

Article

# Model-Based Analysis of Nitrate Concentration in the Leachate—The North Rhine-Westfalia Case Study, Germany

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**Abstract:** Reaching the EU quality standard for nitrate (50 mg NO<sub>3</sub>/L) in all groundwater bodies is a challenge in the Federal State of North Rhine-Westfalia (Germany). In the research project GROWA+NRW 2021 initiated by the Federal States' Ministry for Environment, Agriculture, Nature and Consumer Protection, amongst other aspects, a model-based analysis of agricultural nitrogen inputs into groundwater and nitrate concentration in the leachate was carried out. For this purpose, the water balance model mGROWA, the agro-economic model RAUMIS, and the reactive N transport model DENUZ were coupled and applied consistently across the whole territory of North Rhine-Westfalia with a spatial resolution of 100 m × 100 m. Besides agricultural N emissions, N emissions from small sewage plants, urban systems, and NO<sub>x</sub> deposition were also included in the model analysis. The comparisons of the modelled nitrate concentrations in the leachate of different land use influences with observed nitrate concentrations in groundwater were shown to have a good correspondence with regard to the concentration levels across all regions and different land-uses in North Rhine-Westphalia. On the level of ground water bodies (according to EU ground water directive) N emissions exclusively from agriculture led to failure of the good chemical state. This result will support the selection and the adequate dimensioning of regionally adapted agricultural N reduction measures.

**Keywords:** nitrate; groundwater; source apportionment; modelling; nitrogen sources; leachate rate

## 1. Introduction

Excessive nitrate inputs into groundwater have been recognized as a main reason for failing drinking water standards for decades [1–6]. Agricultural N emissions originating from mineral or organic fertilizers are regarded as the most relevant source of nitrate in groundwater worldwide [7]. Accordingly, strategies to cope with the nitrate pollution of groundwater are focused on controlling the agricultural sources of nitrate [8,9]. In Europe, this is reflected in the water legislation at the EU level, that is, the EU Water Framework Directive (EU-WFD) [10], the EU Marine Strategy Framework Directive [11], and the EU Nitrates Directive [12], obliging the polluter to implement measures to reduce the nitrogen impact on groundwater.

The EU-WFD [10] requires the assessment of the groundwater status at the level of groundwater bodies for both quantitative and qualitative status. The latter is assessed by comparing measured concentrations and trends at groundwater observation wells to groundwater quality standards or

threshold values [13] and by extrapolating the findings at the monitoring sites to the area represented by these monitoring sites. As suggested by the European Commission in a guidance document on groundwater status and trend assessment [14] groundwater bodies in the EU are classified as being not in good status in cases of 20% or more of the total groundwater body area being polluted [15–17]. Consequently, a groundwater body is classified as failing in terms of good status due to nitrate in cases where the area represented by the monitoring station(s) shows nitrate concentrations above 50 mg NO<sub>3</sub>/L and/or rising trends exceed 20% of the total groundwater body area.

In the groundwater bodies failing in terms of good status due to nitrate, measures reducing the nitrogen input into the aquifer have to be implemented [10,11]. Taking nitrate concentrations in groundwater above 50 mg NO<sub>3</sub>/L as a reference, the implementation of measures is limited to oxidized aquifers. Significant denitrification capacities are lacking in oxidized aquifers, and thus nitrate concentrations in the upper groundwater are directly correlated to the nitrate input [18,19].

In reduced aquifers, such a relationship is missing due to denitrification processes [20–23], and thus the related groundwater bodies are in good status with regard to nitrate in spite of high nitrogen inputs. Consequently, no measures to reduce *N* input have to be implemented in such cases. In North Rhine-Westfalia, such aquifers occur in the Northern parts of the Lower Rhine Embayment and parts of the Westphalian lowland. In this context, it must be remembered that the fossil pyrite and/or lignite particles involved in the denitrification process in aquifers are exhaustible resources [24,25]. Once this inventory of an aquifer is consumed, a dramatic nitrate concentration rise in groundwater can be observed [26,27]. Therefore, it is in generally not expedient to allow higher nitrogen inputs for reduced aquifers as is done for oxidized aquifers [28].

In order to ensure that the nitrate concentrations in oxidized aquifers will not exceed 50 mg/L and to conserve the natural denitrification capacity of reduced aquifers, the German Working Group on water issues of the Federal States and the Federal Government (LAWA) requires that the nitrate concentration in the leachate should not exceed 50 mg NO<sub>3</sub>/L [28]. Similar considerations are reflected in the groundwater strategies of other countries [29,30]. Against this background, the nitrate concentration in the leachate can be considered as the decisive starting-point to determine the *N* reduction required [31].

In order to implement measures efficiently, a stepwise procedure can be used [18,32]. At first, the source areas contributing to measured nitrogen concentrations in groundwater beyond quality standards are identified within the groundwater bodies failing good chemical status. This is achieved by using modeled land use specific nitrate concentrations in the leachate to indicate nitrogen emission into groundwater. Subsequently, the absolute *N* reduction required to reach the groundwater quality target in the areas concerned is determined. Finally, regionally adapted and accurately dimensioned *N* reduction measures are selected and implemented.

Thus far, the model approach developed by the authors has focused on *N* emissions from agriculture, assuming that these *N* sources mainly have to be considered for determining the *N* reduction need [33–35]. The predominance of agricultural *N* sources in rural areas is quite obvious. In densely populated and industrialized regions, however, there are clear indications that also non-agricultural *N* sources may contribute to high nitrate concentrations [36,37].

With an average population density of 525 inhabitants/km<sup>2</sup> [38], the Federal State of North Rhine-Westfalia represents a prime example for a densely populated region in Germany. In light of the above, there is a debate as to what extent non-agricultural *N* emissions contribute to high nitrate concentrations. In cases where the nitrate concentrations in the leachate above 50 mg/L can be attributed to *N* sources other than agricultural *N* sources, agriculture alone cannot be obliged to implement *N* reduction measures according to EU-WFD requirements [10]. In the regions where this is the case, *N* reduction measures to counteract non-agricultural *N* sources would have to be implemented.

Against this background, a simultaneous consideration of the *N* emissions from all relevant *N* sources is indispensable for assessing the entire *N* loading of the leachate as well as the *N* inputs into groundwater and surface waters. In practical terms, this means that in addition to the agriculturally produced *N* emissions (agricultural *N* balance surplus, atmospheric *NH<sub>x</sub>* deposition), the *N* emissions

