Total nitrogen concentration modeling for European river basins

Master thesis sustainable development

J.M.Malotaux – 0264415
Department of Innovation and Environmental Sciences, Utrecht University
Supervisors: P. Schot (Utrecht University), E. Meijers and H.Duel (Deltares)
January, 2010

Cover image used from: www.sylvatravel.com

Foreword

This research project took place in 2009 in the framework of the final thesis for the master of Environmental Sciences at the Utrecht University (UU). The project was carried out in combination with an internship at the consultancy and research institute Deltares, the Netherlands.
From the University, supervision was provided by Paul Schot and from Deltares supervision was given by Erwin Meijers and Harm Duel. Karin Rebel (UU) was involved as the second reader of this thesis.
This research was part of the SCENES project (Water Scenarios for Europe and for Neighbouring States) which is a European research project (2006 – 2010) on the development of scenario's for future water availability and quality in Europe and neighbouring states for up to 2030
(www.environment.fi/syke/scenes).

Table of Contents

Introduction

1.1 Problem description

Nitrogen (N) is naturally present in all global ecosystems and is required for plant and crop growth and is essential for sustaining living organisms as it is a building block for proteins and DNA (MEA, 2005; Salminen and De Vos, 2007). However, presently N exported by rivers have increased up to 5-fold compared to pre-industrial times (Green et al., 2004) and is caused by increased amounts of N that are fixed and eventually emitted from fertilizer production, legume cultivation and energy production (Seitzinger, 2008). This lead to an increase in N that is emitted to surface waters, which is also seen on the scale of Europe where higher N concentrations in its water bodies have led to eutrophication and acidification. Eutrophication is typically described as the phenomenon of (toxic) algal blooms in surface waters, leading to light and oxygen depletion in the water, fish kills, loss of biodiversity, and overall deterioration of water quality, due to excessive inflow of nutrients (Stevenson, 1986; Mourad, 2008). Acidification can occur when high amounts of HNO_3 enter into aquatic ecosystems with low acid buffering capacity (Van der Perk, 2006; Nieder and Benbi, 2008). High acidity levels are lethal to plants an organisms, and an example of this are the major fish kills in rivers and lakes in the southern part of Norway and along the Swedish west coast in the 1970's (Erisman et al., 2003). Besides HNO_3, N in the form of NH_4^+ and NO_2^- are also toxic to plants and organism at high concentrations. NO3- is less harmful, although high levels drinking water can cause methemoglobinemia (blue-baby syndrome) with infants under six months (Wolfe and Patz, 2002). Other effects have of increased N emissions to surface waters have been deterioration of bathing water quality and an increase in water purification cost for the drinking water and the manufacturing sector (Saunders and Kalff, 2001; Fogelberg, 2003; EEA, 2005; Billen et al., 2009; Velthof et al., 2009). The process of N fixation as mentioned above, involves the transformation of unreactive N_2 (dinitrogen) from the atmosphere into reactive forms of nitrogen such as NH_4^+ (ammonium), NH_3 (ammonia), NO_3^- (nitrate), NO_2^- (nitrite), and NO_2 (nitrous oxide) (Van Egmond et al., 2002).

N emissions to the aquatic environment from point sources have been reduced since the implementation of the Urban Waste Water Treatment Directive (CEC, 1991a) and the Nitrate Directive (CEC, 1991b) in 1991 due to improved connectivity to waste water treatment plants (WWTP's) of households and industries, increased N removal efficiency in these plants, and decreased N content in detergents (OSPAR, 2003; EEA, 2005). Although some progress is made in decreasing nitrogen emissions, the guideline concentration of 5.6 mg/l as given by the Surface Water for Drinking Directive (CEC, 1975) is still exceeded in many surface waters (EEA, 2001). In European catchments, agricultural is the largest contributors to N in surface waters (Behrendt and Opitz, 1999; EEA, 2002).

The state of N pressure and the associate problems led to the implementation of the Water Framework Directive (WFD) in 2000 (CEC, 2000), which stated that a 'good ecological status' and 'good chemical status' of all European water resources should be reached by 2015 (EEA, 2006). This created a demand in measurement to be taken by river basin managers, policy makers and other stakeholders in order to further reduce N concentrations in European rivers and lakes (Nixon et al., 2003).

1.2 Research context and aim

The SCENES (Water Scenarios for Europe and for Neighbouring States) project has been set up as a reaction to the request of policy makers to have tools to better understand the interaction between the environment and socio-economic development which is needed to achieve the goals as defined by the WFD. The aim of SCENES is to develop a tool that can help investigate change in water availability and water quality in European catchments for different scenarios.

The research described in this report is part of the SCENES project and has a focus on water quality concerning nitrogen concentration in surface waters. The aim of this research is to develop a model that can simulate TN concentration for European surface waters. With this model quantitative information can be provided on possible changes in TN concentrations for the different scenarios. Application of the model for scenarios is not within the scope of this study.

1.3 Research questions

The main research question of this thesis is: 'How can total nitrogen concentration be modeled for surface waters in European catchments?' Total nitrogen refers to all dissolved nitrogen transported by water with the main constituents being NO3-, NO2-, NH4+, and Dissolved Organic Nitrogen (DON), while surface waters refer to all water bodies that are part of a river network, which include river branches, lakes, wetlands and reservoirs. To guide the research the following eleven sub-question were defined:

1) What type of output should the model generate to suit the needs its user ?
2) What are the main N sources and what is their contribution to N emission to surface water in European catchment?
3) What are the physical and biochemical N processes involved?
4) What type of N - concentration / N - load models already exists, what are the differences, and how do these model differences affect the performance of the model?
5) What are the available tools for making the model?
6) What data can be used relevant for modeling N concentrations in surface waters?
7) How can the obtained data be harmonized?
8) How can a nitrogen concentration model be built?
9) How can the model be calibrated?
10) How can the model be validated
11) How does the model perform and what are possibilities for model improvement?

1.4 Study area

The study area in the SCENES project covers all river basins within Pan-Europe which reaches from Scandinavia in the north to the northern countries of Africa in the south, and reaches from Western Europe up to the Ural Mountains in the east. This area is shown in blue in figure 1. Due to data limitations for N emissions and validation, the area covered by the model was significantly reduced to the basins that are located within the hexagon depicted in figure 1.

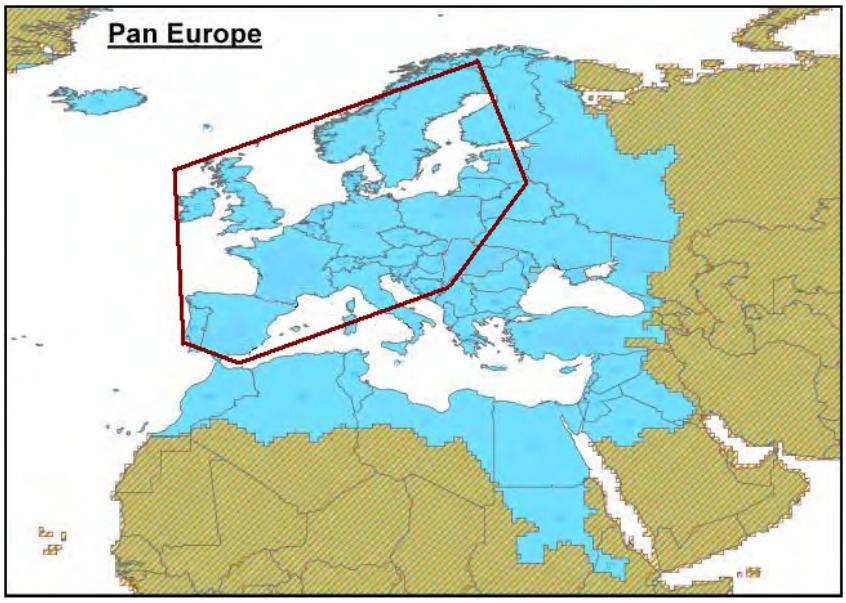


Figure 1 Area covered by the SCENES project (*blue*), and the area cover by the TN concentration model (*basins in hexagon)* - Source: *(SCENES, 2008)*

1.5 Thesis outline

The following chapter contains the research methods which is followed by Chapter 3 that contains all the results concerning the research sub-questions as defined above. A description of the model requirements is given in paragraph 3.1. Paragraph 3.2 to 3.4 contain a literature overviews on N sources, N processes and existing N models, respectively. In paragraph 3.5 and 3.6 a description is given on the choices made for model construction and on the data that was used as model input. 3.7 explains the proceedings on model calibration and the data used for calibration and validation. In 3.8 model results are presented followed by model validation in 3.9. In chapter 4 the performance of the model is evaluated and possibilities for model improvements are discussed.

2 Methods

As an approach for the model development, the steps as described in the model development cycle by Karssenberg (2002) were followed. This cycle is depicted in figure 2 and in this figure the sub-questions are ordered according to the steps in the cycle.

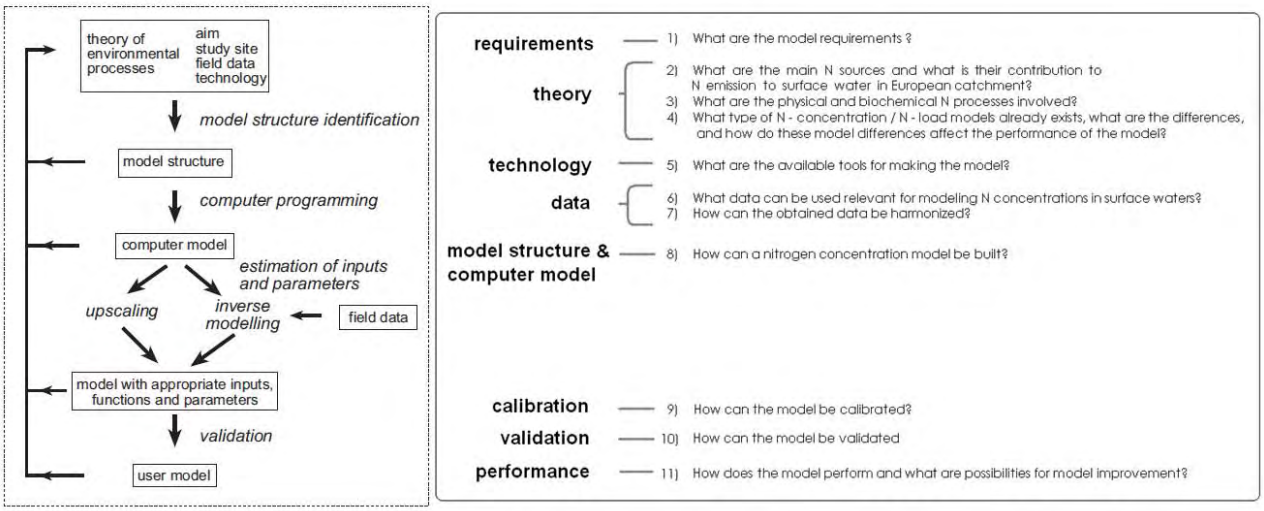


Figure 2 the model development cycle. Source: (Karssenberg, 2002)

- Some basic requirements were formulated as starting point for the modeling development process to determine what kind of output the model should generate. This was done by communication with supervisors and reading documentation on the SCENES project.
- A literature study was done on potentially relevant N sources, N transformation processes and N transport pathways to surface waters, and on already existing nitrogen models. An overview of this study is presented in this report.
- Tools and facilities available at Deltares and the Utrecht University were used for data processing and construction of the model.
- From the findings from the steps described above, a concept of the model was made to be able to determine the type of data that was required. Data was obtained from the SCENES project database, from literature and from web-sites of various research institutes and agencies.
- Quantification methods were defined and applied to the model once sufficient data was found available to serve as input. If sufficient data was not available estimation or assumption were used.
- Data representative for the year 2000 were used as input for the model. If no data was found for the year 2000, data was accepted if it was representative for a year between 1995 -2005.
- After model completion a sensitivity analysis and calibration was carried out. A sensitivity analysis was conducted through a source apportionment study and the model was calibrated for the most sensitive and uncertain parameters with monitoring data from the Vistula river basin (WATERBASE, 2009).
- Measured data of TN concentration that was used for calibration and validation were obtained from the EEA (WATERBASE, 2009) and from literature. For some catchments monitoring data was not available. Literature on DON and NO_3^- contributions to TN loads were investigated to see if this data could be used for as alternative calibration/validation data. Subsequently monitoring data and TN load estimation from literature were compared with modeled results to assess model performance.

3 Results

3.1 Model requirements

Before the model was built model requirements were defined to determine what type of output the model should generate and how well it must perform to be fit scenario application.

One of the requirements was that a source apportionment assessments per river basin could be generated from the model. The contribution of the various sources of N can vary per river catchment and a source apportionment can provide policy makers and stakeholders with information on the relative and absolute contribution of a N source to the total N load in surface waters. Such information can give an indication on what TN concentration reduction measures should be most effective. The model should also match the scale at which policy measures are implemented and to the scale at which the water quality status is assessed by the WDF which are both on the scale of river basins (Horn et al., 2004).

The aim is to built a model that can generate results in average TN concentrations per month, so that inter-annual variation can be reflected. Monthly output can give a better indication on environment suitability of a certain aquatic system for ecosystem and human use. However, if data is too limited for monthly simulation, then the model will be built to generate average annual TN concentrations. The model was required to be a TN - *concentration* model instead of a TN - nitrogen *load* model, as water safety or suitability threshold values are expressed in concentrations, not loads. However, calculations and routing of N within the model was done with N loads as it would have been cumbersome to calculate with concentrations. The aim is to generate model outcomes for average annual TN concentration that do not deviate more than 20 % from measured data.

