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Determination of process factors for surface water and groundwater to evaluate the nitrate residue standard

Extended Summary

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Introduction

The aim of this study is to evaluate and differentiate the current nitrate residue standard based on a review of historical nitrate residue measurements and to link these values to the nitrate concentrations measured in surface waters and groundwater.

This study consists of three phases. In a first phase the nitrate residue measurements of the Flemish Land Agency (VLM) are evaluated and models for the prediction of the nitrate residue are constructed. These models are used in phase two of the study to assess the nitrate residue in unsampled parcels.

In a second phase process factors for surface water and groundwater were calculated. A process factor is an empirical "black box" factor that includes all processes that occur between the leaching of nitrate from the soil profile (starting from the nitrate residue in the fall) and the measured nitrate concentrations in surface water or groundwater. These process factors thus impose a link between the nitrate leached out of the soil on the one side and the water quality measurements in surface water or groundwater on the other side. A third phase of this research focuses on translating this new process factors into maximum nitrate residues based on the scientific assumptions of the study in order to comply with the European Nitrates Directive (50 mg per litre of water).

<u>Phase 1: Statistical analysis of the available nitrate residue measurements of the VLM</u> (Flemish Land Agency)

The data that were used in the first phase of this study, have been provided by the VLM-Mestbank, specifically the nitrate measurements for the years 2000 to 2008 for parcels with a "management agreement water" (BOW), control measurements and follow-up samples for the period from 2004 to 2008, parcel specific data and farm specific information for the same period. The database of the Belgian Soil Service (BDB) regarding nitrate measurements was also intensively used. This database contains information concerning the pH and the organic carbon content of the soil, the use of organic fertilizers and green manure crops, etc. In addition, a large number of meteorological and soil data were collected.

From these data sets 37 variables were extracted, for which the influence or relationship with the nitrate residue was analyzed (descriptive analysis) and which were then used to construct a model for predicting nitrate residues (MANCOVA model). Although the available data sets are not fully representative for all agricultural parcels in Flanders, a number of conclusions can be formulated from the <u>descriptive analysis</u>.

Substantial differences between plots with a Management Agreement Water (dataset BO-BDB) on the one hand and plots in which control measurements were carried out by the Mestbank (MB-BDB dataset) on the other hand are clearly demonstrated. The mean nitrate residue of all parcels in the dataset BO-BDB is 22 kg N/ha lower than the mean nitrate residue in the dataset MB-BDB. These differences are mainly due to differences in fertilization practices. The variables with a significant influence on the nitrate residue in both groups were quite similar, although their influence was generally lower on parcels with a Management Agreement Water.

Of all the analyzed variables, following variables are the most important ones: the main crop (crop group), the fertilization practice in the year of sampling (BPJS: combined effect of the evolution of general fertilization practices, implementation of the manure policy, fertilization history, ...), the agricultural region and the soil texture, the carbon content and pH, the aftercrop associated with land cover at the moment of sampling and time of sampling (depending on the harvest date of the main crop or the growing period of the after crops) and, to a lesser extent, weather conditions (precipitation and temperature) and farming type (farms with or without animals).

In figure 1, the influence of fertilization practices in the year of sampling (BPJS) and the Agricultural Region are shown. The differences between control plots of the Mestbank and plots with a "Management Agreement Water" are reflected in this figure.





Figure 1 - Effect of fertilization practices in the year of sampling (BPJS) on the average total nitrate residue per agricultural region, for the control plots of the "Mestbank" (top) and the plots with a Management Agreement Water (below).

Derogation had no effect on the nitrate residue for the crops "grass" and "winter wheat" in the years 2007 and 2008. Derogation plots with "maize" showed a slightly higher mean nitrate residue, but when maize fields with grass as aftercrop were examined, no effect could be observed. Regarding vegetables, the highest nitrate residues in both data sets are found on parcels with cauliflower, spinach and beans and the lowest nitrate residues for sprouts. In parcels where several measurements were made (parcels > 2 ha), the coefficient of variation for the nitrate residue was calculated as a measure of the variability within fields. The mean coefficient is 0.25, which means that the nitrate residues within a parcel differ relatively little from each other.