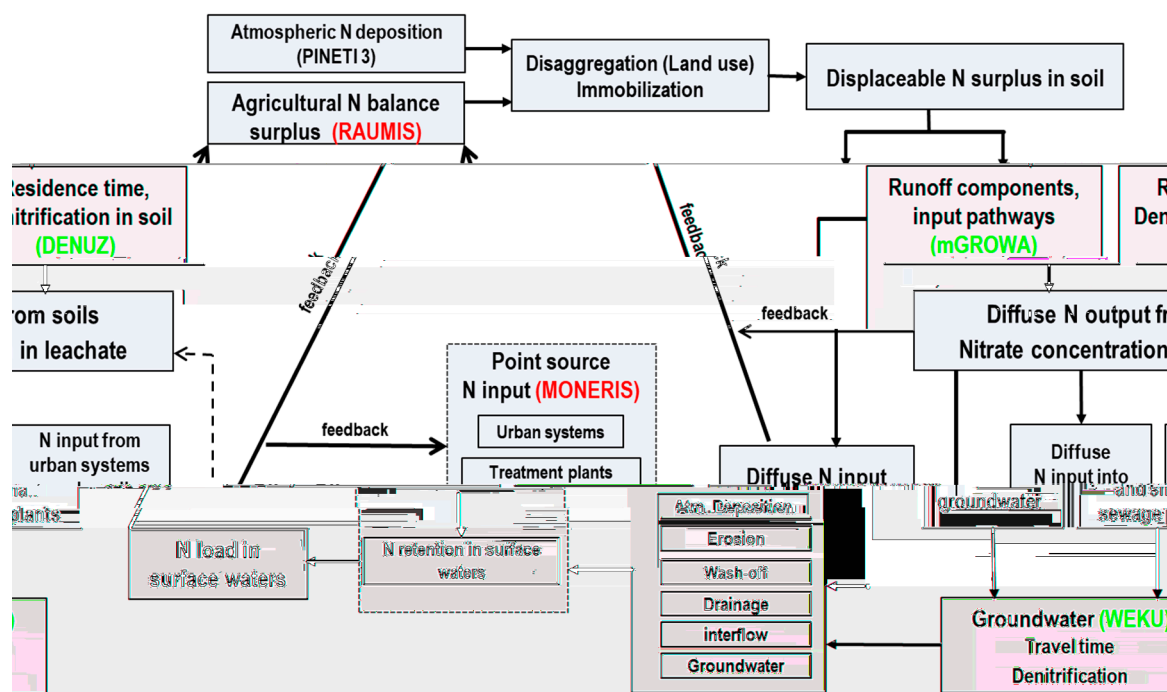
from urban systems; small sewage treatment plants seeping into groundwater; and the atmospheric  $NO_x$  deposition from industry, household, and traffic should also be determined, doing so enables the identification of the “hot-spot areas”, wherein the nitrate concentration in the leachate exceeds 50 mg/L. Additionally, the proportion of the individual  $N$  sources with regard to the modelled nitrate concentration in the leachate in a certain region can be assessed objectively. The latter is an important prerequisite for addressing the regionally relevant  $N$  emission source(s) and for deriving correctly dimensioned  $N$  reduction measures.

## 2. Materials and Methods

The co-operation project GROWA+ NRW 2021 initiated by the Federal States’ Ministry for Environment, Agriculture, Nature and Consumer Protection started at the end of 2015. In the context of the GROWA+ NRW 2021 project, the coupled agro-economic-hydrologic model network RAUMIS-mGROWA-DENUZ-WEKU-MONERIS [31] is applied and further developed in order to support the implementation process of the EU-Water Framework Directive, the EU Nitrates Directive, and the EU Marine Strategy Framework Directive in the Federal State of North Rhine-Westphalia. The questions to be answered in the GROWA+ NRW 2021 project include;

- The determination of the actual  $N$  input into groundwater and surface waters;
- The identification of actual “hot spot” areas of  $N$  pollution;
- The assessment of the necessary reduction of  $N$  emissions to reach the EU quality standards;
- The prediction of the time lags until  $N$  reduction measures will show effect (target achievement).

Nitrate concentration in the leachate is determined within the framework of an area-differentiated modeling of the diffuse and point source  $N$  inputs into groundwater and surface waters. For this purpose, the model system [31,32], which had already proven its suitability in macro-scale applications on the level of States and river basins in Germany, was applied in NRW on the basis of statewide available input data. The individual sub-models and their interplay are documented in the literature [32–36] and will only be briefly described here. The interplay of the individual sub-models is summarized in Figure 1.



**Figure 1.** Simulation of nitrate concentration in the leachate in the framework of the coupled model system RAUMIS-mGROWA-DENUZ-WEKU-MONERIS.

In the agricultural sector model RAUMIS [39], a set of agro-environmental indicators is linked to agricultural production. Currently, the model comprises indicators such as fertilizer surplus (nitrogen, phosphorus, and potassium), pesticides expenditures, a biodiversity index, and corrosive gas emissions. These indicators help to evaluate direct and indirect environmental impacts of policy-driven changes in agricultural production. Regarding diffuse water pollution, the indicator “nitrogen surplus” is of particular importance. Agricultural statistics with data, for instance on crop yields, livestock farming, and land use, were used to balance the nitrogen supplies and extractions for the agricultural area. The long-term nitrogen balance averaged over several vegetation periods is calculated by considering the organic nitrogen fertilization, the mineral nitrogen fertilization, the symbiotic *N* fixation, the atmospheric *N* inputs, the compost and sewage sludge spreading, and the *N* removal with the crop substance [40,41]. As a rule, the difference between nitrogen supplies, primarily by mineral fertilizers and farm manure, and nitrogen extractions, primarily by field crops, leads to a positive *N* balance.

A certain amount of the mineral *N* surpluses in soils is denitrified to molecular nitrogen. Denitrification losses in the soil are calculated using the DENUZ model as a function of the diffuse *N* surpluses, denitrification conditions, and the residence time of percolation water in the soil according to Michaelis–Menten kinetics [31,34]. The kinetical parameters are assessed on the basis of observed denitrification rates in soils [42,43] according to the geological substrate, the influence of groundwater, and perching water of the soils and the average residence time of perching water in the soil.

In order to determine the diffuse *N* inputs into groundwater and surface waters according to individual pathways, the *N* outputs from soil were subsequently coupled to runoff components. The latter were quantified with the water balance model mGROWA [44,45]. The mGROWA modelling approach comprises several sequential parts. Within the basic part, the hydrologic processes at the earth’s surface and in the root zone of soil are simulated. In particular, soil moisture dynamics including percolation water movement, capillary rise from groundwater to the root zone, actual evapotranspiration, and total runoff generation are calculated on the basis of the multilayer soil water balance model BOWAB [46]. Total runoff values are used to derive runoff components including the leachate rate and input pathways for nutrients into groundwater and surface water.

Nitrate inputs into an aquifer may be reduced in groundwater by denitrification processes in a reduced (oxygen-free) groundwater milieu. This reactive nitrate transport in reduced groundwater is modelled using the WEKU model [47,48] assuming a first-order denitrification kinetics depending on the nitrate inputs and the residence time in groundwater with a reaction constant of 0.17–0.56 a<sup>-1</sup> [49–51].

*N* inputs from point sources and urban areas were taken into account using the procedures elucidated in the MONERIS model [52]. The nitrogen load in surface waters within a catchment is calculated by integration of the diffuse nitrogen inputs into the surface waters via the considered pathways calculated for each grid cell over the catchment area of the considered station plus the sum of the *N* inputs from point sources. The observed *N* loads, however, are influenced by nitrogen retention processes in the river itself, which may reduce the nitrogen loads of rivers. Nitrogen conversion in rivers is considered using the size of the catchment area, total runoff, the size of open water areas and temperature as inputs [53].

The summation of the modelled *N* inputs from diffuse and point sources minus the riverine *N* retention were compared to the measured *N* loads from monitoring stations. The observed discharge and *N* total concentrations were transformed into  $N_{\text{tot}}$ -loads according to the OSPAR method [54].

The results of three sub-models were used for the simulation of the nitrate concentration in the leachate, namely, the mean long-term leachate rate determined with the water balance model mGROWA [44], the agricultural *N* balance surplus assessed on the basis of the agro-economic model RAUMIS [39], and the reactive *N* transport in soils determined on the basis of the DENUZ model [31].

Atmospheric *N* deposition was taken into account, separated for the agricultural-related  $NH_x$  emission and the atmospheric  $NO_x$  deposition originating from households, industry, and transport [55].

Both atmospheric  $N$  sources contribute to the diffuse  $N$  output from soils. Additionally, the  $N$  emissions from urban systems and small sewage treatment plants were considered.