Consequently the model requirements can be summarized as follows:

1. Model results should be generated on a catchment scale
2. The model should be able to indicate the contribution of each source to the total nitrogen load (source apportionment)
3. Model results should be presented as the number of months that a threshold is exceeded per year, or an average annual value with an indication of the range in which it may vary over the year
4. Model outcomes should be given in total nitrogen concentrations
5. Model output should not deviate more than 20 % from average annual values derived from monitoring data.

3.2 Nitrogen sources and processes

The geosphere and the atmosphere contain large amounts of N of 1.6 *10^8 and 3.9 * 10^6 Tg N (Tg = 10^{12} g) respectively. However, this is nitrogen that is not readily available to the biosphere. N becomes available to organisms, when it comes in the form of NO_3^-, NO_2^-, NH_4^+, NH_3, or N_2O. All activities that result in N emissions to the soil, the hydrosphere or the atmosphere in bio-available form are described here as N sources. N sources are closely interrelated with various N transformation processes. Together, N sources and processes form the N-cycle as schematically depicted in figure 3.

This paragraph presents an overview of N sources and are categorized as natural or anthropogenic. For each source an estimation is given on its quantity on a European scale, to give an indication of the significance of the source. This is followed by an overview on the different N transformation processes. How these sources and processes were taken into account and quantified in the model is discussed in paragraph 3.6.

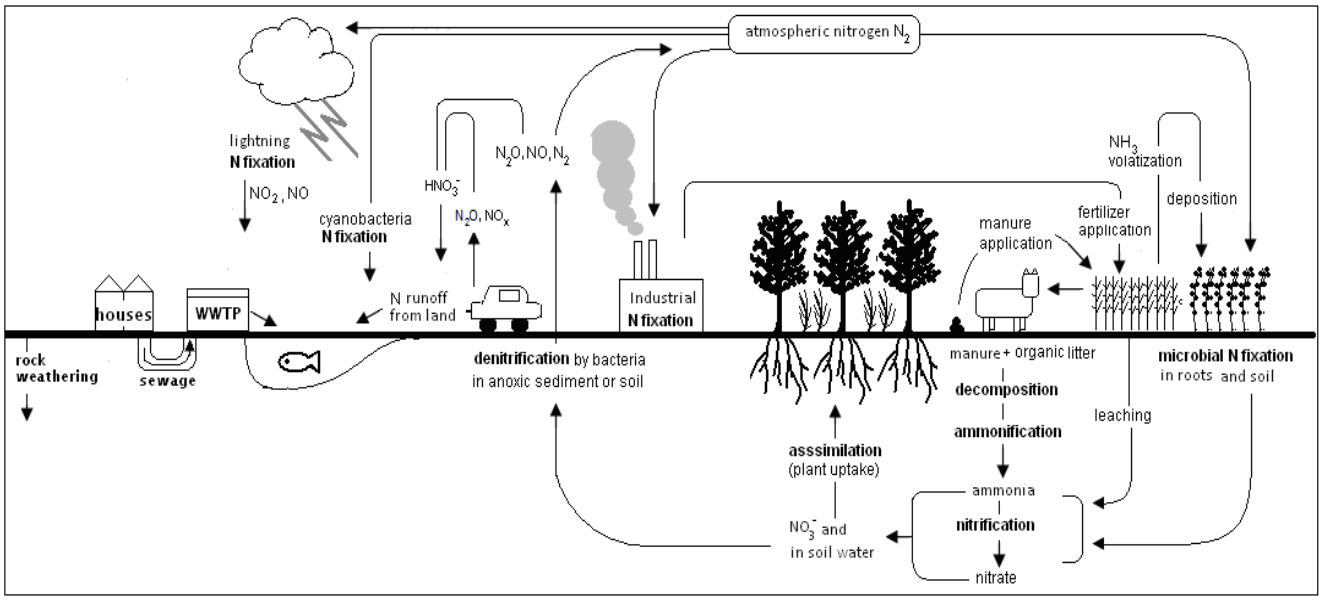


Figure 3. N sources and N processes in the human influenced N-cycle.

3.2.1 Natural sources

Natural N sources, are source of N emissions not induced by human activities. Natural sources are N fixation by lightning, N fixation by microbial activity, and N release due to rock weathering. The chemistry involved and controlling factors in these processes are discussed in further detail in section 3.2.2

Globally lighting N fixation is responsible for an input of reactive N of approximately 5.4 Tg N yr^{-1} (Lelieveld and Dentener, 2000) and enters surface waters through deposition or via the soil groundwater system. Information on the contribution of lightning fixation to N emissions in Europe was not found.

Certain types of microorganism are also capable of N fixation, which is process often referred to as ***biological nitrogen fixation (BNF).*** The N that is fixed is emitted during decomposition of organic matter into soil or water.

In the process of ***rock weathering*** N contained in rock minerals can be released in a reactive form. Generally, igneous and metamorphic rocks have a N content of about 20 ppm and with sedimentary rocks this can range between 200 – 4000 ppm of which highest nitrogen content is generally found in shales (Van der Perk, 2006; ISWS, 2009). N stored in sediments and sedimentary rocks is several of orders magnitude larger than the amount in the biosphere and hydrosphere, but it is also cycled much slower. No information was found on the contribution of rock weathering to nitrogen inputs in Europe, but studies by Dahlgren (1994) and Holloway and Dahlgren (1999) in the U.S.A. showed that nitrogen input from rock weathering can be significant in undisturbed ecosystems.

3.2.2 Anthropogenic sources

Anthropogenic sources emit N resulting from human activities. This involves emissions from households, industry, urban areas, agriculture, and the transport sector.

Households emit N in the form of human excreta and disposal of detergents (Behrendt, 1994). Some households are not connected to a sewage system and emit their waste water directly to water, to land, or the waste water is stored in a septic tank. N emissions from households that are connected to a sewage systems are emitted to surface water directly or after treatment in a waste water treatment plant.
In the ***industrial sector*** various processes induce N fixation. On the one hand N is fixed during industrial processes associated with high temperatures or electrical discharges. The N that is fixed is subsequently emitted to the air. On the other hand N is fixed by the Haber Bosch process to include N compounds into products like fertilizers, plastics, or synthetic fibers. Some of the fixed N are emitted directly to water and some is emitted later when the industrial products are used or disposed of (CEC, 2006). Emissions through waste water discharge from both industry and households is estimated to be 2.6 Tg N yr^{-1} for Europe (Van Egmond et al., 2002).
In **urban areas** N is emitted due to N contained in litter and excreta from pets falling on paved areas. When there is sufficient rainfall, the N on paved urban areas is transported into the sewage system or it is transported to unpaved areas (soil) where it can infiltrate. In times of heavy rain urban runoff is directly transported through sewage pipes to surface waters as sewage overflow. A schematic representation of two types of sewer systems, combined sewage system and a separate sanitary and storm sewer system, are depicted in figure 4. The combined sewer system is predominant in Europe (Sundberg et al., 2004) and so urban runoff is partly treated in WWTP's.

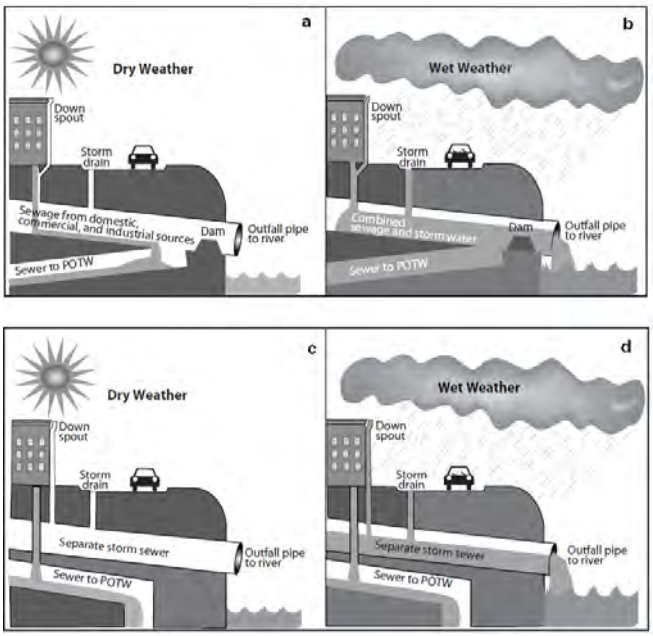


Figure 4 Schematic representation of a combined sewer system (a,b) and a separate sanitary and storm sewer system (c,d). In a combined sewer, sewage overflow occurs only during heavy rainfall and then also a part of the waste water flows directly to surface waters (b) Image-source: EPA, 2008

Due to **agricultural activities** large amount of fertilizer and manure N are applied to agricultural fields from which N is emitted to surface waters by transport via the soil and groundwater. N is also emitted due to leakage of dissolved N compounds of N from manure storage systems or volatization of N in the form of NH_3 (Velthof et al., 2009). An additional increase in reactive N is induced by cultivation of N fixing crops in agriculture. In Europe N put through fertilizer application is estimated to be approximately 11.8 Tg N yr^{-1} fertilizer application, while N fixed by BNF (natural and crop cultivation) was estimated to be 2.2 Tg N yr^{-1} (Van Egmond et al., 2002).
In the **transport sector** high temperatures and pressures that are involved in combustion processes lead to N fixation. During combustion of coal, also N that is stored in the coal is released (Nieder and Benbi, 2008).
Also electricity generation and use of electrical utilities in transport and industrial sectors and in households lead to N fixation (Hill, 2004; Chernikov and Bruskov, 2005).The amount of N that is fixed due to fuel combustion and other industrial processes is estimated at 3.3 Tg (Van Egmond et al., 2002).
Reactive N in the atmosphere originates from anthropogenic and natural sources and occurs in the form of N_2O, NO_x, NH_y or HNO_3, and can be deposited on the earths' surface through either wet or dry **atmospheric**

deposition. Wet deposition can be in the form of rain, snow, or dew, while dry deposition is deposition in the form of dust particles (Langmuir et al., 1997).
In table 1. an overview is given on the N in- and outputs for Europe as estimated by Van Egmond et al. (2002).

Table 1 Total N inputs in Europe - Source: (Van Egmond et al., 2002)

Input or output	**Process or activity**	**specification**	**Quantity of N (Tg)**
input	N fixation[1]	*biological N fixation*	2.2
		N-fertilizer production	14
		fuel combustion + other industry	3.3
	Atmospheric deposition (NH_3 + NO_y)	*aquatic*	2.2
		terrestrial	5.1
	imports into Europe		7.6
output	Denitrification N_2, N_2O	*aquatic*	6.2
		terrestrial	7.6
	N emissions	NH_3 *from manure*	3.5
		NO_y, *terrestrial*	0.7
		NO_y *from N fixation by transport sector and industry*	3.3
	Exports from Europe		6.3
	Export through rivers		6.2

[1] *11.8 Tg of industrially fixed N is used in Europe as fertilizer, 2.9 Tg of fixed N is emitted by households to air (0.3) and to water (2.6).*

Emissions of N vary widely in different regions in Europe (Velthof et al., 2009). Total nitrogen (TN) loads are highest in England/Wales, Denmark, the Netherlands, Belgium and the western part of Germany, and in the Po river catchment in Italy. TN loads in Eastern Europe and the Baltic countries relatively low, and even lower in the Scandinavian countries. In major European catchments the main N source is agriculture except for example for catchments in Nordic countries where background input from soil can contribute up to 90 % (Lepistö et al., 2006) and the Axios river catchment in Greece where point sources are the largest contributor (EEA, 2005) .

3.3 Processes

In this paragraph an overview is given on N processes and what environmental factors control the process rates. Basic understanding of these relations are required before sound decisions can be made on if, and how processes need to be represented in the model.

3.3.1 Chemical processes

The processes responsible for N transformations are: N fixation, nitrate assimilation, ammonification and denitrification (Zumft and Cardenas, 1979; Stevenson, 1986)).

As mentioned in the previous paragraph ***N fixation*** is a process that is driven by microbial activity, by electrical discharge, by heat generation, or by the Haber-Bosch process in industry. N fixation by microorganisms is driven by symbiotic or free-living bacteria species (e.g. Rhyzobium, cyanobacteria) that are capable of fixing N_2 from the into NH_4^+, followed by further transformation into to organic compounds and assimilation into bacteria and plants (Nieder and Benbi, 2008). The process of *N assimilation* is the process in which NH_4^+, NO_2^-, or NO_3^- is taken up by organisms and transformed into organic compounds.

Cleveland (1999) conducted a study on biological N fixation rates in various natural ecosystem and found that nitrogen fixation can vary strongly per ecosystem type. The range of BNF rates was 0.1 to 160 kg N ha^{-1} yr^{-1}. This wide range was accounted to temperate forest ecosystems, while BNF rates in short grasslands were estimated to range between 1 – 30 kg N ha^{-1} yr^{-1}. Estimations on N fixation rates of various agricultural crop types (e.g. legumes, cereals) lie between 3 – 350 kg N ha^{-1} yr^{-1} (Smil, 1999; Nieder and Benbi, 2008).