The variability within parcels was smaller in the Loamy region and on loamy soils than for parcels with lighter textures. It was also smaller for parcels with cereals and sugar beet than for parcels with maize or for orchards. The variability within parcels was largest for grassland. For the parcels which were both sampled in 2007 and 2008 by the "Mestbank", the mean nitrate residue for 2008 was significantly lower than the mean nitrate residue for 2007.

For the vast majority of parcels which had a higher nitrate residue than 90 kg N/ha in 2007, the residue decreased in the following year due to the accompanying measures and increased focus on fertilization practices, and this for all observed crops.

For parcels with a "Management Agreement Water" which were sampled for several years and which repeatedly exceeded the nitrate residue standard (90 kg N/ha) no correlation could be found between the multiple exceedence of the nitrate residue standard and the carbon content of the soil, the ammonium content or the application of organic manure.

In 2008, for parcels with a "prolonged manuring regulation" the mean nitrate residue was significantly higher than for parcels without. The effect of the prolonged manuring regulation was not dependent on soil texture or on the agricultural region.

For each crop group a separate <u>MANCOVA predictive model</u> was developed, based on the control measurements and follow-up samples. These models can be used to predict the total nitrate residue and the nitrate residue per soil layer for unsampled parcels. Despite the large number of explanatory variables which were included in these models, only a relatively small portion of the variation of the corresponding dataset (per crop group), could be explained: the R-square values ranged from 0.09 (maize) to 0.19 (Potatoes) for the total nitrate residue.

The overall R-square values of the combined MANCOVA model (consisting of the submodels of the various crop groups) for total nitrate residue and nitrate residue for each soil layer, were between 0.23 and 0.25. This means that about 1/4 of the total variation of the (log transformed) nitrate residue of the Manure control measurements and follow-up samples is explained by this combined model.

The semivariogram analysis of the model error shows that the model errors only display slight spatial autocorrelation on a catchment scale. This means that it is likely that introducing additional explanatory variables with a clear spatial structure over the parcel boundaries will not yield any substantial improvement of the model.

The large "nugget" variance indicates that an improvement of the model can only be expected with input from additional field-specific information (such as fertilization, management history). Only 15 to 25% of the total variance consisted of structural variance. Therefore we can neglect any spatial dependency in further calculations of the confidence interval on the estimation of the process factor for a certain catchment.

Phase 2: Determination and evaluation of process factors for surface water and groundwater

Phase 2 of this research focused on determining process factors for both surface water and groundwater, as well as the spatial differentiation of these factors. The empirical process factor characterizes the degree of dilution and degradation of nitrate from the moment that the nitrate leaches out of the root zone at 90 cm below the surface until the moment that it reaches the surface water or the groundwater (where it is being measured). Low process factors (\approx 1) mean that the nitrate leached out of the root zone will be found in an almost equal concentration in the surface water or groundwater, whereas high process factors mean that the nitrate is diluted and/or denitrified and thus that a lower concentration will be measured in surface water or groundwater.

In figure 2, the groundwater flow through a hypothetical profile is showed. The process factor for surface water is the ratio between the average nitrate concentration below the root zone at -90 cm and the mean nitrate concentration in the surface water recipient. The water leaching from the root zone can reach a surface water body trough runoff and interflow or by groundwater transport.

In turn, the process factor for groundwater is the ratio between the average nitrate concentration at -90 cm and the average nitrate concentration in the first filter of the multi-level monitoring well of the phreatic groundwater monitoring network.





The process factor surface is defined as the ratio between the average nitrate concentration below the root zone over the winter period and the average concentration in surface water (red dotted line).

The process factor groundwater is defined as the ratio between the average nitrate concentration below the root zone and the average concentration in the first filter of a multi-level groundwater monitoring well (yellow dotted line).

The EU Nitrates Directive (91/676/EEC) states that the nitrate concentration in surface water or groundwater should not exceed 50 mg NO_3^- per litre of water.

Process factors for surface water and ground water are therefore a useful mean to determine the maximum nitrate concentration below the root zone of a parcel, in order not to exceed this limit of 50 mg/l.