Equation (1) shows the general relation between the  $N$  sources and the leachate rate in order to determine the nitrate concentration in the leachate. For an area covering analysis on the Federal State level, the individual terms of Equation (1) were determined:

$$C_{NO_3} = \frac{4.43 \times (N_{soil} + KKA + KS)}{0.01 \times Q_{sw}} \quad (1)$$

where

$C_{NO_3}$ : nitrate concentration in the leachate (mg/L);

$Q_{sw}$ : leachate rate (mm/year);

$KKA$ :  $N$  emissions from small sewage treatment plants (kg N/(KKA and year));

$KS$ :  $N$  emissions from urban systems (kg N/(community and year));

$N_{soil}$ : diffuse  $N$  output from soils (kg N/(ha and year));

4.43: factor to convert nitrate-N (mg/L) to nitrate- $NO_3$  (mg/L)(-);

0.01: factor to convert mm in liter (-).

The leachate rate ( $Q_{SW}$ ) was determined on the basis of the mGROWA model [39], which simulates in the basic part the hydrologic processes at the earth's surface and in the root zone of soils. In particular, soil moisture dynamics including the movement of the leachate in soils, capillary rise from groundwater to the root zone, actual evapotranspiration, and total runoff generation were calculated in daily time steps on the basis of grass reference evapotranspiration, land use-specific crop coefficients, and a topography correction function. Additionally, mGROWA calculated the water balance for impervious surfaces (e.g., sealed surfaces in urban areas) and open water surfaces using approaches adapted to specific storage characteristics. The second part in mGROWA separated total runoff into the direct runoff components (natural interflow, drainage runoff, surface runoff, direct runoff from urban areas) and groundwater recharge from the total runoff by using base flow indices [56]. The leachate rate results from the difference between surface runoff including runoff from urban areas and total runoff and designates the water volume leaving the root zone downwards. It is in this regard not identical to groundwater recharge, which designates the water volume infiltrating into the aquifer.

The diffuse  $N$  output from soil ( $N_{soil}$ ) included  $N$  originating from two  $N$  sources, on one hand the  $N$  output from soil originating from agriculture ( $N_{soil}(agri)$ ), and on the other hand the  $N$  output from soil originating from  $NO_x$  deposition. The diffuse  $N$  output from soil originating from agriculture ( $N_{soil}(agri)$ ) was derived according to Equation (2) considering the agricultural-related  $N$  loads. The corresponding diffuse  $N$  output from soil originating from  $NO_x$  ( $N_{soil}(NO_x)$ ) was derived according to Equation (3). In both cases, two important processes controlling the  $N$  losses from soils, these being  $N$  immobilization ( $NI$ ) and denitrification ( $ND$ ), needed to be considered.

The diffuse  $N$  output from soil originating from agriculture ( $N_{soil}(agri)$ ) included the agricultural  $N$  balance surplus ( $N_u$ ) on a community level averaged over several vegetation periods provided by the regionally differentiating agricultural sector model RAUMIS [40]. As a rule, the difference between nitrogen supplies, primarily by organic and mineral fertilizers, and the nitrogen extractions, primarily by field crops, leads to a positive  $N$  balance for the agriculturally used areas ( $N_u$ ).

$$N_{soil}(agri) = N_u + NHx - NI - ND \quad (2)$$

$$N_{soil}(NO_x) = NO_x - NI - ND \quad (3)$$

where

$N_{soil}(agri)$ :  $N$  output from soil originating from agriculture (kg N/ha-year);

$N_{soil}(NO_x)$ :  $N$  output from soil originating from  $NO_x$  (kg N/ha-year);

$N_U$ : mean agricultural  $N$  balance surplus (kg N/ha·year);  
 $NH_x$ : mean atmospheric  $NH_x$  deposition (kg N/ha·year);  
 $N_I$ : mean  $N$  immobilization in soil (kg N/ha·year);  
 $N_D$ : mean denitrification in soil (kg N/ha·year).

The  $NH_x$  emission ( $NH_x$ ), particularly from livestock, is the second most important agricultural  $N$  source that contributes to the diffuse  $N$  output from soil originating from agriculture (see Equation (2)). It can be assumed that the entire agricultural share in atmospheric deposition was represented by the  $NH_x$  deposition. Equivalent to the  $NH_x$  deposition, it was assumed that the entire  $NO_x$  deposition originating from households, traffic, and industry represented the diffuse  $N$  output from soil originating from non-agriculture  $N$  sources ( $N_{soil}(NO_x)$ ).

Both  $NH_x$  and  $NO_x$  were derived from an official German-wide dataset on atmospheric  $N$  deposition determined in the framework of the PINETI project series (PINETI-3, Pollutant Inputan EcosystemImpact) [55] for the time series 2013–2015. In order to adapt the spatial resolution of the PINETI-3 datasets to the spatial resolution of the modelling on NRW scale, the land-use specific  $NH_x$  and  $NO_x$  values available as  $1 \times 1$  km grids were disaggregated according to the land use grids of  $100 \times 100$  m. Apart from its impact on agriculturally used land, the atmospheric  $NH_x$  and  $NO_x$  deposition also affected forests and settlement areas, and thus it had to be considered as area-covering data in the modelling of the nitrate concentration in the leachate.

The  $NO_x$  deposition, as well as the sum of agricultural  $N$  balance surpluses and atmospheric  $NH_x$  deposition, do not correspond to the diffuse  $N$  output from soils as two important processes controlling the  $N$  losses from soils, that is,  $N$  immobilization ( $N_I$ ) and denitrification ( $N_D$ ) have to be considered. For pasture and forested areas, it is assumed that a certain part of the  $N$  input into soils is immobilized in the soil organic matter [57] and contributes to the development of biomass. The immobilization rates depend on the interplay of certain site conditions, for instance, leachate rates, soil texture, and topography. They can consequently be regarded as regionally variable and are determined in the framework of the model calibration for pasture and forested areas. For arable land, however, a significant  $N$  immobilization in soil can be neglected [33].

The  $N$  load resulting from the summation of agricultural  $N$  balance surplus, atmospheric  $NH_x$  and  $NO_x$  deposition, and  $N$  immobilization in soil is defined as the displaceable  $N$  surplus in soil (see Figure 1). From this intermediate result, the  $N$  output from soil is derived by subtracting the  $N$  losses in soil due to denitrification. In contrast to  $N$  immobilization, denitrification in soil takes place independent from the type of land cover. Equation (3) specifies the DENUZ approach to determine denitrification rates in soil.

$$\frac{dN_s t_{soil}}{dt_{soil}} + D_{max} \cdot \frac{N_s t_{soil}}{k + N_s t_{soil}} = 0 \quad (4)$$

where

$N_s t_{soil}$ :  $N$  output from soil from agricultural  $N$  sources and  $NO_x$  deposition after residence time ( $t_{soil}$ ) (kg N/(ha·year));

$t_{soil}$ : residence times in soil (year);

$D_{max}$ : maximum yearly denitrification rate in soil (kg N/(ha·year));

$k$ : Michaelis-constant (kg N/(ha·year));

$0$ : displaceable  $N$  surplus in soils (kg N/(ha·year)).

Using observed denitrification rates as a reference, the maximum denitrification rate ( $D_{max}$ ) was assessed [18]. This was performed on the basis of a ranking of the soils predominantly according to their groundwater and perching water influence, as well as their organic carbon content [34,35]. Denitrification rates in soils were determined as a relationship between the realizable maximum annual denitrification rates assigned by the denitrification conditions and the related soil-specific reaction rates of denitrification ( $k$ ) under consideration of the effective residence times of the leachate in the

root zone ( $t$ ). In this way, it is assumed that, for example, in a case were the residence time in a certain soil amounts to 6 months, the extent of denitrification is half of the maximum denitrification rate per year for the given soil.

The final result of the DENUZ model, that is, the diffuse  $N$  output from soils from agricultural  $N$  sources and  $NO_x$  deposition, was subsequently used to calculate the nitrate concentration in the leachate according to Equation (1). Additionally, the  $N$  outputs from urban systems (KS) and small sewage treatment plants (KKA) (see Equation (1)) were derived from directories about inhabitants and data about water management facilities (for the North Rhine-Westfalia-specific numbers, see Section 3.2.1).