Electrical discharge and heat generation causes conversion of N_2 and O_2 into NO_x, which can subsequently be oxidized further into NO_2 and HNO_3. NO_x, are emitted to the atmosphere and can travel significant distances before deposited to (Jonson et al., 1998) land or water surfaces. Emission rates depend on local activity in lightning, power plants, use of electrical utilities and activity in the transport sector. The Haber-Bosch process is used in industry for the fixation of N_2 into NH_3, and these compounds are emitted mostly though fertilizer application on agricultural land.

Ammonification, also referred to as **mineralization**, is the transformation process of organic N into NH_4^+, and is driven by microorganisms. Both anaerobic as aerobic bacteria are capable of transforming mineralizing organic N (Stevenson 1986). In surface waters ammonification occurs as a photochemical process, but process rates are generally lower.

Nitrification is the process of oxidation of NH_4^+ to NO_2^-, which is often transformed in a relatively short time into NO_3^-. The conversion of NH_4^+ into NO_2^-, as well as the transformation of NO_2^- into NO_3^- are bacterial processes and requires the presence of dissolved HCO_3. Microorganisms responsible for nitrification require availability of oxygen, so the process will only occur in oxic conditions (Stevenson, 1986).

Denitrification is a bacterial process in which nitrate and nitrite are reduced to N_2 and a smaller fraction is transformed into N_2O. The process requires an electron donor which is usually carbon, but minerals like pyrite can fulfill a similar role (Schwientek et al., 2008). Denitrification requires anoxic condition and starts at oxygen concentrations below 2.0 mg/l (Schwientek et al 2008). Denitrification is highest at oxic/anoxic interfaces as the denitrification rate is dependent on the supply of NO_3^- from the nitrification process, and the nitrification occurs at oxic conditions (Inwood et al., 2005). Favourable condition for denitrification are generally found in areas such as riparian zones, stream beds, heavily irrigated regions, animal manure folding facilities, wetland rice cultivated areas, and water saturated soils (Galloway et al., 2004; Seitzinger, 2008; Thieu et al., 2009).

All processes described above that are driven by microbial processes are dependent on general factors controlling microbial activity, which are: temperature, moisture, pH, substrate NH4+, O2 concentrations, microbial biomass, nutrient availability and soil C and N concentrations (Booth et al., 2005).

Transformation of NH_4^+ to volatile NH_3 is the process of **N volatization** and largest N emissions from volatization occur during the decomposition of manure (Van der Perk, 2006). Residence time of ammonia in the atmosphere is generally short (hours, days), which results in most of the NH3 being re-deposited close to the place from where it was emitted. Also plants interact with NH_3 in the atmosphere. They can take up or release NH_3 dependent on the relative concentration in the plant, air and soil (Jenkinson, 2001).

3.3.2 Anthropogenic influence on N processes

Anthropogenic influence does not only relate to direct increase of N emissions to surface waters, but also indirect effects are can influence overall N emissions to the water. This influence is caused by activities such as deforestation, damming, drainage, water extractions and pavement constructions (Heathwaite and Johnes, 1996; Galloway et al., 2003)

Deforestation can lead to mobilization of N due to increased erosion and loss of soil organic matter (Heathwaite and Johnes, 1996). Damming has globally tripled the average residence time of water in river works and increased the amount of standing water stock up to 7-fold (Vörösmarty et al., 1997) which led to an overall increase of instream nitrogen retention (Harrison et al., 2009). Drainage leads to acceleration of nutrients flowing from the soil to surface waters, it increases oxygen concentration in the soil, which may decrease denitrification rates (de Wit, 1999). Drainage in peat lands can lead to increased N emission due to decomposition of organic matter and subsequent mineralization (Heathwaite, 1990).

Due to anthropogenic influence catchments have changed from naturally forest dominated to pasture or agricultural dominated ones over a period of a few thousand years (Salminen and De Vos, 2007). In a study on the relationship between N export and environmental factors on a global scale by Alvarez-Cobelas et al. (2008) cropland dominated catchments exported twice and four times as much TN compared to pasture and forest dominated catchments, respectively.

3.3.3 Pathways

There are various pathways through which nitrogen compounds are transported to surface waters from the location from which it was emitted. These pathways can be distinguished between surface runoff and groundwater runoff. Information on how N load is distributed over these pathways, the travel time of N per

pathway, and the retention per pathway control the N load that enters surface waters at a certain period in time, and therefore these factors are relevant for estimating TN concentration in surface waters from data on N emissions.

Estimation of the input from point sources such as waste water discharge from WWTP's is relatively easy compared to estimation of N input from diffuse sources. Direct emissions have limited travel time to surface waters, N input from these emissions are relatively constant throughout the year and can be monitored more easily. Due to heterogeneities in the distribution of diffuse source in the landscape and the diffuse pathways, input from these sources are much harder to estimate (De Wit, 1999)

According to Kunkel et al. (2004) two main different aquifer types can be distinguished in Europe: lowlands where the subsurface consists of unconsolidated rocks and areas where it consists of consolidated rocks. In unconsolidated rock areas the groundwater runoff component was estimated to be of higher importance and travel times towards surface waters was also higher compared to consolidated rock areas.

TN concentration in surface waters of a catchments with low nitrogen storage capacity is expected to be more strongly related to water flow, than in catchment with high storage capacity. In catchments with higher storage a more damped effect is expected due to buffering in the aquifer (Wade et al., 2004). This may also be a reason why in many catchment limited effect of nitrogen reduction measures in agriculture have been reflected in surface water N concentration, as there is a significant time lag between input to the soil and emissions to surface waters.

As the main pathways of N are hydrological pathways it is not surprising that N export from catchments was found to be related to area specific runoff (Behrendt and Opitz, 2000; Smith et al 2003; Böhlke et al., 2007; Alvarez-Cobelaz et al., 2008,). In various studies runoff showed a positive relation with both TN loads and TN concentration (Brunet and Astin, 1996; Sigleo and Frick, 2007; CBS and PBL, 2009a).

The amount that is transported from one place to another through various pathways depends on the total N input and the amount that is retained during transport. At a certain level of nitrogen input the amount of N is too high to be removed by crop uptake and denitrification, and this excess N can be transported towards surface waters. Figure 6. by Stevenson (1986) shows that this excess N in not necessarily linear to N input.

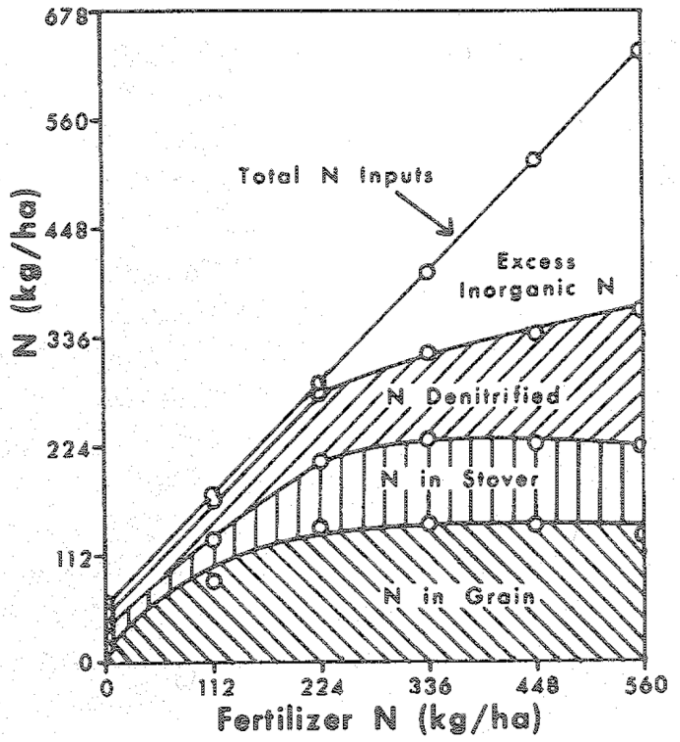


Figure 5 – Excess inorganic N in relation with fertilizer application on agricultural soils (Legg and Meisinger, 1982)

3.3.4 Seasonal variation related changes in processes and sources

Seasonal variations of TN concentrations in and N export through rivers can be significant as was shown by in studies by various authors (Böhlke et al., 2007; Sigleo and Frick, 2007; Mourad, 2008). These variations are caused by differences in temperature, precipitation, N plant uptake and organic matter decomposition rates over the year.

In studies conducted on rivers in north-western and north-eastern Europe higher TN concentrations, DIN concentrations and TN loads were found in winter compared to summer months (Loos et al., 2009; Mourad, 2008; Ahad et al, 2006 (Salminen and De Vos, 2007)). As high concentrations coincided with higher river water discharges in winter months this lead to a 'double' increase of the TN loads (Ahad et al, 2006). In the Ahja river TN concentrations could range by a factor 3 or 4 over the seasons (Mourad, 2008). The general lower concentrations of TN in summer, were attributed to higher plant N uptake, higher

denitrification rates and lower water discharge during the summer period (Ahad et al., 2006; Böhlke et al., 2007; Van Gerven et al., 2009). N concentration and loads can also depend on preceding weather condition as was demonstrated by Sigleo and Frick (2007) in which unusually high TN concentrations were measured after the first winter storm runoff, after a relatively dry year.
In catchments with significant agricultural land coverage, nitrogen loads in rivers can become significantly higher during periods of fertilizer application. In the Ardour river catchment in the south of France, fertilizer application from February to July 1992, caused for increased TN concentrations in the Ardour river during this period, except for May, in which relatively low agricultural N flow into the river was appointed to crop uptake and retention in the riparian zone (Brunet & Astin, 1996). Pathways of N transport towards surface water can also vary over the year due to frost and snow cover that can limit N transportation from the soil (Silgram et al., 2008). All this intra-annual variations indicates that when looking at TN concentrations on an annual scale different process dominate compared to if one looks at it on a monthly scale.

3.3.5 Retention

In a study by (Van Gerven et al., 2009) retention was defined as "the absolute or a relative difference between incoming and outgoing loads within certain spatial borders within a certain period of time". On different spatial and temporal scales this retention could result in either an increase or a decrease of N. However, various authors have pointed out that on a catchment scale N loads entering a catchment is generally higher than the amount leaving the catchment through the outlet. So at the catchment scale retention can generally be expressed as a reduction of N loads.
The factors that influence N loads are denitrification, N volatization, immobilization of N due to plant or microbial uptake, temporary N storage in soils and sediments, residence of N in groundwater and decomposition of organic matter (Lepistö et al., 2006; Böhlke et al., 2007). The process of denitrification is the only process that leads to permanent loss of bioavailable N to the atmosphere (Laursen and Seitzinger, 2002). An overview of retention processes and controls of the process rates are listed below in table 2.

TABLE 1 - RETENTION PROCESSES AND FACTORS CONTROLLING THE PROCESS RATES.

N retention component	**Controlling factors**	**comments**
denitrification	Availability of DOC or other electron donors, pH, nitrate concentration, oxygen concentration, temperature, pH, residence time, stream flow regime*	Most N is transformed into N2 which is 'permanently' lost to the atmosphere and leads to a decrease in bioavailable N (Inwood et al., 2005)
volatization	NH3 load, temperature, pH, moisture content	Volatized N is generally redeposited not far from where it was emitted, on a temporal scale of hours or days (Jenkinson, 2001; Van Breemen et al., 2002)
plant uptake	Season, soil moisture content, N availability	Plant N uptake is high in the growing season (spring/summer). In autumn and winter N uptake is limited and possibly there is a net release of N due to plant N decomposition. If net export of crops N uptake > N release ny plants (Van Gerven et al., 2009)
Storage in soil and sediment	Soil texture, soil organic matter content, soil moisture content.	NH4+ can be permanently bound in silicate minerals, and then this N becomes non-exchangeable with the bulk solution (ref).
Residence in groundwater	Groundwater residence time	N is retained by groundwater by delay the N load from reaching surface waters. So it functions as temporary storage. During groundwater residence certain amounts of N may be lost due to denitrification Note that groundwater becomes a source rather than a storage if outflow of N becomes larger than the inflow of N

* De wit, 1999

Various studies indicate that TN load and water residence time are the main controls of instream N retention in a catchment (Saunders and Kalff, 2001; Lepistö et al., 2006). Residence time is influenced by climate, and the occurrence of stagnant water systems. Saunders and Kalff (2001) conducted a literature review on N retention in rivers, lakes, and wetlands, which indicated that these systems retained 64%, 34%, 2% of entering TN loads, respectively.
For Europe the major contributor to catchment scale retention was found to be denitrification (Velthof et al., 2009). However, some river basins where lake densities are relatively high, like in the Oulujoki catchment (Finland) sedimentation of organically bound N was estimated to contribute more to overall basin N retention (Lepistö et al., 2001; Lepistö et al., 2006). In a study done by Alvarez-Cobelas (2008) TN load was found to be a good predictor for N retention in lakes (r^2 =0.80) and wetlands (r^2 = 0.82), although it did not give good prediction for retention in rivers (r^2 = 0.10). And although lentic systems like wetlands are generally thought to decrease the TN load, some studies that conducted sampling during storm events indicated that during these events wetlands can actually act as an N source (Wade et al., 2004).

According to various authors (Alexander et al., 2000; De Klein, 2008; Van Gerven et al., 2009) retention rates decrease with stream size. This is explained by the presence of macrophytes in smaller sized river channel, which lead to N uptake, and lower flow velocities which promote sedimentation and denitrification due to longer residence times. Furthermore, contact between the water and the channel bed is higher in smaller sized upstream channel reaches, which also promotes denitrification (Gerven et al., 2009)..