Determination and evaluation of process factors for surface water.

In the N-(eco)² project (2002), the process factor for surface water was defined as the ratio between the average nitrate concentration in the leachate of the root zone (at -90 cm) and the average nitrate concentration in surface water, and this for small catchments mainly influenced by agriculture. In this study the process factor for surface water has been determined for 50 sampling points of the MAP surface water monitoring network. Based on a statistical analysis, the explanatory variables for the variation in these process factors are investigated in order to make area covering predictions for the process factors for Flanders.

The MAP surface water monitoring network is a monitoring network of 794 sampling points in small watercourses, for which the catchment area predominantly consists of agricultural parcels. For each of these 794 sampling points the catchment area was calculated for a 5 m x 5 m grid using the ArcGIS extension "ArcSWAT". The catchment area demarcates the area within which rainfall water flows to the MAP sampling point.

For each catchment a number of characteristics were calculated, such as the area of the catchment, the length of the river system within the catchment, the percentage of agricultural parcels, the Hydrogeologically Homogeneous Zone (HHZ) to which the catchment belongs, the dominant texture of the soil, the land use within the catchment and some indicators for nitrate exceeding in the sampling point.

The 50 best catchments were selected, based on a maximum possible homogeneity for every criterion within each catchment and on contrasting characteristics between the catchments.

To calculate the process factor for surface water, the average nitrate concentration at 90 cm depth over the winter period was modelled for each of the 50 catchments. The nitrate concentration below the root zone was calculated, by modelling the nitrate leaching over the winter period (November 1st to March 31st) with an analytical nitrate leaching model. The nitrate leaching is calculated for 4 winter years (2004-2005, 2005-2006, 2006-2007 and 2007-2008), and then averaged over these four years winter. In this way, an average process factor was obtained for this period, as the actual travel time of the water is unknown.

Before the nitrate leaching can be calculated, a number of data should be linked to each catchment. Initially, for each parcel within each catchment the nitrate residue was calculated for each of the four winter years. The nitrate residues were either measured (control measurements) or estimated using the MANCOVA models from the first phase of the study. For non agricultural parcels (forest, nature, buildings,...) nitrate residues were estimated using the atmospheric nitrogen deposition of that year. Subsequently, based on the Belgian soil map, the soil type for each parcel was determined (sand, sandy loam, loam or clay) and for each soil type a mean particle size distribution and an average organic carbon content was given. For deeper layers (deeper than 90 cm), the particle size distribution was determined based on drilling reports of the phreatic groundwater monitoring network. Each plot was ultimately given the average groundwater level and the average rainfall excess over the winter period.

Based on these data, it is possible to use an analytical leaching model (analytical solution of the convection-dispersion equation) to model the nitrate concentration below the root zone over the winter for each parcel. The mean nitrate concentration below the root zone for the entire catchment is then calculated as the weighted mean of the concentrations of the individual parcels weighed over the relative area share for each parcel. For each winter year (2004-2005, 2005-2006, 2006-2007 and 2007-2008), an average nitrate concentration below the root zone is obtained.

The next step in the determination of the process factor for surface water is the calculation of the average nitrate concentration in the surface water for each of the 50 selected sampling points. For this, the available time series for the nitrate concentration in the 50 sampling points was used. The evolution of the nitrate concentration over time was analyzed for each sampling point for the presence of a month effect, the presence of autocorrelation or the presence of a trend. The final model used to calculate the mean nitrate concentration is a combination of a year and/or month effect (with or without autocorrelation). If a month effect is present, the nitrate concentration is determined as the mean of the average monthly concentrations, weighed by a discharge factor (average discharge in that month divided by the sum of the monthly discharges), for which the sum of the factors is one. If a year effect is present, the arithmetic mean of the measurements is calculated.



Figure 3 - Histogram of the process factor for surface water (x-axis in logarithmic scale)

The process factors were obtained by dividing the mean nitrate concentration below the root zone by the (weighted) mean nitrate concentration in the MAP sampling point. The process factors show a lognormal distribution, with a median value of 3.3 (Figure 3).