### 3. Results

All input parameters and model results to calculate the nitrate concentration in the leachate were processed as area-covering data for the entire state of Northrhine-Westfalia with a spatial resolution of  $100\text{ m} \times 100\text{ m}$ . This resulted in a subdivision of the area of the Federal State into around 3.4 Mio individual grids.

The leachate rate (see Figure 2) diluted the  $N$  emissions from agricultural and non-agricultural  $N$  sources, as specified in Equation (1). It was calculated with the mGROWA model [39] for the hydrological reference period of 1981–2010. Using mean long-term leachate rates as a reference has two advantages with regard to the modelled nitrate concentrations in the leachate. On one hand, as a short-term climate-induced blurring of leachate rates was excluded, the modelled nitrate concentrations in the leachate were representative of the regional long-term hydrologic conditions. On the other hand, the regional varying  $N$  emissions were related to a uniform leachate rate, which was of importance when the impact of  $N$  reduction measures was assessed.

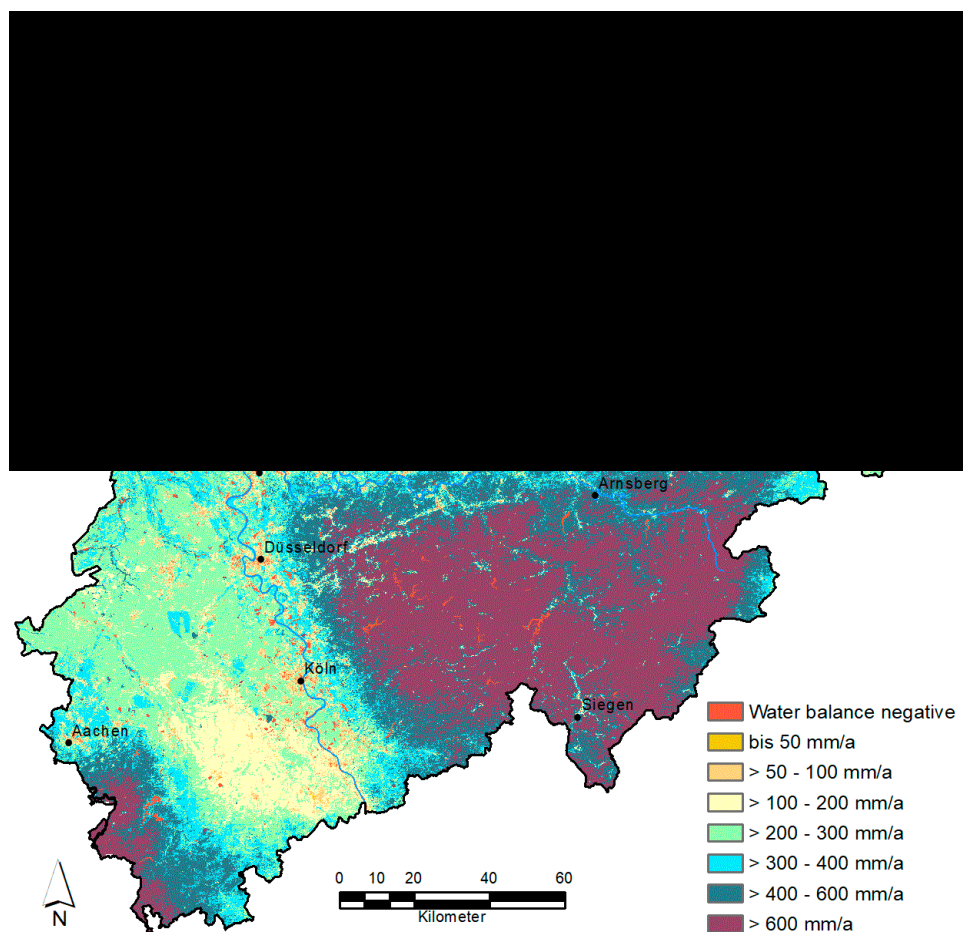


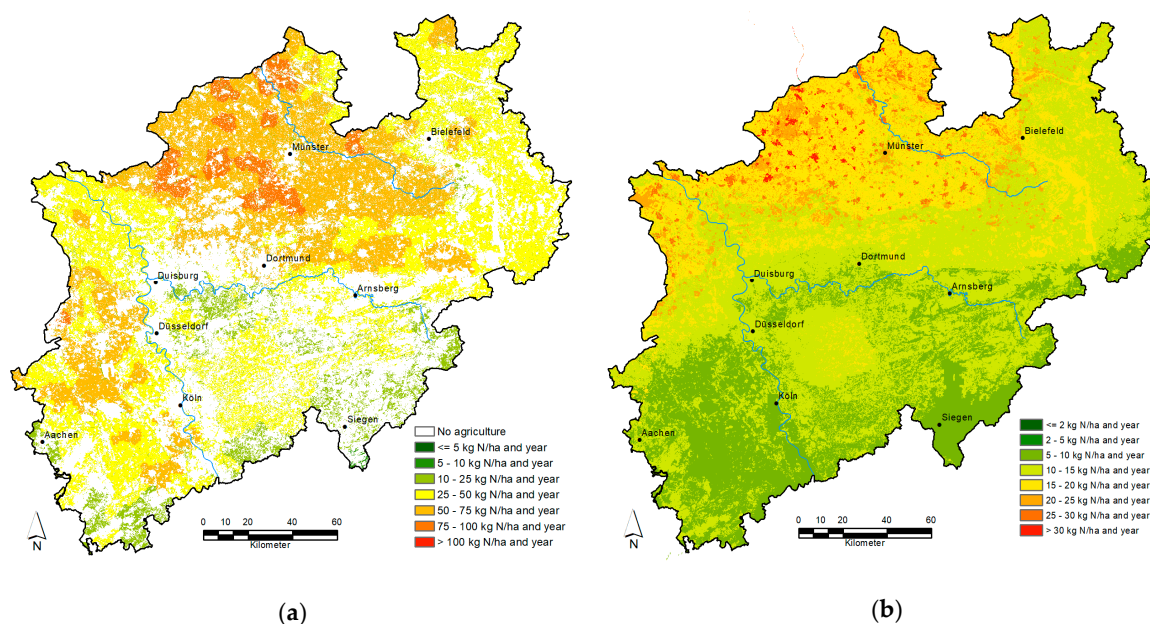
Figure 2. Mean long-term leachate rate of the hydrologic period of 1981–2010.

The mean long-term leachate rates shown in Figure 2 reveal wide disparities between the regions. Whereas leachate rates of 600 mm/year or more frequently occurred in all consolidated rock regions (e.g., Rhenish Massif), leachate rates of less than 200 mm/year may have occurred in the southern part of the Lower Rhine embayment. There, the dilution of *N* emissions from the different *N* sources was up to three times higher in the consolidated rock regions.

### 3.1. Nitrogen Emissions from Agricultural Sources and Resulting Nitrate Concentrations in the Leachate

#### 3.1.1. Agricultural *N* Sources

The *N* sources taken into account for determining the *N* output from soil originating from agriculture, that is, the agricultural *N* balance surplus and the atmospheric *NH<sub>x</sub>* deposition, are shown in Figure 3a,b, respectively.