Estimation on denitrification in groundwater was done by Kunkel et al (2004) for the German lowlands, nitrogen loads were halved within 1 – 4 years, due to oxygen free conditions and presence of organic carbon and pyrite. For consolidated rock regions in Germany it was estimated that 30 % of the diffuse nitrogen load entering groundwater is denitrified before reaching surface water, while this was estimated at 90% for unconsolidated regions. These higher denitrification rates in unconsolidated rocks was appointed to higher availability of cation exchangers and longer groundwater residence times in these areas.

Various estimation on instream retention, soil groundwater retention and overall catchment retention factors were found in literature (see appendix 2). Instream retention estimates varied from 10 -50 %(Lepistö et al., 2006), soil –groundwater retention varied from 20 –50% (Thieu et al., 2009), and overall catchment retention was estimated between 40 -60 % on a global scale by Van Breemen et al. (2002).

3.4 Existing N models

Various models have been developed for source apportionment, scenario or environmental assessment studies. The models that are of interest for this study were those that could model N transport on a catchment scale (Billen et al., 1994; Arheimer and Brandt, 1998; Arnold et al., 1998; Krysanova et al., 1998; Whitehead et al., 1998) on a continental scale (Howarth et al., 1996; Grizzetti and Bouraoui, 2006b) or on a global scale (Kroeze and Seitzinger, 1998; Caraco and Cole, 1999; Van Drecht et al., 2001; Dumont et al., 2005), as the scale of the model that was to be developed in this project is comparable to the scales to which these model were applied. Generally N transport models can be distinguished between *process oriented* and *data oriented* models. Process oriented models try to describe 'real' processes and therefore generally are more complex and have higher data requirements compared to data oriented models. Empirical models do not model processes explicitly, but contain equations based on statistical relationships. An example of such a relation is the positive relation that was found between TN concentrations in surface waters and population density within a certain catchment (Caraco and Cole, 1999). The relation between model type and level of complexity as depicted by Schouwmans and Silgram (2003) is schematically depicted in figure 6. Resolution of the models vary from 1 x 1 km to approximately 50 x 50 km (Van Drecht et al., 2001), and output on N flow or concentrations are generated on a daily, monthly or annual basis.

Consistent datasets that cover areas at the catchment, continental or global scale are scarce, which is often why data oriented models are generally preferred for large scale modeling (Grizzetti and Bouraoui, 2006a). A disadvantage of empirical models is that they are less suitable for making future prediction, as the empirical relationships of environmental factors and N load might change under different circumstances such as a change in climate.

Since recently the artificial neural networks (ANN) approach has also been applied in nitrogen concentration modeling (Lischeid and Langusch, 2004). This approach is based on the principle that a computer can learn from relationships between variables and was inspired by the workings of the human brain. A model comparison study by Srivastava et al. (2006) showed that the ANN model performed better compared to the process based SWAT model in monthly N concentration predictions. Due to limited knowledge and later discovery of this model type, the ANN approach was not considered to be used in the TN concentration model.

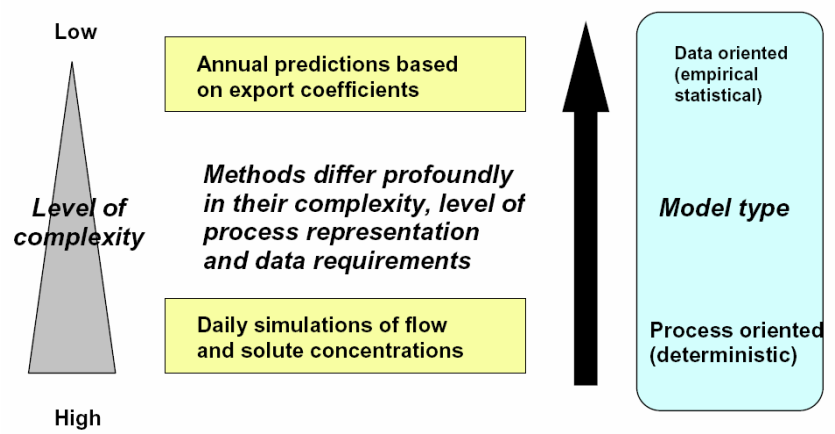


Figure 6 Relation between model type and model complexity. Source: (Schoumans and Silgram, 2003)

Description of retention processes in models can be done by explicit description of retention processes such as denitrification or plant uptake (Whitehead et al., 1998) but can also be represented by a fixed or variable dependent retention parameter (Grizzetti Bouraoui, 2006). Explicit descriptions of retention processes is of importance in models that generate output on a sub-annual scale (daily - monthly) as individual processes rates vary over the year and are controlled by different factors (Van Gerven et al., 2009). The fixed or variable parameter approach is generally more suitable for modeling on annual scales. N load that is exported has been expressed in models as a function of temperature (Whitehead et al., 1998), proportion of water in a catchment (Lepistö et al., 2001), river length (Grizzetti and Bouraoui, 2006), or hydraulic load and specific runoff (Behrendt and Opitz, 1999).
In a number of case studies statistical models performed to a similar extent or better compared process oriented models(De Wit and Pebesma, 2001; Grizzetti et al., 2005). But how the models perform is also dependent on the input data and the suitability of the model for application to a certain catchment. In the Euroharp project(Schoumans and Silgram, 2003), a number process oriented and conceptual models were compared and applied to a number European basin. No 'best' was identified. Rather it was recognized that a specific models is suitable for a specific purpose.

3.5 Modeling tools

The TN concentrations model was built in the spatial analysis tool HABITAT. For the preparation of the input data both a spreadsheet (MS-Excel 2003), and a GIS-tool ArcGis (Version 9.2) was used.
The HABITAT tool can calculate with spatially referenced data in the format of bil-files that can transformed from asci-files within HABITAT. Data that serve as input for the model should be spatially referenced before calculation can be made with them in HABITAT and ArcGis was used to make the spatial reference of all data sets consistent and to adjust the format. In HABITAT results can be visualized in the form of maps and tables. It is a program which is based on PCRaster modeling language (Van Deursen and Wesseling, 1995) which is a language especially developed for environmental modeling.

3.6 The TN concentration model

3.6.1 Choices on model construction

The model developed in this research project became a static, semi-distributed, and data oriented model and uses a lumped approach to describe N processes. The model simulates TN concentrations at the river outlet of river catchments on an annual scale. How the decisions for this model were made is described in this section.

In the model requirements it was stated that the aim was that the model would be able to simulate TN concentrations per month. However, this was not possible due to data and time limitations. Overall N emissions from source like fertilizer and manure N application vary over the year. And other factors that vary over the year are factors like river discharge, retention of N loads. During different periods in the year different processes dominate that control retention as was explained in paragraph 3.3.4. Making a model that could generate TN concentrations per month would require descriptions of the individual processes, and information on how N emissions from sources like N fertilizer application are distributed over the months for European catchments. It was concluded that time was too limited to find the data and to apply a process oriented approach. From this is was decided to built the model on an annual scale and the model describes retention with parameters that lump these processes together. For the annual scale it is easier to quantify N emission as data are mostly available on an annual scale, and it is easier to estimate the annual effect of retention, as inter-annual variation of TN loads and concentrations are smaller than intra-annual variation (Loos et al., 2009).

The hydrological data that was available in this research was data on water discharge at river outlets of European river basins. It was decided to calculate TN concentrations at the river outlet and not model TN concentrations in more detail, like for example at the scale of river branches as was done in the study by Mourad et al. (2008). This was found acceptable as a model that could generate annual average TN concentrations data per basin on an annual scale could still provide quantitative data for the purpose of a scenario study.

The difference between present day N emission compared to historical N inputs is not taken into account in the model. And so it is assumed that estimation of N emitted via groundwater in 2000 can be based on N applied to the soil in 2000. This can generally be true for aquifers that consist of consolidated rock as runoff as N transport to surface waters in these aquifer types are relatively short (Kunkel et al., 2004), but is unlikely for basins with large groundwater residence times.

The model covers the major watersheds of Europe including the Upper-Danube, Douro, Elbe, Göta, Loire, Po, Oder, Rhine, Rhone, and the Vistula, and also some smaller ones like the Thames, the Scheldt, and Shannon as shown in orange-colours in figure 7. The resolution of the model was chosen at 5 x 5 arc minutes, since most datasets (e.g. data on land cover, urban areas) were available at this or a higher resolution, or were expected to become available at this resolution in the near future. The spatial resolution of 5 x 5 arc minutes represent approximately 9 x 4[1] km in the north of Scandinavia, and 9 x 8 km in the south of Spain.

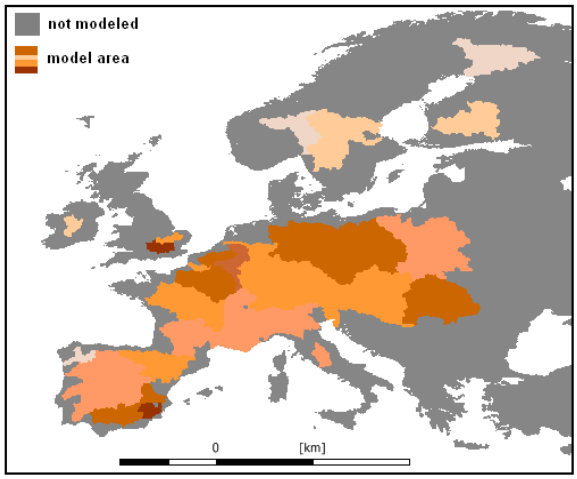


Figure 7 - Modelled area

[1] 9 x 4 km: 9 km in the North-South direction, 4 km in the East-West direction.

3.6.2 Model description

TN concentrations in surface waters were estimated by quantification of the following factors: N emissions, N retention processes, and the water volume to which N is emitted. Land use data was used to define the various pathways through which N emitted was transported to surface waters. The N sources as discussed in paragraph 3.2.2 were quantified, which were: lightning N fixation, and biological N fixation from natural ecosystems and crop cultivation, manure and fertilizer application, rock weathering, and emissions from households, industry, urban areas, fossil fuel combustion, and electricity generation. Some sources are represented in the model by one variable. For example, N input from lightning, fossil fuel combustion and electricity generation are assumed to be represented by emission data for *atmospheric deposition* of reduced (NH_y) and oxidized N (NO_x). N emission from rock weathering, biological N fixation in natural ecosystems and agricultural land are lumped under an estimated value for *background N emissions*. In the model, N emissions due to lightning and BNF are quantified by assuming that these sources lead to an fixed amount of N emissions to surface waters per area of natural or agricultural land. This approach was chosen, as data on individual emissions per N sources were difficult to quantify. Spatial distribution of emissions from biological N fixation with help of land cover maps on ecosystems types and crop types was not applied due to the high uncertainty involved. Quantification of N emissions from the sources that are represented by atmospheric N deposition is cumbrous and not required as the pathways and the overall emission to surface waters remain the same.

In the model three different types of retention factors were applied to TN loads dependent on the area this load was emitted to. A retention factor was applied to TN loads that entered non-agricultural land surface areas, another retention factor was applied to the N load emitted to agricultural, and the third one representing instream retention that is applied to all emissions entering surface waters. A distinction between these three retention factors was made as literature gave different estimations on their values, which are discussed in section 3.6.4. The three retention factors were set at the same value for all catchments in the model. This approach for the model structure was inspired by the models of de Wit (1999) and Grizzetti and Bouraoui (2006). Emissions that first enter soil (either in agric or non-agric areas) and possibly also enter groundwater before reaching surface waters will be further referred to as *indirect emissions*, and N emission that directly flow into surface waters will be further referred to as *direct emissions*. The model approach is schematically depicted in figure 8.

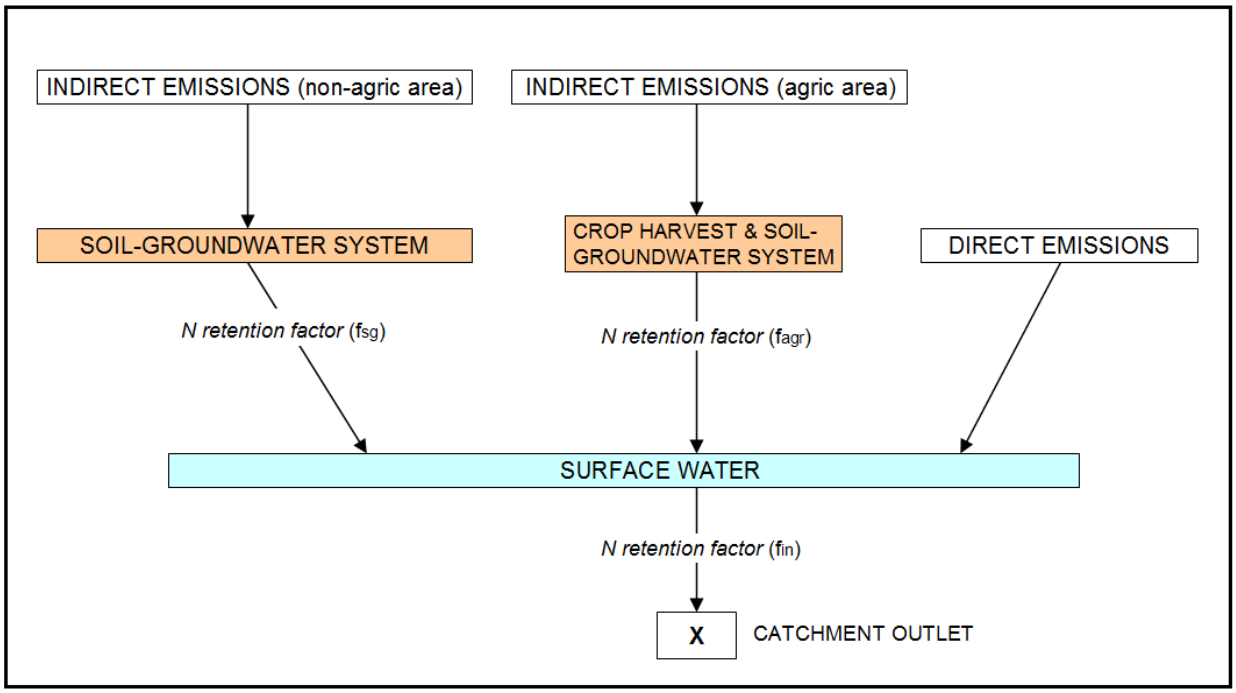


Figure 8 - Model structure modified from De wit (1999) and Grizzetti and Bouraoui (2006).