Based on a statistical analysis, the dominant texture of the catchment and the redox potential of the underlying aquifer, proofed to be significant explanatory variables. These two variables were then used to build a predictive regression model. With this model, area covering predictions were done for the whole of Flanders (Figure 4). The process factor for surface water exhibits a clear regional variation, which can only partly be explained with the model.



Figure 4 - Raster map showing the predicted process factor for surface water for Flanders with the 50 catchments and their observed value for the process factor (Grid of 500 m \times 500 m).

The WEKU model, a grid-based, stochastic travel time denitrification model, was used to model the nitrate load to surface water for each of the 50 selected catchments. The WEKU model assumes that rainfall reaches the river system trough a rapid runoff component (overland flow, interflow, drainage) and a slow runoff component (through groundwater flow). During the transport of nitrate via the rapid runoff component, denitrification is not expected, while during transport by means of the slow component trough groundwater, nitrate is degraded in a first order reaction at a rate that depends on the aquifer properties. The prediction of the nitrate load to the surface water with the WEKU model is acceptable. However, no significant correlation exists between the modelled and observed process factors. However, the modelled process factors are of the same magnitude as the observed ones. Presumably some uncertainties on the input data for the model are too large to give a good correlation between the modelled and measured process factors. Also the catchments used in this study are probably too small for the model.

Determination and evaluation of process factors for groundwater

The quality of the phreatic groundwater in Flanders is monitored in a network of monitoring wells (phreatic groundwater monitoring network), where the sampled water originates from a small number of parcels upstream of the monitoring well, following the groundwater flow. The

first filter of each monitoring well is preferentially installed in the oxic zone of the aquifer because the nitrate is not denitrified by microorganisms in this zone. The measured nitrate concentration is therefore a reflection of the intensity of manuring on the parcels, from where the water in the well originates. The first filter is not always installed in the oxic zone, but sometimes in the reduced zone, where much of the nitrate has already been denitrified.

Because of the stability of nitrate in the oxidized zone of the phreatic groundwater, this zone is considered to be a reference for the groundwater quality where the Nitrates Directive should be met, because the highest nitrate concentrations measured are generally measured in this zone. Characterizing oxidized or reduced filters based on chemical characteristics seemed to be difficult and it was therefore decided not to exclude any monitoring wells a priori from further analysis.

The process factor for groundwater was determined for a subset of 525 monitoring wells of the phreatic groundwater monitoring network, based on their location in some contrasting HHZs (contrasting in use of nitrogen and potential nitrogen leaching), their location in different Flemish agricultural zones and main Flemish river catchments. Those wells for which the travel time is longer than 5 years, were excluded from the selection because of the range of available measurements of nitrate in groundwater and nitrate residue measurements

For each monitoring well, the contributing recharge area was determined as an elliptical region, upstream of the sampling point, from the water measured in the sampling point originates which with 75% certainty (Figure 5). For each sampling point, the travel time through the unsaturated and saturated zone is calculated.



Figure 5 - Top view of a hypothetical agricultural parcel with a sampling point of the phreatic groundwater monitoring network and associated contributing area.

Similar to the process factor for surface water, the necessary data were coupled to the parcels in the contributing area to model the nitrate leaching from the root zone with the analytical model. The mean nitrate concentration below the root was determined for the winter year 2004-2005, starting from measured or estimated nitrate residues for 2004.

The nitrate concentrations for different parcels were however weighted over the contributing areas, where the weighing factor decreases from the centre to the edge of the ellipse.

In order to calculate the process factor for groundwater, the weighed average nitrate concentration below the root zone was divided by the nitrate concentration in the filter of the corresponding sampling point for that year, equal to the winter year of 2004-2005 plus the travel time of the water.

The frequency distribution of the process factors shows two prominent peaks, with a first peak value around 2.1 and a second peak around 200 (Figure 6).



Figure 6 - Frequency distribution of the ln-transformed process factor for groundwater for the 525 groundwater sampling points. On the X-axis, the untransformed values of the process factor are shown for the upper limit of each class.

When the process factors are plotted against the redox potential, two groups are observed. One group with low process factors and high redox potential and one group with high process factors and a low redox potential (Figure 7).