**Figure 3.** (a) Agricultural *N* balance surplus and (b) atmospheric *NH<sub>x</sub>* deposition.

In order to guarantee that crop- and withdrawal-related fluctuations were biased out, the agricultural *N* balance surplus on a community level provided by the RAUMIS model [40] was determined as an averaged value for the period of 2014–2016. In total, the agricultural *N* balance surplus in North Rhine-Westphalia summed up to around 82.400 t N/a. Major differences became evident in cases where this sum was considered regionally differentiated (see Figure 3a). Agricultural *N* balance surpluses of less than 25 kg N/ha and year were found in regions where extensive grassland dominates (e.g., Rhenish Massif). In the food crop cultivation regions (e.g., Lower Rhine Embayment), where the *N* demand was predominantly covered by well-controllable mineral fertilizer applications, the agricultural *N* balance surpluses ranged between 25 and 50 kg N/ha per year. In contrast, nitrogen surpluses above 50 kg N/ha per year were determined for regions where livestock density was so high that the amount of organic fertilizers (and additionally applied mineral fertilizers) exceed the *N* demand of the agriculturally used land. Areas in white indicate the non-agriculturally used forest and settlement areas.

In the agricultural regions with intensive livestock production in the north, the atmospheric *NH<sub>x</sub>* deposition provided by the PINETI model summed up to more than 20–25 kg N/ha per year and locally to more than 30 kg N/ha per year [58] (see Figure 3b). To the south, that is, in greater distance from the regions with intensive livestock production, *NH<sub>x</sub>* deposition rates between 10 and 20 kg N/ha per year predominated. This region extended from the northern part of the Lower Rhine embayment in the

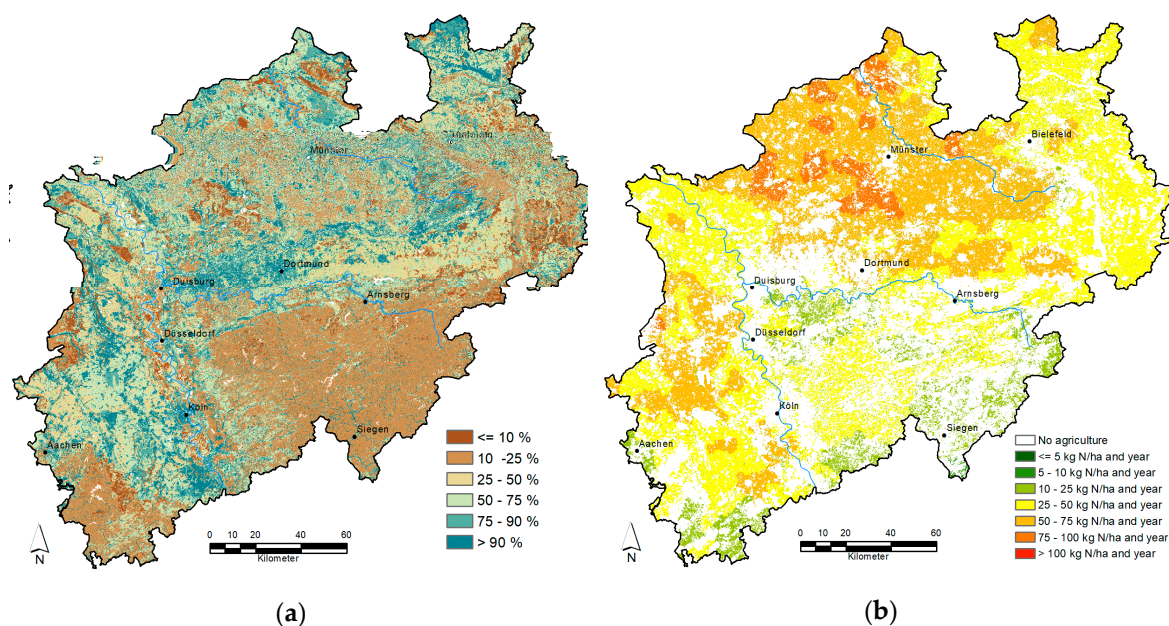


west to the Weserbergland in the east. In the southern part of the Lower Rhine Embayment, crop farms predominate. There, the atmospheric  $NH_x$  deposition rarely exceeded 10 kg N/ha per year. The same  $NH_x$  deposition rates were determined for the most southern parts of the Rhenish Massif situated in the lee of the Sauerland Mountains. Averaged over the entire Federal State of North Rhine-Westfalia, the atmospheric  $NH_x$  deposition corresponded to a total of around 44,000 t N/a.

### 3.1.2. N Output from Soils Originating from Agricultural N Emission Sources

In order to determine the N output from soils, N immobilization and denitrification (in soil) was considered. N immobilization is related to the sum of the agricultural N balance surpluses and atmospheric  $NH_x$  deposition. Whereas the determined N immobilization rates comprised around 50% for the land-use category pasture, the N immobilization rates for the land-use categories of coniferous forests and deciduous forests were in the range of 10% and 20%, respectively. Averaged over the entire Federal State of North Rhine-Westfalia, N immobilization retained around 18,500 tons N/a. Consequently, the displaceable N surplus in soil, that is, the sum of agricultural N balance surpluses plus atmospheric  $NH_x$  deposition minus N immobilization was in the range of around 108,000 t N/a.

The displaceable N surplus in soil minus the N losses in soil due to denitrification modeled with the DENUZ model (Figure 4a) determined the N output from soils (see Figure 4b). In the shallow brown earth soils of the Rhenish Massif, denitrification reduced the displaceable N surplus in soil to less than 25%. The low denitrification rates were due to the interaction of small residence times in the soil (often less than 3 months) and poor denitrification conditions in the soil.



**Figure 4.** (a) Denitrification losses in soil relative to the displaceable N surplus in soil, and (b) N output from soils originating from agricultural sources.

In the fertile loess regions of North Rhine-Westfalia (Lower Rhine embayment, Soester Börde), up to 50% of the agricultural N input into soils was denitrified. Although the denitrification capacity of the predominantly occurring luvisol was quite unfavorable, these soils displayed a high water storage capacity and relatively low leachate rates (see Figure 2). Consequently, residence times in soil was often in the range of 1 year (or more), and thus the maximum possible denitrification rates in soil could nearly be reached or even be exceeded. As shown in Figure 4b, the resulting N output from soils in these regions ranged between 25 and 50 kg N/ha per year.

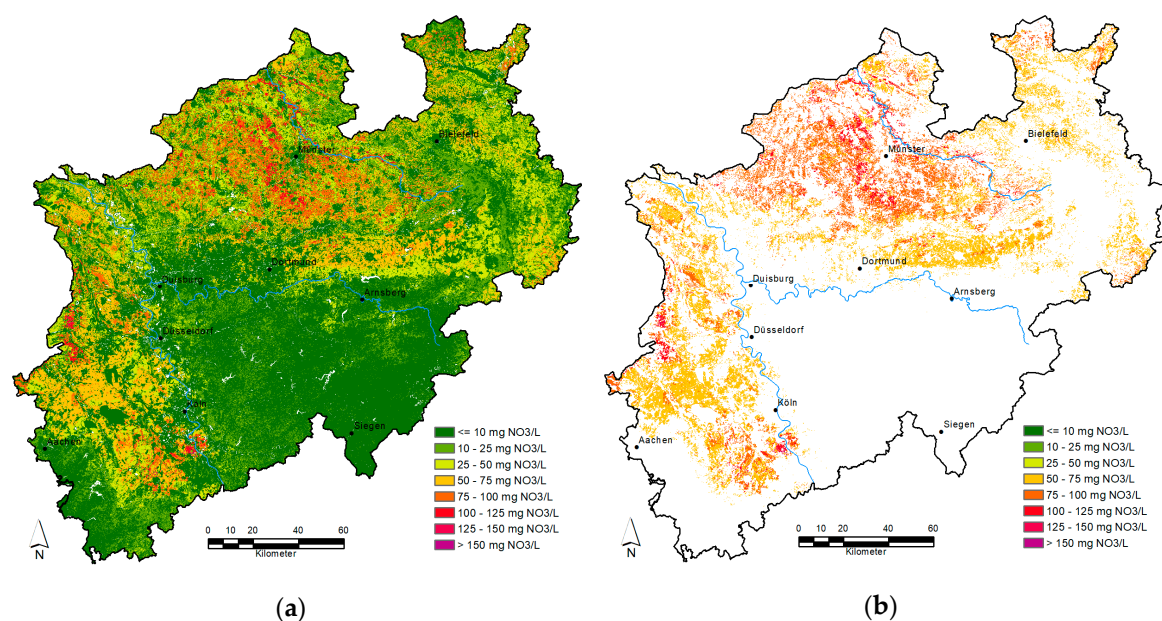
Generally, high displaceable N surpluses in soil occurred in the Münsterland basin in the Northern part of North Rhine-Westfalia. There, sandy podzol soils showing poor denitrification