The governing equation for the calculation of TN load is as follows:

$$N_{tot} = a^* (N_{dir} + (b * N_{in\_non}) + (c * N_{in\_agr}))$$

Where: $a = 1 - f_{in}$
$b = 1 - f_{sg}$
$c = 1 - f_{agr}$

And where:

N_{tot}	is the total nitrogen load at the catchment outlet (kg)
N_{dir}	represents all direct N emissions (kg)
N_{in_non}	represents the indirect N emissions emitted to non-agricultural areas (kg)
N_{in_agr}	represents the indirect N emissions emitted to agricultural areas (kg)
f_{in}	is the in-stream retention factor (-)
f_{sg}	is the soil-groundwater retention factor for N loads entering non agricultural areas (-)
f_{agr}	is the retention factor which is applied to all N inputs to agricultural areas before reaching surface waters (-)

The TN concentration at the outlet can be calculated from the total nitrogen load N_{tot} and water discharge (Q) as follows:

$$C = (N_{tot} * 1000) / Q$$

Where:

- C is the average annual TN concentration (mg l^{-1})
- N_{tot} is total dissolved nitrogen (kg)
- Q is the water discharge (m^3)

3.6.3 *Quantification of N emissions*

In this section a general overview is given on the methods and data that were used for quantification of N emissions. A detailed description on the quantification methods and on metadata can be found in appendix 4 and appendix 5, respectively.

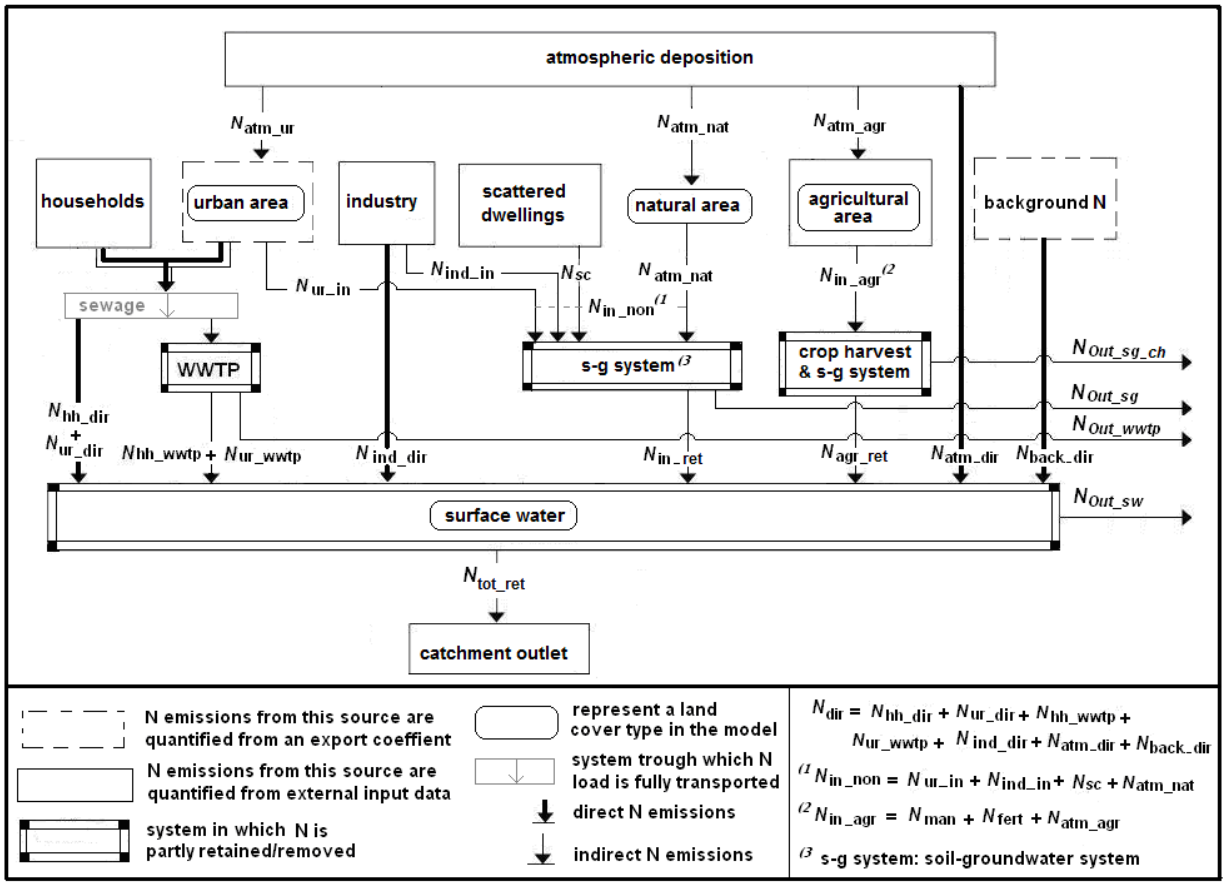


Figure 9 - Indirect and Direct Nitrogen emissions from sources and their pathways towards surface waters and the catchment outlet.

- **Emissions from industry**

Emissions from industry were quantified with a dataset from the website of the European Pollutant Emission Register (EPER, 2001) which is a dataset that contains data on N emissions of industrial facilities that emit more than 50.000 kg N per year. This data set covers the EU-15 member states, Hungary and Norway and represents emissions data of the year 2001. Information used from this dataset was the total amount of N emitted per facility, the location of the industrial facility in geographical coordinates, and the emission type. The emission types are distinguished between emissions *to air, directly to water*, and *indirectly to water* (via land). Emissions labelled as 'water direct' in the dataset are assumed to flow directly into surface water while 'water indirect' treated as indirect emissions to non-agricultural soil in the model. Inherently, emission data is missing in the EPER due to the threshold of 50.000 kg N that before N emissions are registered. Comparing data from the Dutch Emission Register (ER) and EPER data on Dutch industrial N emissions, the ER data gave N emission (95 Gg N) that were more than ten times the amount as the amount that was registered in the EPER (6.6Gg) for the Netherlands. In the model data from EPER is multiplied by a factor 7 in the entire modelled area. It is recognized that this data has high uncertainty on the 'real' industrial emissions and suggestions for data improvement are given in the discussion.

- **Emissions from households**

Household emissions were estimated from population data and an assumed value for the average N emission per persons for people in Europe. Population data was available on a 30 x 30 min scale covering the pan-Europe area from the Centre for Environmental Systems Research (CESR, 2007), and estimations of

N emissions per capita were derived from literature which ranged from 9 - 18 g N day^{-1} (De Wit, 1999; Van Drecht et al., 2003) At first the guideline value of 12 g N cap^{-1} day^{-1} by OSPAR was used, but this changed into 11 after calibration. It was assumed that per capita emissions was the same over in all regions.
Three different pathways of transport of household N emissions to surface waters were described in the model: 1. households connected to the sewage system, of which the waste was treated in a WWTP 2. households connected to a sewage system of which waste water was not treated in a sewage system, and was directly emitted to surface water, and 3. households not connected to a sewage system The third type of households will be further referred to as ***scattered dwellings.*** Data on the connectivity of household to sewage system, the fraction of the waste water that is treated in WWTP's, and percentage of waste water treated per treatment type was available per country from the SCENES database. This data was obtained from national statistics, the WHO, EUROSTAT, and UNICEF, and an overview of this data is included in appendix 6. Table 2. below contains the percentage of N reduction that was assumed for the three various treatment types, and we derived from (Grizzetti and Bouraoui, 2006a). All emissions from scattered dwellings were assumed to enter the soil-groundwater system.

TABLE 2 - FIGURE 8 - PERCENTAGE OF N REDUCTION IN WWTP'S PER TREATMENT TYPE.

Treatment type	% of N reduction
primary	15
secondary	30
tertiary	60

Modified from: (Grizzetti and Bouraoui, 2006a)

- **Emissions from agriculture**

Emissions from agriculture were quantified from estimations on N fertilizer and manure application rates and data on agricultural land cover per basin. Data on N fertilizer and manure application rates were obtained from visual estimation from two maps by Mulligan et al (2006). One map depicted fertilizers N application and the other depicted manure N application rates for EU-27 on a 10 x 10 km grid in kg N ha^{-1} per agricultural area (AA). The estimated value ranged from 10 kg ha^{-1} yr^{-1} per AA for river basins in the north of Scandinavia and to up to 320 kg ha^{-1} yr^{-1} for the Weser river basin in Germany. Spatial information on agricultural areas was obtained from that was compiled by the CESR and combined the Corine land cover map (CLC2000)(EEA, 2007) and the Global land Cover Characterization database (USGS, 2007). This map distinguished between various natural land cover types and four different agriculturally related land cover types, which were 'grassland', 'cropland', 'fruit farms', and 'cropland/natural vegetation mosaic'. It was assumed that total N application rates are equal for all areas classified as grasslands, cropland, and fruit farms and is 50 % less for areas classified as 'cropland/natural vegetation mosaic'.

- **Atmospheric deposition**

Atmospheric N deposition data is obtained from the website of the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) which contained 50 x 50 km gridded N deposition data for the year 2000. The pathways of atmospheric N deposition to surface waters are dependent on what land cover type (urban, natural, agricultural, water) N is deposited on as is visualized in figure 9.

- **Background N emissions**

Background N emissions were quantified from data on the amount of natural and agricultural allocated within a catchment and a fixed N export parameter per (natural/agricultural) area. An estimation of background N emissions was made from data on 1. estimated value of background concentration of TN for European rivers 2. River water discharge from at the outlet of a catchment 3. The total catchment area for that same catchment. The estimation was done based on European background concentrations of NO_3^-- N of 0.2 - 0.3 mg/l (Meybeck, 1982; EEA, 2001; Nixon, 2004) and Rhine characteristics with a river discharge of 2300 m^3/s and a catchment area of 160.000 km^2. Assuming that NO_3^-- N of 0.2 - 0.3 mg/l equals TN concentrations of about 0.3 - 0.5 mg/l, then estimated background N emission range between 1.4 -2.3 kg ha^{-1}. And assuming that 0.5 kg ha^{-1} of this background N emission is from natural atmospheric deposition, (which is quantified together with non-natural atmospheric deposition under '*atmospheric deposition*')

background N emissions from biological N fixation and rock weathering is estimated to range between 0.9 to 1.8 kg ha^{-1}. All vegetated areas like agricultural land and all natural areas are assumed to contribute equally to N loss per unit area, except for the areas classified as covered with snow and ice and barren or built up areas. These areas are assumed to emit no background N. Although it is recognized that N emissions from rock weathering and from biological N fixation do not enter water directly, background N emission is treated as a direct emission in the model, as the emission rate is defined as the N emissions of these sources *to surface waters*. After calibration of the model the background N emissions rate was set at 150 kg ha^{-1} yr^{-1}.

3.6.4 Quantification of retention factors

In this section the three retention factor of the model are quantified.

- **Retention in soil and groundwater**

The soil/groundwater retention parameter (f_{sg}) is assumed too lie between 0.3 and 1.0. This range is derived from the estimation by Kunkel et al., (2004) that in catchments with a subsurface of unconsolidated rocks, a factor 0.9 of the transported TN load is retained due to denitrification in groundwater before reaching surface waters. This fraction was 0.3 for catchment with a subsurface of consolidated rocks. The upper value of this range is derived from the graph by Stevenson (1986) which shows that if there is no excess nitrogen, then all nitrogen is retained within the soil/groundwater system and the retention factor is 1. In the model soil and groundwater retention factor was set at 0.4 after calibration of the model.

- **Retention in surface water**

The instream retention parameter (f_{in}) is based on literature data as described in section 3.3. and ranges between 0.10 – 0.50. This retention factor is assumed to represents retention due to denitrification, N sedimentation and re-suspension, vegetation N uptake and N release due to decomposition of organic matter. It is also assumed that this factor takes into account the effect of the presence of wetlands, reservoirs, lakes on these processes. In the model this instream retention factor was set at 0.1 after calibration.