Figure 7 - Relationship of the process factor groundwater to the redox potential

From these observations it appears that the 525 samples come from two distinct populations, which are filters from the oxic zone and filters from the reduced zone. The filters in the oxic zone were statistically analyzed, because in these filters the influence from manuring practices can be measured. However for these oxic filters no significant differences based on texture or HHZ can be found. Since the process factor for groundwater could not be spatially differentiated, the median of the oxic filters (2.1) is therefore the best estimate as process factor for groundwater.

Combined process factors surface water-groundwater for Flanders

In order to meet the EU nitrates directive of 50 mg per litre water both for surface water and ground water, the lowest of the two process factors in that zone should be respected. This means that where the process factor for surface water is larger than 2.1, it is topped at that value. Where the process factor for surface water is smaller, the latter value applies. One can speak of the combined process factor for surface water-groundwater. Spatially this is represented in Figure 8.



Figure 8 - Spatial representation of the combined process factor for surface water-groundwater

Based on this spatial pattern, new nitrate residues are proposed to improve water quality in Flanders. New combined process factors are somewhat stricter in comparison with the process factor of 2.4 from the N-(eco)² study, especially for Limburg and the loamy region between Leuven and Diest.

Phase 3: Proposal of nitrate residues based on the combined process factors

Based on simulations with the nitrogen balance model WAVE, in the N-(eco)²-project, maximum nitrate residues were derived for different crops on sandy soils and non-sandy soils in order to meet the EU nitrates directive (50 mg nitrate per litre of water).

These nitrate residues (Table 1) were based on a process factor of 2.4, which was then considered as the process factor for Flanders.

Table 1 - Nitrate residues (kg NO_3^- -N/ha) for Flanders, proposed within the N-(eco) ² study (2002) based on a process factor of 2.4.

	Maximum nitrate residue values, proposed in the N-(eco) ² -study			
Сгор	Sand	Non- sand		
Maize	60	90		
Beets	50	70		
Vegetables without removal of harvest remnants	40	50		
Grass	70	100		
Cereals with green manure crop	70	100		
Other crops	50	80		

The new combined process factors in the present study were in turn translated into maximum nitrate residues. First the process factors were aggregated into three classes, namely 1.5 (for process factors between 1.3 and 1.7), 1.9 (for process factors between 1.7 and 2) and 2.1 (for process factors between 2 and 2.1). Hereafter, the nitrate residues from the N-(eco)²-project were interpolated for the new combined process factors (with the same textures and crop groups). This led to the interpolated maximum nitrate residues which are presented in table 2.

Table 2 - Interpolated nitrate residues for three classes of process factors for six crop groups in sand and non-sandy soils by analogy with the N-(eco)²-study.

	Nitrate residue kg NO ₃ ⁻ - N/ha for process factors:				Nitrate residue kg NO ₃ - N/ha for process factors:		
Sandy soils	1.5	1.9	2.1	Other soils	1.5	1.9	2.1
Maize	34	44	49	Maize	54	71	79
Beets	29	38	42	Beets	40	53	59
Vegetables without removal				Vegetables without			
of crop residues	30	34	37	removal of crop residues	37	43	46
Grass	44	57	63	Grass	63	81	90
Cereals with green manure				Cereals with green manure			
crop	40	51	57	crop	57	73	81
Other crops	34	46	51	Other crops	47	62	69

The interpolated nitrate residues are displayed cartographically in figure 9 to figure 14.



Figure 9 - Cartographic representation of the interpolated nitrate residue for "maïze" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.



Figure 10 - Cartographic representation of the interpolated nitrate residue for "other crops" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.



Figure 11 - Cartographic representation of the interpolated nitrate residue for "beets" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.



Figure 12 - Cartographic representation of the interpolated nitrate residue for "cereals with green manure crop" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.



Figure 13 - Cartographic representation of the interpolated nitrate residue for "grass" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.



Figure 14 - Cartographic representation of the interpolated nitrate residue for "vegetables without removal of crop residues" based on the new combined process factors. The agricultural regions of Flanders are represented by red lines.

A further decline of the current measured nitrate residues can be expected if better fertilization practices and accompanying measures are taken.