capacities alternated with loamy lowland soils (e.g., Gleyic soils) showing high denitrification capacities. Consequently, denitrification losses of more than 75% may be achieved in the lowland soils, whereas denitrification rates in the pozol soils hardly exceeded 25% (see Figure 4a). Accordingly, soils with  $N$  outputs of less than 25 kg N/ha per year and soils with  $N$  losses of more than 75 kg N/ha per year occurred closely adjacent to one another (see Figure 4b). In the core of the Münsterland, vast areas with  $N$  outputs from the soil in the range of 75 kg N/ha per year were identified. There, soils with moderate denitrification capacities coincided with very high displaceable  $N$  surpluses in soil. Clearly recognizable in Figure 4b is the metropolitan area Rhein-Ruhr. As there were no other agricultural  $N$  inputs other than the atmospheric  $NH_x$  deposition, the  $N$  output from soil that can be assigned to agricultural  $N$  emissions was below 5 kg N/ha per year.

Averaged over the entire Federal State of North Rhine-Westfalia, around 45% of the displaceable  $N$  surplus in soil (around 108,000 t N/a) was denitrified, and thus the  $N$  output from soil originating from agricultural  $N$  emissions was reduced to approximately 69,000 t N/a.

### 3.1.3. Nitrate Concentration in the Leachate Originating from Agricultural Sources

The  $N$  output from soil attributed to agricultural  $N$  emissions (Figure 4b) were combined with the leachate rates (Figure 2) to determine the nitrate concentration in the leachate originating from agricultural sources (see Figure 5a). In Figure 5b, the areas where a nitrate concentration in the leachate exceeded 50 mg  $NO_3/L$  are highlighted.



**Figure 5.** (a) Nitrate concentration in the leachate originating from agricultural sources, and (b) areas showing nitrate concentrations in the leachate above 50 mg  $NO_3/L$  due to agricultural  $N$  emissions.

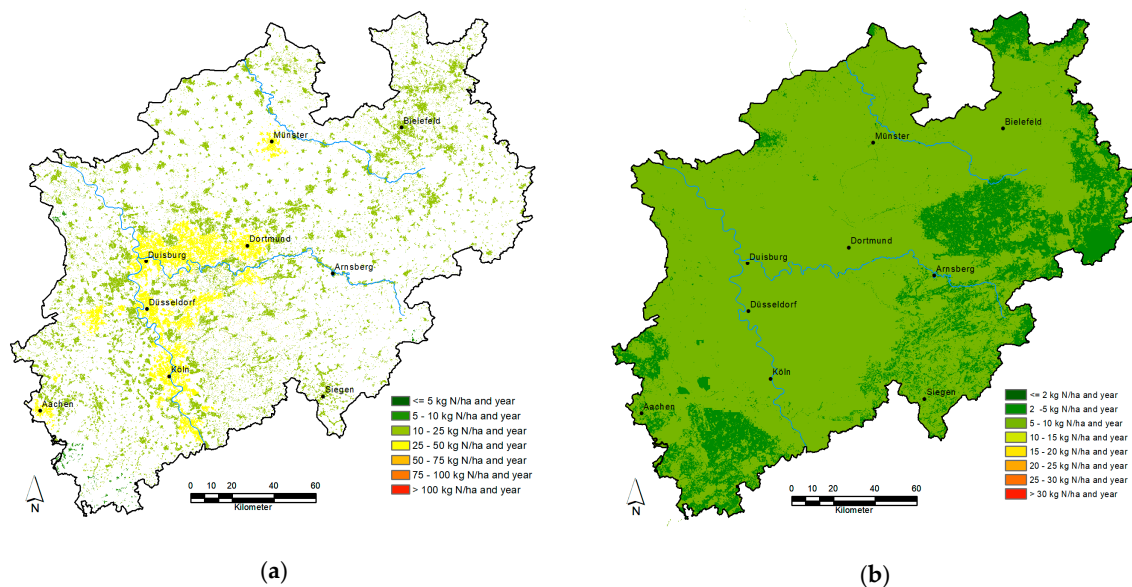
For many areas in the Münsterland, particularly high values arose due to the high livestock density, which led to an accordingly high nitrogen balance surplus. In the Lower Rhine Embayment, nitrate concentrations in the leachate between 50 and 75 mg/L predominated. There, moderate nitrogen balance surpluses arising from cash crop farms were combined with low leachate rates. Nitrate concentrations in the leachate below 25 mg/L could be found in the urbanized areas of North Rhine-Westfalia, as well as in the Rhenish Massif, where high leachate rates coincided with low  $N$  emissions. Figure 5b illustrates in this regard how yet again there was a remarkable extent of areas with nitrate concentrations in the leachate above 50 mg/L in the Lower Rhine Embayment and the Münsterland.

### 3.2. Nitrogen Emissions from Non-Agricultural Sources and Resulting Nitrate Concentrations in the Leachate

The calculation of the nitrate concentration in the leachate due to non-agricultural *N* sources included on one hand the *N* emission from small sewage treatment plants and urban systems. On the other hand, it included the *N* outputs from soil attributed to the *NO*<sub>x</sub> deposition from industry, traffic, and households (see Equation (3)).

#### 3.2.1. Non-Agricultural *N* Sources

The *N* output from urban systems (Figure 6a) was quantified on the basis of data provided by an actual management report about the development and level of sewage disposal in North Rhine-Westphalia [59]. According to this report, the total amount on nitrogen emitted from municipal waste water disposals (including indirect discharges) divided by all inhabitants resulted in 11 g *N* per day. Under the assumption that 15% of this disposal was released into groundwater due to leakage from the waste water systems, a uniform nitrogen release from urban systems into groundwater of 1.65 g *N* per inhabitant per day was estimated. The *N* losses from urban systems determined in this way ranged between 10 kg and 50 kg *N*/ha per year. The highest values occurred, as expected, in densely populated regions along the river Rhine and the Ruhr area. On Federal State scale, the total *N* losses from urban systems accumulated to approximately 11.200 t *N*/a.