- **Retention in agricultural soils (f_{agr})**

The range of N retention (f_{agr}) for N inputs entering agricultural soils is derived from data from reports from Dutch agencies and was estimated 0.90 to > 95 (STOWA, 2008; 2009b; CBS and PBL, 2009c). At higher N emissions at the soils surface the retention fraction is expected to be lower excess N is higher and as crops have a maximum amount of N they can take up and the soil can get N saturated (Stevenson, 1986) as described in section 3.3.3. However, these retention estimations were derived from a country where agricultural N application are one of the highest in EU-27 (EEA, 2006) In this model one fixed value for this retention value was assumed to be representative for each river basin in the model area, and was set at 0.95. In table 3. the value for all three parameters are presented.

TABLE 3 – SETTINGS OF THE RETENTION PARAMETERS FOR THE TN CONCENTRATION MODEL

retention parameter	description	Value in model
f_{sg}	Retention of N entering in non-agricultural areas before reaching surface waters	0.4
f_{agr}	Retention of N loads in agricultural soils before reaching surface waters	0.95
f_{in}	Retention of N entering surface waters before reaching catchment outlet	0.1

3.6.5 Quantification N emission to water and from the catchment outlet.

The amount of N that reaches the catchment outlet depends on the load emitted and the amount that was retained on the way since it was emitted, which depends on whether it was emitted directly or indirectly to surface waters according to the model structure as described above. N input from some sources like atmospheric deposition and households both have direct or indirect pathways towards surface waters. In this section a description is given on how the pathways of N loads from source to outlet are determined in the model. A schematic depiction of these pathways is given in figure 9 (section 3.6.3).

Direct inputs of N (N_{dir}) that are taken into account into this model are as follows:

- household emissions from sewage systems without treatment (N_{hh_dir})
- urban emissions from sewage systems without treatment (N_{ur_dir})
- households emissions led to a sewage system and treated in WWTP's (N_{hh_wwtp})
- urban emissions from sewage system and treated in WWTP's (N_{ur_wwtp})
- emission via industrial waste water discharge (N_{ind_dir})
- atmospheric N deposition onto surface waters (N_{atm_dir})
- background N emissions from agricultural and natural areas (N_{back_dir})

Total direct N emissions to surface waters can then be calculated as follows:

$$N_{dir} = N_{hh\_dir} + N_{ur\_dir} + N_{hh\_wwtp} + N_{ur\_wwtp} + N_{ind\_dir} + N_{atm\_dir} + N_{back\_dir}$$

N_{dir} represents the N load of all direct N emissions to surface waters within a catchment. All N loads are expressed in kg yr^{-1}.

Indirect inputs of N in *non-agricultural* (N_{in_non}) areas are:

- urban runoff infiltrating into the soil (N_{ur_in})
- industrial waste disposal to land (N_{ind_in})
- emissions from scattered dwellings (N_{sc})
- atmospheric N deposition on natural areas (N_{atm_nat})

Indirect N emissions to non-agricultural areas can be calculated as follows:

$$N_{in\_non} = N_{ur\_in} + N_{ind\_in} + N_{sc} + N_{atm\_nat}$$

Indirect inputs of N in *agricultural* (N_{in_agr}) areas are:

- manure N application (N_{man})
- fertilizer N application (N_{fer})
- atmospheric N deposition on natural areas (N_{atm_agr})

Indirect N emissions to agricultural areas can be calculated as follows:

$$N_{in\_agr} = N_{man} + N_{fer} + N_{atm\_agr}$$

3.6.6 Data harmonization

Data harmonization can be described as the adjustment of data with the aim to make them spatially and temporally comparable and consistent. Data sets can be inconsistent in a number of ways. For example, data can represent measurements obtained in different time periods (e.g. different year, season) or locations, and there can also be differences in the measuring methods applied like laboratory analysis methods, and difference in measurement density and frequency (Wahlin and Grimvall, 2008)
In this research the datasets obtained represented annual averages except for the water discharge data. Water discharge data was given on a monthly scale and was transferred to annual values by summation of discharge values for all months of the year 2000. Data on population, atmospheric deposition were scaled down to match the model resolution. This was done with the help of ArcGis. Transfer of data on N emissions or population number to a different resolution is done while keeping the total mass balance, or population number intact. When data is scaled up or down , the N load or population number is allocated proportionally to the change in grid cell area. Data that represent emission rates, like with the agricultural data, can be directly transferred without modification of the values as the emission rates stay the same at any spatial resolution. All gridded data sets were set to the WGS -1984. For details on the projection see appendix 3.

3.7 Calibration and validation data

Data that is to be used for validation of the model need to be representative for the year for which input data was provided and the temporal extent for which the output is generated is average TN concentration for the year 2000. Some monitoring data on TN concentration close to outlets of a number of river catchments were available from a water quality dataset of the EEA (WATERBASE, 2009), which contained measurement data from between 1995 -2007. This data was used for validation of the model. Some of the station from which monitoring data was used were some distance away from the river outlet (e.g. for the Oder). This decreased the representativeness of the data. However, due to lack of alternatives the data was still used if the larger cities in the catchment and water bodies like lakes and wetland, lay upstream of the monitoring location.

The monitoring stations were checked on their proximity to the catchment outlet, was with done with the coordinates of the measurement locations and GoogleMaps. For quite a number catchment TN concentrations measurement data was not available, or was not representative for either the year 2000 or for the concentration at the catchment outlet. For these catchments literature was addressed to find representative monitoring data. Measured TN concentrations or estimated loads for the Po, Scheldt, and Göta were obtained literature sources and are listed in appendix 5 on metadata. During this research it was found that the data on N concentrations were usually measured for limited number of N-species and mostly for NO_3^- as this is relatively easy to measure (Raat et al., 2004; Salminen, 2005; Saraiva et al., 2007). This raised the question whether TN concentrations could be estimated if data on concentration of N-species were available. Klepper et al. (1995) used data on NO_3^- concentration as validation data for TN concentration and assumed a ratio between TN and NO_3^- of 0.7. Other authors also stated that NO_3^- usually was the dominant N species making up the TN load (Dumont et al, 2005; Mourad, 2008), which implies that NO_3^- concentration can be used as some indicator for TN concentrations, and might serve as validation data. However, a number of studies on N speciation (Klepper et al, 1995; Willet, 2004; Mourad, 2008; Loos et al., 2009; Kessel et al, 2009) showed that ratio's of NO_3^-, NH_4^+ and DON varies strongly depending on N source types, season, and the prevailing conditions for N transformation. In these studies ratio's of contribution of NO_3^- to the TN load were found to vary from close to 0 to up to 87 %, and DON ratio's varied from < 30 to 80 % in surface waters. Therefore it was concluded that data on concentration of NO_3^- or other N species cannot be used model validation in this study.

Calibration is the activity of tuning model parameter values, or estimated emissions values to make its outcomes better fit to measured data (Brimicombe, 2003) with the aim to reduce the uncertainty of parameters and compensate for errors in input data (Thielman et al., 2001). Calibration can be done with help of statistical approaches like the Monte Carlo procedure (Grizzetti and Bouraoui, 2006a) or manually by a trial-and-error approach. This latter approach, trial-and-error, was used for the calibration of the model built in this research. The model was calibrated for the Vistula river basin (Poland). This basin was chosen as it was positioned relatively central on the North –South line, and the station from which the monitoring data was obtained lay very close to the catchment outlet which would make the model output suitable for comparison with this monitoring data. The model was calibrated for 5 different parameters. These parameters were the three retention factors for non-agricultural areas, agricultural areas and surface waters, and the values for background N emissions and N emissions per person. These parameters were all tuned within their uncertainty ranges as described in paragraph 3.6. The initial settings and the settings after calibration are listed in table 3.

TABLE 4 PARAMETER SETTINGS BEFORE AND AFTER CALIBRATION.

Tuned parameter	Initial settings	Settings after calibration	unit
f_{agr}	0.90	0.95	-
f_{sg}	0.6	0.4	-
f_{in}	0.2	0.1	-
Background N loss factors	100	150	kg ha^{-1} yr^{-1}
Per capita N emission	12	11	kg cap^{-1} yr^{-1}
Factor for multiplication of industrial N emissions	5	7	

In complex models the effect of change of input values on output values is not always straightforward, for example due to feedback mechanisms. For these models a structural and step by step sensitivity analysis by adjustments of uncertain parameters is necessary to determine sensitivity of the model output to these factors. A sensitivity analysis for the TN concentration model would give different results per river basin. As a basic sensitivity analysis a source apportionment was conducted and this presented in figure 11 in section (3.8.2). This gives an indication of the contribution of each source to the total N emissions to water and from the catchment outlet. For catchments where agriculture is a major source, the catchment will be more sensitive to changes in setting influencing the amount agricultural emissions. A catchment where background N emissions are mainly responsible tor the TN is not as sensitive to changes in settings for agricultural N emissions.

3.8 Model results

3.8.1 TN concentration

In this paragraph the model result on calculated TN concentration per river catchment is presented. The model results are classified according WFD water quality status classification as shown in table 4.

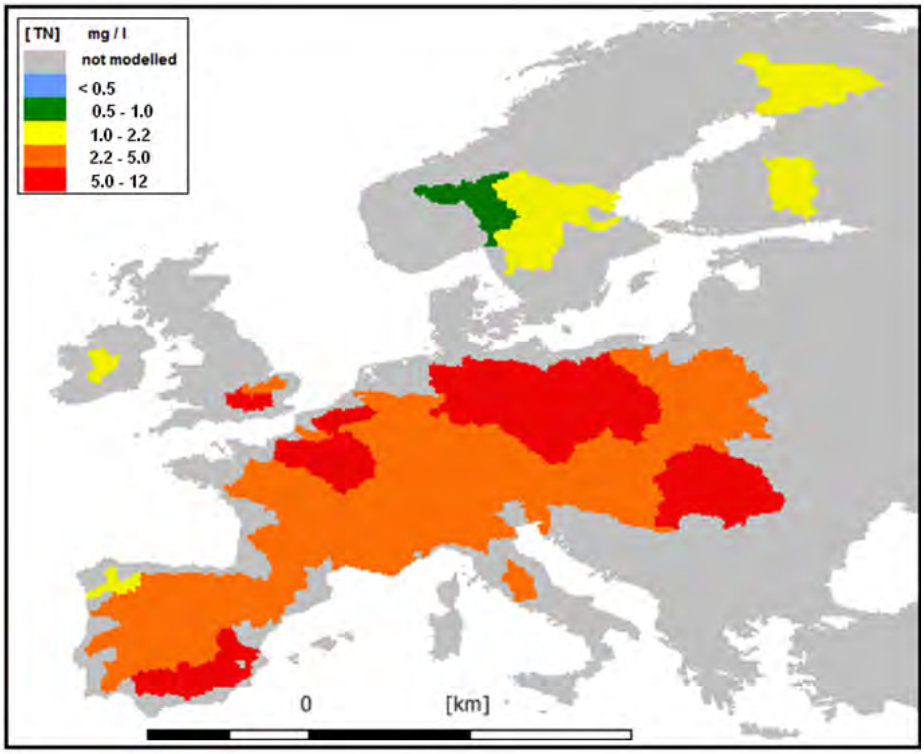
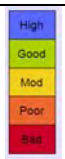


Figure 10 - Modeled average annual TN concentrations at river catchment outlets for the year 2000.

TABLE 5 CLASSIFICATION OF WATER QUALITY STATUS OF SURFACE WATERS FOR TN CONCENTRATIONS

colour	status	TN concentration (mg/l)
	High	< 0.5
	Good	0.5 – 1.0
	Moderate	1.0 – 2.2
	Poor	2.2 – 5.0
	Bad	5.0 - 18

According to the model results a 'bad status' for TN concentrations can be found in basins in North-West of Europe which include the Thames, Scheldt, Meuse, Seine, Weser, Elbe and the Oder river basins. Other river basins for which the surface water at the catchment outlet was classified to be of 'bad quality' were the Guadalquivir, Segura, and Jucar river basins (Southeast Spain), and the Central-Danube basin (Hungaria). All other modeled river catchments, depicted in yellow or orange in figure 8. came out the model to be of low or moderate quality concerning average annual TN levels at the catchment outlet.

3.8.2 Source apportionment

The present model area is limited by the coverage of Europe by industrial data. The following figure takes into account a larger amount of river basins than for which TN concentrations are modeled and presents a source apportionment per river basin, without taking into account emissions from industrial activities. The fractions of the pie-diagrams are based on the contribution per source to the TN load at the catchment outlet. The sources that are represented are households, agriculture, atmospheric deposition and background N.

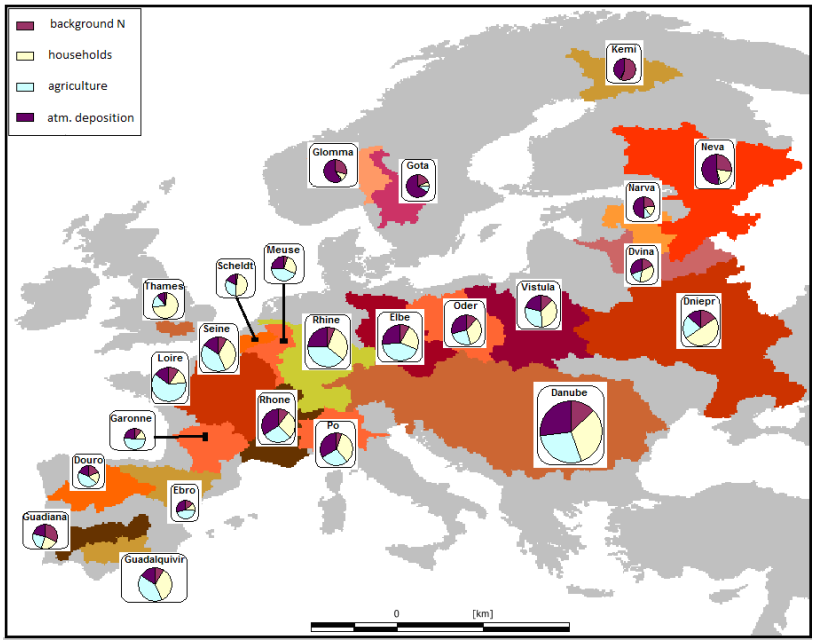


Figure 11 - Contribution to TN concentration of surface waters at catchment outlets per source, per river catchment, excluding contribution from industrial emissions.

