one grid element; $l_{max}$ flow path of maximum residence time for $R_{i,j}$ groundwater level; $l_{min}$ flow path of minimum residence time for $R_{i,j}$; UZ unsaturated zone; A aquifer

tion of the denitrification conditions at the site and of time (Böttcher and others 1989):

$$C = CGw \cdot \exp(-KN \cdot t)(\text{mg NO}_3/\text{l})$$

where $C$ is nitrate concentration after residence time is aquifer (mg $NO_3$/l); $CGw$ is nitrate concentration in recharged groundwater (mg $NO_3$/l); $t$ is residence time (yr); and $KN$ is reaction constant of denitrification depending on denitrification conditions in the aquifer (l/yr).

The denitrification conditions in the groundwater provinces are estimated using about 10,000 groundwater analyses from the measuring networks of several state offices for water and waste management or water management offices from the entire federal territory. A selection of sensitive parameters of groundwater analysis, which indicate denitrification events in the aquifer, are presented in Table 1.

Reducing groundwaters show unrestricted denitrification conditions. These groundwaters are often nitrate-free and the $O_2$ concentrations are typically below 2 mg $O_2$/l. On the contrary, the concentrations of $Fe^{2+}$, $Mn^{2+}$, and DOC are raised. This hydrochemical type of groundwater occurs in Germany predominantly in aquifers of Pleistocene lowlands and moor countries.

Oxidizing groundwaters show insignificant denitrification conditions. The oxygen concentration exceeds 5 mg $O_2$/l, preventing denitrification in large amounts. Groundwater-bearing formations in Germany showing predominantly this hydrochemical type are found in, e.g., karst aquifers and sandstone aquifers. The denitrification conditions are typified by different reaction constants of denitrification in the aquifer following investigations of Obermann (1982), Mull (1987), and Böttcher and others (1989).

**Table 1** Sensitive parameters of reducing and oxidizing groundwaters

| | Groundwater | |
|---|---|---|
| Parameter | Reducing[a] | Oxidizing[b] |
| $O_2$ (mg/l) | <ca. 1 | >ca. 5 |
| $NO_3^-$ (mg/l) | <ca. 1 | Variable |
| $Fe^{2+}$ (mg/l) | >ca. 2 | <ca. 0,1 |
| $Mn^{2+}$ (mg/l) | >ca. 0,1 | <ca. 0,05 |
| DOC (mg/l) | >ca. 1,5 | <ca. 0,5 |

[a] Unrestricted denitrification conditions
[b] Insignificant denitrification conditions

The reaction constants for denitrification lead to a half-life of approx. two years under unrestricted denitrification conditions (reducing groundwaters, max. degradation 100 percent) and to a half-life of approx. 35 years under insignificant denitrification conditions (oxidized groundwaters, max. degradation 16 percent). Intermediate values were found for aquifers which cannot be uniquely allocated to these denitrification conditions.

## Assessment of the regional risk potential in Germany

In the present paper groundwaters are regarded as potentially endangered by nitrate if, after their residence time in the aquifer, they still display nitrate concentrations above the EC norm of 50 mg/l for drinking water. As compared to a single approach, the maxima–minima evaluation makes it possible to identify more clearly any endangered, potentially endangered, and currently not endangered groundwater provinces. However, knowledge of the average nitrate concentration upon entry into the receiving body does not permit conclusions to be drawn about the nitrate distribution and possible peak loads in the aquifer.

Fig. 5 shows the nitrate concentration of the groundwater after the maximum residence time in the aquifer. The final concentrations are shown in the initial grid, i.e. the grid, for which the nitrate concentration in recharged groundwater has been determined. This type of representation has the advantage that the origin of a load on the earth's surface is immediately identified. Due to the long flow distance of the groundwater, the highest possible nitrate degradation rates were calculated. There is a high risk potential close to river courses. Even with good denitrification conditions, which can account for a complete degradation of the nitrate in the aquifer, the brief residence time in the water-bearing formation is not sufficient to achieve any perceptible degradation of high nitrate inputs. Furthermore, there is also a potential risk in many regions where high nitrate inputs are associated with relatively low residence times for the groundwater, as well as restricted and/or insignificant degradation conditions in the aquifer.

In Germany this situation occurs in most solid rock regions such as the Thuringian Basin and the Franconian and Swabian Jura. In contrast, for the aquifer of the North German Plain, even with high nitrate concentrations in the recharged groundwater, only very low nitrate concentrations result as a whole upon transfer into the main receiving water. The long residence time of the groundwater and hydrochemical conditions enabling unrestricted nitrate degradation as a rule mean that the groundwater of the North German Plain is almost nitrate-free when it enters the surface waters (after the maximum residence time). Nevertheless, this fact does not reduce the need for a general reduction of the nitrate input into the groundwater nor is it a reason to delay remedial measures. Nitrate degradation is associated with the consumption of iron sulfide compounds and/or organic carbon. When the natural content of these components in the aquifer is exhausted, then a rapid rise in nitrate concentration in the groundwater results, the so-called nitrate breakthrough.

Based on the minimum residence time of the groundwater, only low nitrate degradation rates are achieved due to the short residence time in the aquifer (Fig. 6). The minimum residence time illustrates the load situation which arises if large-area groundwater runoff conditions are disturbed. Groundwater withdrawal for drinking water supply plays a particular role in this connection. Regions with a potentially low nitrate pollution risk after the minimum residence time have relatively low concentrations in the recharged groundwater. In addition to the regions already indicated in Fig. 5 with a potentially high pollution risk, the Lower Rhine Basin, the Münsterland and Lower Franconia must also be mentioned. In addition, some areas of the North German Plain should also be included in this category, such as the hilly country of Holstein, the area around Vechta, and the North Frisian marshy areas. In all these regions there is a danger that the norm of 50 mg/l nitrate for drinking water is exceeded in groundwater samples. There is an urgent need for action towards comprehensive groundwater management on the part of the water utilities, the regional water boards, and the legislature.

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