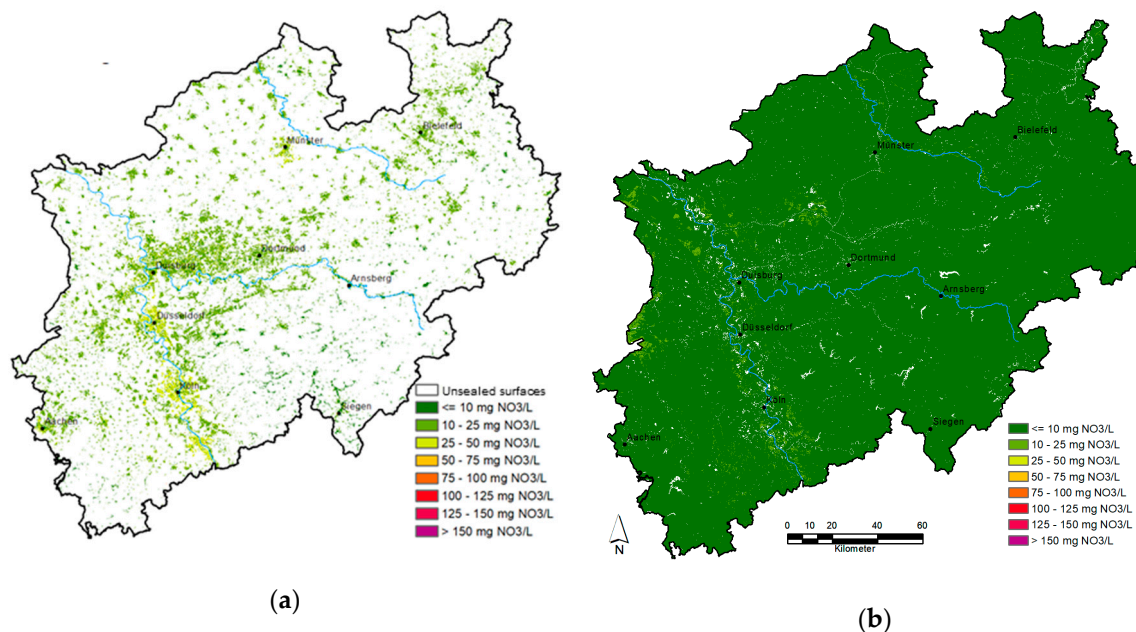
**Figure 6.** (a) Nitrogen output from urban systems and small sewage treatment plants, and (b) atmospheric *NO*<sub>x</sub> deposition (2013–2015).

For considering the *N* output from small sewage treatment plants, the recorded annual *N* emissions of around 20,000 individual facilities emitting into groundwater were taken into account [60]. For this purpose, the recorded *N* loads were assigned to the corresponding 100 × 100 m grids. In most of all grids concerned, the *N* outputs from small sewage treatment plants showed values below 25 kg *N*/ha per year. Higher *N* outputs occurred locally only, but could reach 100 kg *N*/ha per year and more. At the Federal State level, the total *N* loss of the small sewage treatment plants summed up to around 500 t *N*/a. As the visibility of the individual 100m grids was limited, the *N* outputs from small sewage treatment plants are shown in Figure 6a, together with the *N* output from urban systems.

The atmospheric *NO*<sub>x</sub> deposition originating from households, industry, and transport was provided from a Germany-wide dataset on atmospheric *N* deposition [58]. Depending on the region, the *N* output from soils from *NO*<sub>x</sub> deposition ranged between <5 to >10 kg *N*/ha per year (see Figure 6b). For the total area of NRW, this relatively low average annual atmospheric *NO*<sub>x</sub> deposition summed up to around 20,000 tons of *N*/a.

### 3.2.2. Nitrate Concentration in the Leachate Originating from Non-Agricultural N Sources

The N output attributed to urban systems and small sewage treatment plants (Figure 6a), as well as the N output from soil resulting from  $NO_x$  deposition (Figure 6b) was combined with the leachate rates (Figure 2) to determine the nitrate concentration in the leachate originating from non-agricultural sources (Figure 7).



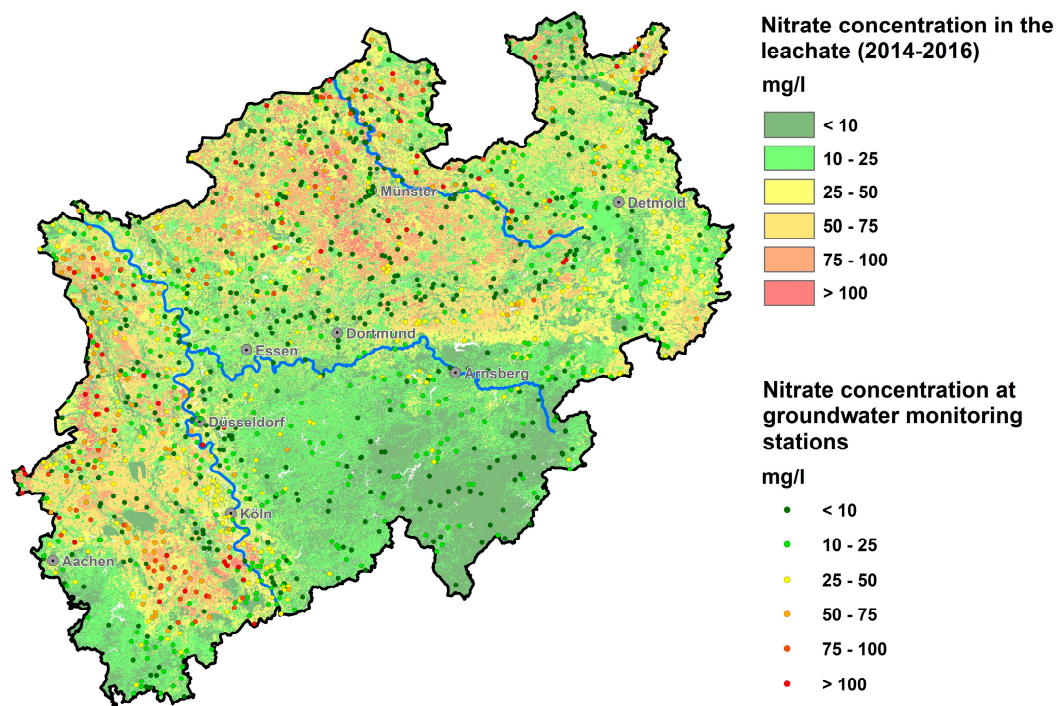
**Figure 7.** (a) Nitrate concentration in the leachate originating from urban systems and small sewage treatment plants, and (b) nitrate concentration in the leachate originating from the N output from soil due to  $NO_x$  deposition.

Figure 7a shows that the nitrate concentration in the leachate originating from urban systems and small sewage treatment plants ranged in most areas between 10 and 25 mg/L (e.g., in the entire Ruhr area). It was evident that the nitrate concentration in the leachate originating from these sources only to a minor extent and locally exceeds 50 mg/L. As the areas concerned did not exceed 20% of the area of a groundwater body, no measures to reduce the N emissions from urban systems and small sewage treatment plants had to be included in the program of measures according to EU-WFD requirements [14]. This, however, does not detract from the fact that measures to reduce N output from urban systems may be necessary to improve surface water quality.

Figure 7b shows the nitrate concentration in the leachate originating from  $NO_x$  deposition. For the latter, the denitrification in soil was accounted for as described in Equation (3). In most areas of North Rhine-Westphalia, the nitrate concentration in the leachate originating from  $NO_x$  deposition was less than 10 mg/L. In the southern part of the Lower Rhine Embayment, values of up to 25 mg/L occurred due to the low leachate rates (Figure 2). In conclusion,  $NO_x$  deposition did not at all lead to  $NO_3$  concentrations in the leachate above 50 mg/L.

### 3.3. Plausibility Check of Modelled Nitrate Concentration in the Leachate

For comparing (modeled) nitrate concentrations in the leachate with (observed) nitrate concentrations in groundwater, it was necessary to merge the N emissions from the individual N sources. The corresponding nitrate concentrations in the leachate are represented in Figure 8 as the underlying colored areas.