In figure 12 the contribution of different N sources to overall TN emissions to surface waters is expressed in area specific loads. Highest loads can be found in North West European, the Po and the Guadalquivir river catchments. Lower areas specific N loads are found in catchment of the Northwest part of Spain and the Scandinavian, and also in the Dnieper and the Danube catchments. Area specific N load for The Thames, Scheldt, Meuse, Rhine and the Po are high mainly due to household and agric N emissions, which can be explained by the high population densities in these catchment and the high amount of fertilizer and manure N application. In the catchments lying in parts of Scandinavia like the Glomma, the Neva, and the Kemi the area specific input from all sources are relatively low, which can be explained by low population densities, less agricultural activity and smaller fertilizer and manure N application rates and agricultural input are very.

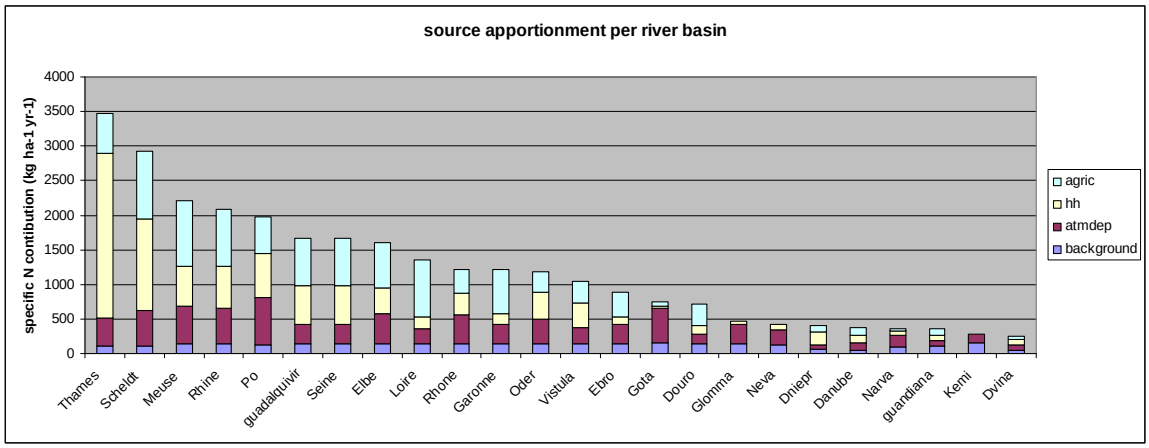


Figure 12 Contribution to TN emissions to surface water per source, expressed in area specific load.

3.8.3 Validation results

The TN concentration model was validated for those catchment for which measured data was available on average annual TN concentration. The deviation between the modeled and the measured TN concentration values is depicted here as the ratio between modeled and measured value as shown in figure 13. The model was calibrated for the Vistula catchment, and therefore the fraction of modeled to measured is 1. Little deviation of model results is found for the Guadalquivir, the Po, the Rhone, and the Scheldt.

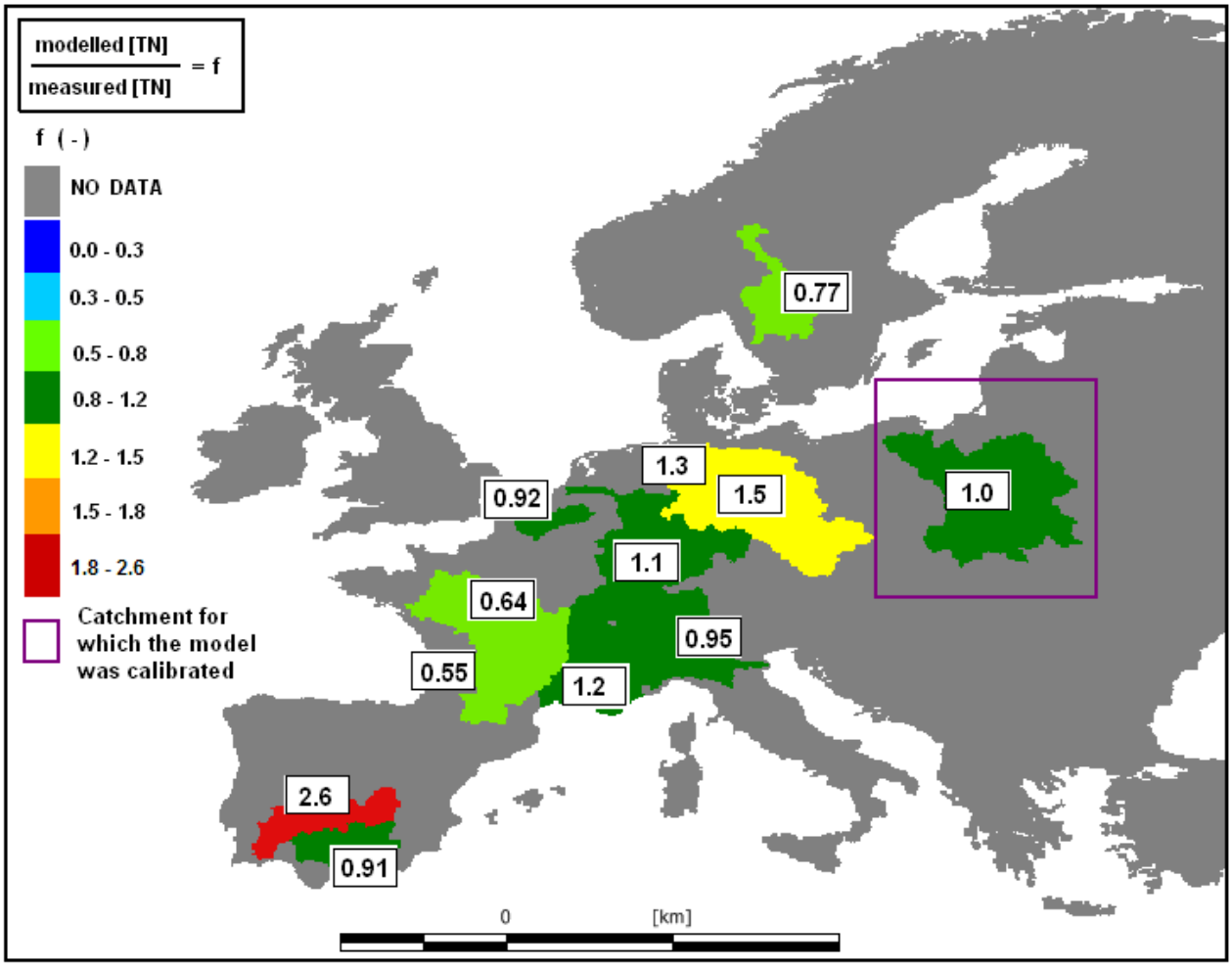
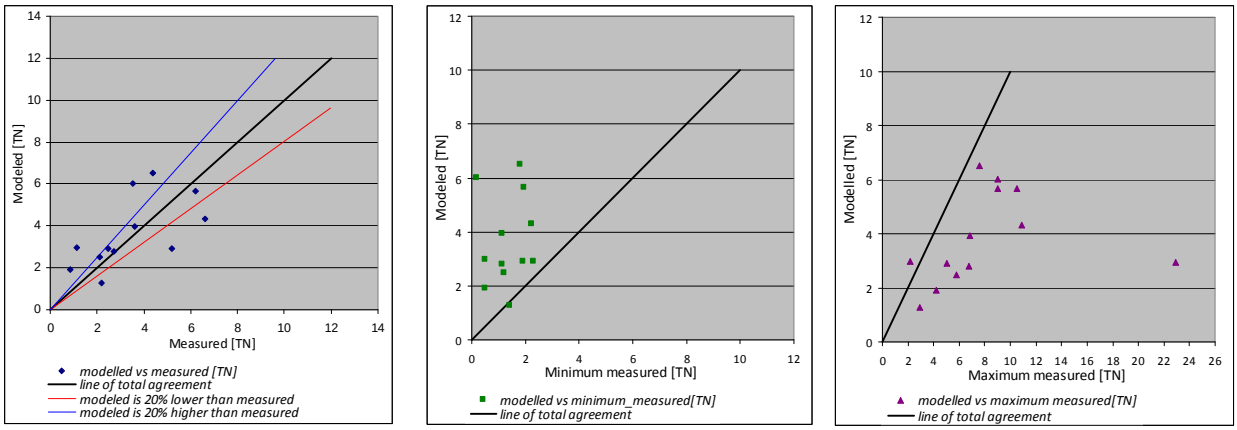


Figure 13 Ratio between modeled and measured annual average TN concentration at the catchment outlets

Results in figure 14 show that the model performance was good for five out of the twelve catchments, as the modeled result for these catchments did not deviate from the measured ones for more than 20%, that was aimed for. The largest deviation in the model results was for the Guadiana catchment, where the model overestimated the TN concentrations by a factor 2.6. The largest underestimation found was for the Garonne by a factor 2.3. Modeled average annual TN-concentrations remained between the minimum or maximum measured values at the catchment outlets for most catchments, as can be seen in figure 3.7(a,b).



a. b. c.

Figure 14 a) deviation of modelled results compared to measured TN concentrations; b) modelled average TN concentration values compared to minimum measured concentrations; c) modelled average TN concentration compared to maximum measured concentrations.

4 Conclusion and Discussion

The model performed well for about half of the catchments for which the model was validated, and for the majority of remaining catchment the model gave results that stayed within the maximum and minimum measured values for TN concentration at the catchment outlet. For a model with simplistic representation of N transport pathways and transformation processes the model performance is reasonable.

Theoretically the model could be used for scenario applications, as the most important function is to see the relative effect of the various socio-economic development scenario's on TN concentrations in surface waters. However, only general variables can be changed in the model for scenario application like population number, waste water treatment efficiency in WWTP's, and change in river water discharge related to change in human water consumption patterns. The model is not found suitable for estimating the effects of measures like development of riparian zones, or estimating the net effect of various processes. For this type of application a more detailed description of individual N processes is required. This was not accomplished in this research project due to time limitations.

For more consistency in the representation of N emissions in the model it is suggested to check the industrial data input into the model. This can be done by comparing model values on industrial emissions with data on industrial N emissions from other sources, such as national statistics. It is also suggested that EPER data on industrial emissions for 2004 is used. The reason for this is that 2001 was the first time the EPER was implemented. Using data from 2004, would lead to a larger coverage of the model (EU-27 and Norway, instead of EU-15 and Hungary and Norway), the reporting is expected to be more complete, and emission values for 2004 are expected to be sufficiently representative for the year 2000.

Other data that can be improved are agricultural N emissions. Present estimation on agricultural and manure N emissions in river basins are relatively uncertain as they were estimated visually. Reducing uncertainty in data for agricultural emission estimates is relevant as agricultural N is a significant N source for most European river basins. Alternative fertilizer and manure N emission data can be found for example in Oenema et al. (2009), or alternatively from the FAO.

Another adjustment that might improve emissions quantification concerns the methods used to quantify N emissions from households. It is expected that more accurate estimations can be made on household emissions and the N emission pathways by allocating N emission from scattered dwelling to rural areas, while relating households connected to sewage systems to urban areas. Households are a large contributor to overall N emissions to surface water, so improved estimation on these emission can lead to a better model performance or, in any case, to a better representation of 'reality'.

Another suggestion for improving model performance is to investigate how its performance changes when N retention is included in the model as a function of temperature, water surface area within a catchment, river length (available in Crouzet, 1999) or precipitation. These factors are suggested as data on these factors are relatively easy to collect on the scale of Europe. This approach would give a better representation of the N retention processes as temperature affects process rates, and river length and water surface area are indicators for water residence time affecting the time in which retention processes can take place.

Acknowledgements

I would like to thank my supervisors Paul Schot, Harm Duel, Erwin Meijers and Sibren Loos for their help and advise and for making this research project possible. Many thanks go to the people of the WKE-department, who were part of the reason that my internship was a very positive experience. I would like to thank Rolf van Buren, Karen Meijer, Marjolijn Haasnoot, Valesca Harezlak, Reinaldo Penailillo Burgos, and Svetlana Obradovic for their willingness to assist and for their contributions.

References

Ahad, J. M. E., Ganeshram, R. S., Spencer, R. G. M., Uher, G., Upstill-Goddard, R. C. and Cowie, G. L., 2006. *Evaluating the sources and fate of anthropogenic dissolved inorganic nitrogen (DIN) in two contrasting North Sea estuaries*. Science of the Total Environment Vol. 372(1), p. 317-333.

Alexander, R. B., Smith, R. A. and Schwarz, G. E., 2000. *Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico*. Nature Vol. 403(6771), p. 758-761.