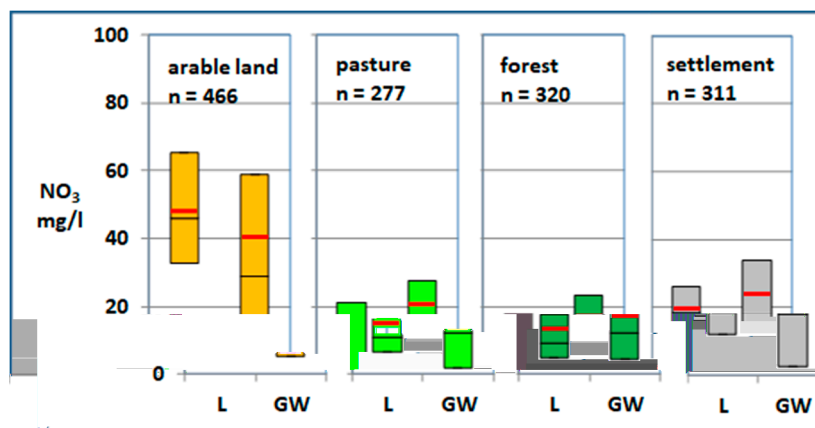
**Figure 8.** Plausibility check of the mean annual nitrate concentration in the leachate. The dots show observed values at groundwater monitoring sites—the underlying colored areas are the modelled nitrate concentrations in the leachate per grid.

The modelled nitrate concentration in the leachate was compared to nitrate concentrations observed at around 1500 groundwater monitoring stations from the upper aquifer for the period 2014 to 2017. In Figure 8, the mean values of the observed nitrate concentrations at the groundwater monitoring stations are represented as dots. For the comparison, the same class widths and the same color gradation were selected for both the underlying areas and the dots. The proportion of the main land use types (e.g., arable land, pasture, forest, settlement) occurring in North Rhine-Westphalia was approximately reflected by the distribution of the monitoring stations within these land use types, thus guaranteeing representability.

As can be seen from Figure 8, the modeled values in the Lower Rhine Embayment, the Weserbergland, and the Rhenish Massif corresponded spatially and with regard to their concentration levels very well to the observed nitrate concentrations in groundwater.

In the Münsterland, however, the modeled nitrate concentration in the leachate systematically exceeded the observed nitrate concentrations in groundwater (see Figure 8). There, due to the occurrence of denitrification capacities in the aquifers, the nitrate concentration in the leachate was decreased once the leachate entered into the groundwater. Consequently, the apparent disagreement between (high) modeled nitrate concentrations in the leachate and (low) observed nitrate concentrations in groundwater was attributable to the considerable denitrification capacity of reduced aquifers and did not indicate wrong model results [24].

The plausibility check described above was accompanied by a statistical evaluation of the modelled nitrate concentrations in leachate and the observed nitrate concentrations at monitoring stations for different land uses (Figure 9).



**Figure 9.** Comparison of modelled nitrate concentrations in the leachate (L) and observed nitrate concentrations in groundwater at monitoring stations (GW) for different land use types. The lower and upper end of the bars indicate the statistical distribution with the 25th percentile and 75th percentile, respectively, and the lines inside the bars mark the median (black line) and mean (red line).

Figure 9 shows that the 25th percentile and 75th percentile values, as well as the median and mean values of the modelled nitrate concentrations in the leachate and the observed nitrate concentrations in groundwater corresponded quite well for the land use classes of pasture, forests, and urban areas. For the land use class of arable land, however, the observed nitrate concentrations in groundwater showed lower values than the modelled nitrate concentrations in the leachate.

A more detailed analysis showed that the absence of denitrification capacities in aquifers explained the good agreement for the land use classes of pasture, forests, and settlements. Groundwater samples from these land use types showed oxidized groundwater, and thus the nitrate concentration in the leachate was preserved after infiltration into the upper aquifer [18,31].

A considerable number of the groundwater monitoring stations from the land use class of arable land were, however, located in aquifers displaying high denitrification capacities, mainly in Münsterland (see Figure 8). As denitrification in groundwater was not accounted for in the modelled nitrate concentrations in the leachate, it was obvious that the modelled nitrate concentration in the leachate showed higher values than the observed nitrate concentrations in groundwater.

#### 4. Discussion

The application of Equation (1) at the Federal State level was indispensable for assessing the entire *N* loading of the leachate as well as the *N* inputs into groundwater and surface waters. The grids showing nitrate concentrations in the leachate above 50 mg NO<sub>3</sub>/L represent the hot-spot areas of nitrate pollution of groundwater. The good correspondence of the modelled nitrate concentrations in the leachate with the observed nitrate concentrations in groundwater detected in the course of the plausibility check demonstrated that the model results were appropriate in indicating the nitrate pollution of groundwater at the Federal State level. Consequently, the modelled nitrate concentration in the leachate can be regarded as a reliable starting point for scenario analyses, for instance as an adequate reference value for assessing the extent to which a nitrate reduction is necessary to reach the EU-WFD quality target for groundwater.

Inside the groundwater bodies failing good quality status due to nitrate, the areas showing nitrate concentrations in the leachate above 50 mg/L were predestined for implementing *N* reduction measures. Modelling nitrate concentration in the leachate apportioned between the individual agricultural and non-agricultural *N* sources facilitated the identification of the main polluter in a certain region. It was obvious that only the latter had to implement measures to reduce the nitrogen impact on groundwater according to EU-WFD requirements.

Results of the model analysis in North Rhine-Westfalia proved that *N* emissions from small sewage plants, urban systems, and *NO<sub>x</sub>* deposition only locally caused nitrate concentrations in the leachate above 50 mg *NO<sub>3</sub>*/L, in spite of the high population density (525 inhabitants/km<sup>2</sup>). Consequently, as the areas concerned did not exceed 20% of the area of a groundwater body, the focus relied on agricultural measures to reduce nitrogen losses. This, however, did not detract from the fact that the implementation of measures to reduce the *N* output from urban systems may have been necessary, but not within the program of measures according to EU-WFD.

Model analysis confirmed instead that *N* emissions from agriculture exclusively led to extended areas of nitrate concentrations > 50 mg *NO<sub>3</sub>*/L, especially in the north (Münsterland) and the west (Lower Rhine Embayment). As in general more than 20% of the areas in the respective groundwater bodies were concerned, the implementation of measures to reduce agricultural *N* emissions in the context of the WFD program of measures was necessary.

Results presented for the Federal State of Northrhine-Westfalia clearly illustrated the importance of systematically considering not only agricultural *N* emissions in modelling nitrate concentrations in the leachate. Especially in densely populated regions, the consideration of the *N* inputs from all *N* sources (as shown in the maps) was the only way to objectively assess the relevant polluter(s) in a region and to evaluate the relative contribution of each polluter to the overall *N* pollution. The latter was once again important to dimension appropriate polluter-specific *N* reduction measures.

A comparison of modelled nitrate concentrations in the leachate and observed nitrate concentrations in groundwater at monitoring stations for different land use types showed that the modelled nitrate concentration in the leachate showed higher values than the observed nitrate concentrations in groundwater due to denitrification processes in groundwater. The modelled high nitrate concentrations in the leachate were an indication that the *N* emissions in groundwater have to be reduced. Even in cases where the observed nitrate concentrations in groundwater were found to be considerably below 50 mg *NO<sub>3</sub>*/L, a reduction of the *N* emissions in groundwater is the only way to conserve the natural denitrification capacity of reduced aquifers for as long as possible [28].

Although the model can be recommended for large-scale assessments on the level of states or entire river basins, the use of the model results for local issues is subjected to several constraints. Most important are limitations in the local representativeness of the model input parameters derived from statewide available databases. It is evident that, for instance, on-site occurring soil properties may not be represented in a statewide available soil map at a scale of 1:50,000. Consequently, local obviously deviating model results may have been due to databases being insufficiently accurate for local issues. Therefore, an effective monitoring network and local expert knowledge will remain indispensable for implementing local nitrogen strategies. In this regard, it must also be remembered, that the modelled values represent reference values characterizing mean long-term conditions rather than fixed values tracing specific nitrate concentrations at certain sites and at certain times.

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