Alvarez-Cobelas, M., Angeler, D. G. and Sánchez-Carrillo, S., 2008. *Export of nitrogen from catchments: A worldwide analysis*. Environmental Pollution Vol. 156(2), p. 261-269

Arheimer, B. and Brandt, M., 1998. *Modelling nitrogen transport and retention in the catchments of southern Sweden*. Ambio Vol. 27(6), p. 471-480.

Arnold, J. G., Srinivasan, R., Muttiah, R. S. and Williams, J. R., 1998. *Large area hydrologic modeling and assessment. I. Model development*. Journal of the American Water Resources Association Vol. 34(1), p. 73- 89.

Behrendt, H., 1994. Stickstoff und Phosphateintrag in die Fließgewässer Deutschlands unter besonderer Berücksichtigung des Eindtragsgeschehens im Lockergestinsbereich der ehemaligen DDR. Book *Stickstoff und Phosphateintrag in die Fließgewässer Deutschlands unter besonderer Berücksichtigung des Eindtragsgeschehens im Lockergestinsbereich der ehemaligen DDR*. Werner, W. and Wodsak, H. P., Agrarspectrum. 22.

Behrendt, H., Kornmilch, M., Opitz, D., Schmoll, O. and Scholz, G., 2002. *Estimation of the nutrient inputs into river systems–experiences from German rivers*. Regional Environmental Change Vol. 3(1), p. 107-117.

Behrendt, H. and Opitz, D., 1999. *Retention of nutrients in river systems: Dependence on specific runoff and hydraulic load*. Hydrobiologia Vol. 410p. 111-122.

Billen, G., Garnier, J. and Hanset, P., 1994. *Modelling phytoplankton development in whole drainage networks: the Riverstrahler Model applied to the Seine River System*. Hydrobiologia Vol. 289(1), p. 119-137.

Billen, G., Thieu, V., Garnier, J. and Silvestre, M., 2009. *Modelling the N cascade in regional watersheds: The case study of the Seine, Somme and Scheldt rivers*. Agriculture, Ecosystems and Environment Vol. 133(3-4), p. 234-246.

Böhlke, J. K., O'Connell, M. E. and Prestegaard, K. L., 2007. *Ground water stratification and delivery of nitrate to an incised stream under varying flow conditions*. Journal of Environmental Quality Vol. 36(3), p. 664.

Brimicombe, A., 2003. *GIS, environmental modelling and engineering*. CRC Press.

Brunet, R. C. and Astin, K. B., 1996. *Variations in mineral nitrogen levels: the River Adour*. Hydrobiologia Vol. 335p. 159-170.

Caraco, N. F. and Cole, J. J., 1999. *Human impact on nitrate export: An analysis using major world rivers*. Ambio Vol. 28(2), p. 167-170.

CBS and PBL, 2009a. *Belasting van het oppervlaktewater, 1990-2007* versie 10, 14 augustus 2009. Retrieved 11 november 2009 from http://www.compendiumvoordeleefomgeving.nl/indicatoren/nl0083-Belasting-van-het-oppervlaktewater.html?i=5-117. Compendium voor de leefomgeving, Den Haag/Bilthoven, Wageningen.

CBS and PBL, 2009b. *Stikstofbalans van bodem en grondwater, 1986-2007* versie 10, 4 september 2009. Retrieved 11 november 2009 from http://www.compendiumvoordeleefomgeving.nl/indicatoren/nl019510-Stikstofbalans-bodem-en-grondwater.html?i=3-17
Compendium voor de leefomgeving, Den Haag/Bilthoven, Wageningen.
.

CBS and PBL, 2009c. *Stikstofbalans van bodem en grondwater, 1986-2008.* (versie 11, 11 december 2009). Retrieved 20 december 2009 from http://www.compendiumvoordeleefomgeving.nl/indicatoren/nl0195-Stikstofbalans-bodem-en-grondwater.html?i=3-17
Compendium voor de leefomgeving, Den Haag/Bilthoven, Wageningen.

CEC, 1975. *Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States* Official Journal Vol. 194p.

CEC, 1991a. *Council Directive 91/271/EEC concerning waste water treatment* Official Journal Vol. L 135p.

CEC, 1991b. *Council directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources*. Official Journal Vol. L 375p.

CEC, 2000. *The implementation of Council directibe 2000/60/EC - Water Framework Directive*. Luxembourg, Luxembourg. European Parliament and of the Council, Official Journal.

CESR, 2007. *Centre of envrionmental Systems Research* SCENES. Retrieves Acces Data Acces 2007

Chernikov, A. V. and Bruskov, V. I., 2005. *Fixation of atmospheric nitrogen in the water by heat or light with the formation of nitrogen oxides*. Doklady Biochemistry and Biophysics Vol. 400p. 40-43.

Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Howarth, R. W., Hedin, L. O., Perakis, S. S., Latty, E. F., Von Fischer, J. C. and Elseroad, A., 1999. *Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems*. Global Biogeochemical Cycles Vol. 13(2), p. 623 - 645.

Dahlgren, R. A., 1994. *Soil acidification and nitrogen saturation from weathering of ammonium-bearing rock*. Nature Vol. 368p. 838 - 841.

De Klein, J. J. M., 2008. *From ditch to delta: nutrient retention in running waters*. Wageningen University. Phd.Wageningen. Retrieves Acces Data Acces 2008

De Wit, M., 1999. *Nutrient fluxes in the Rhine and Elbe basins*. Utrecht Koninklijk Nederlands Aardrijkskundig Genootschap/Faculteit Ruimtelijke Wetenschappen Universiteit Utrecht.

De Wit, M. J. M. and Pebesma, E. J., 2001. *Nutrient fluxes at the river basin scale. II: the balance between data availability and model complexity*. Hydrological Processes Vol. 15(5), p. 761-775.

DER, *Dutch Emission Registration*. Retrieves Acces Data Acces from http://www.emissieregistratie.nl/ERPUBLIEK/erpub/weergave/grafiek.aspx

Dumont, E., Harrison, J. A., Kroeze, C., Bakker, E. J. and Seitzinger, S. P., 2005. *Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially explicit, global model*. Global Biogeochemical Cycles Vol. 19(4), p.

EC, 2006. *Guidance Document for the implementation of the European PRTR.* Retrieved 1st of December 2009 2009. European Commission, Luxembourg, Luxembourg.

EEA, 2001. *Nitrogen and Phosphorus in river stations by river size and catchment type.* Fact Sheet. Retrieved June 2009. European Environmental Agency, Copenhagen.

EEA, 2002. *Are nitrate concentrations in our rivers falling? - Nitrogen and Phosphorus in river stations*. Factsheet. European Environmental Agency. 16.Copenhagen. Retrieves Acces Data Acces 2002

EEA, 2005. *Source apportionment of nitrogen and phosphorus inputs into the aquatic environment*. EEA Report. European Environmental Agency. 46.Copenhagen, Denmark. Retrieves Acces Data Acces 2005

EEA, 2006. *Integration of environment into EU agriculture policy - the IRENA indicator-based assessment report*. European Environmental Agency. 2. 64.Copenhagen, Denmark. Retrieves Acces Data Acces 2006

EEA, 2007. *Corine land cover map* European Envrionmental Agency. Retrieves Acces Data Acces 2007 from http://www.eea.europa.eu/themes/landuse/clc-download

EPER, 2001. *The European Pollutant Emission Register*. European Commission. Retrieves Acces Data Acces 2001 from http://eper.ec.europa.eu/eper/extract_data.asp?i=

Erisman, J. W., Grennfelt, P. and Sutton, M., 2003. *The European perspective on nitrogen emission and deposition*. Environment International Vol. 29(2-3), p. 311-325.

Fogelberg, S., 2003. *Modelling nitrogen retention at the catchment scale: Comparison of HBV-N and MONERIS.* Technical University.Uppsala, Sweden. Retrieves Acces Data Acces 2003

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B. and Cosby, B. J., 2003. *The nitrogen cascade*. BioScience Vol. 53(4), p. 341-356.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A. and Holland, E. A., 2004. *Nitrogen cycles: past, present, and future*. Biogeochemistry Vol. 70(2), p. 153-226.

Green, P. A., Vörösmarty, C. J., Meybeck, M., Galloway, J. N., Peterson, B. J. and Boyer, E. W., 2004. *Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology*. Biogeochemistry Vol. 68(1), p. 71-105.

Grizzetti, B. and Bouraoui, F., 2006. *Assessment of Nitrogen and Phosphorus Environmental Pressure at European Scale*. Technical series EUR 22526. Directorate General Joint Reserch Centre. Institute for Environment and Sustainablility. .Ispra, Italy. Retrieves Acces Data Acces 2006

Grizzetti, B., Bouraoui, F. and De Marsily, G., 2005. *Modelling nitrogen pressure in river basins: A comparison between a statistical approach and the physically-based SWAT model*. Physics and Chemistry of the Earth Vol. 30(8-10), p. 508-517.

Harrison, J. A., Maranger, R. J., Alexander, R. B., Giblin, A. E., Jacinthe, P. A., Mayorga, E., Seitzinger, S. P., Sobota, D. J. and Wollheim, W. M., 2009. *The regional and global significance of nitrogen removal in lakes and reservoirs*. Biogeochemistry Vol. 93(1), p. 143-157.

Heathwaite, A. L. and Johnes, P. J., 1996. *Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments*. Hydrological Processes Vol. 10(7), p. 971-983.

Hill, M. K., 2004. *Understanding environmental pollution: a primer*. Cambridge University Press. p. 118.

Holloway, J. A. M. and Dahlgren, R. A., 1999. *Geologic nitrogen in terrestrial biogeochemical cycling*. Geology Vol. 27(6), p. 567.

Horn, A. L., Rueda, F. J., Hörmann, G. and Fohrer, N., 2004. *Implementing river water quality modelling issues in mesoscale watershed models for water policy demands—an overview on current concepts, deficits, and future tasks*. Physics and Chemistry of the Earth Vol. 29(11-12), p. 725-737.

Inwood, S. E., Tank, J. L. and Bernot, M. J., 2005. *Patterns of denitrification associated with land use in 9 midwestern headwater streams*. Journal of the North American Benthological Society Vol. 24(2), p. 227-245.

ISWS, 2009. *Nitrogen Cycle Project - Geosphere.* Retrieved 12th of August 2009 from http://www.isws.illinois.edu/nitro/detail.asp?lpg=areas&type=geosphere. Illinois State Water Survey, Champaign, USA.

Jenkinson, D. S., 2001. *The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture*. Plant and Soil Vol. 228(1), p. 3-15.

Jonson, J. E., Bartnicki, J., Olendrzynski, K., Jakobsen, H. A. and Berge, E., 1998. *EMEP Eulerian model for atmospheric transport and deposition of nitrogen species over Europe*. Environmental Pollution Vol. 102(1S1), p. 289-298.

Karssenberg, D., 2002. *Building dynamic spatial environmental models*. Koninklijk Nederlands Aardrijkskundig Genootschap/Faculteit Ruimtelijke Wetenschappen, Universiteit Utrecht, Nederland. .

Klepper, O., Beusen, A. H. W. and Meinardi, C. R., 1995. *Modelling the flow of nitrogen and phosphorus in Europe: From loads to coastal seas*. RIVM Rapport. Rijksinstituut voor Volksgezondheid en Milieu, the Netherlands. Retrieves Acces Data Acces 1995

Kroeze, C. and Seitzinger, S. P., 1998. *Nitrogen inputs to rivers, estuaries and continental shelves and related nitrous oxide emissions in 1990 and 2050: a global model*. Nutrient Cycling in Agroecosystems Vol. 52(2), p. 195-212.

Krug, E. C. and Winstanley, D., 2002. *The need for comprehensive and consistent treatment of the nitrogen cycle in nitrogen cycling and mass balance studies: I. Terrestrial nitrogen cycle*. The Science of the Total Environment Vol. 293(1-3), p. 1-29.
Krysanova, V., Müller-Wohlfeil, D. I. and Becker, A., 1998. *Development and test of a spatially distributed hydrological/water quality model for mesoscale watersheds*. Ecological Modelling Vol. 106(2-3), p. 261-289.
Kunkel, R., Bach, M., Behrendt, H. and Wendland, F., 2004. *Groundwater-borne nitrate intakes into surface waters in Germany*. Water science & technology Vol. 49(3), p. 11-19.
Langmuir, D., Hall, P. and Drever, J. I., 1997. *Environmental Geochemistry*. Prentice Hall, New Jersey.
Laursen, A. E. and Seitzinger, S. P., 2002. *Measurement of denitrification in rivers: an integrated, whole reach approach*. Hydrobiologia Vol. 485(1), p. 67-81.
Legg, J. O. and Meisinger, J. J., 1982. Soil nitrogen budgets. Book *Soil nitrogen budgets*. Stevenson, F. J. Madison Wisconsin, USA, American Society of Agronomy, 503 - 566.
Lehner, B. and Döll, P., 2004. *Development and validation of a global database of lakes, reservoirs and wetlands*. Journal of Hydrology Vol. 296(1-4), p. 1-22.
Lelieveld, J. and Dentener, F. J., 2000. *What controls tropospheric ozone?* Journal of geophysical Research Vol. 105(D3), p. 3531-3551.
Lepistö, A., Granlund, K., Kortelainen, P. and Räike, A., 2006. *Nitrogen in river basins: Sources, retention in the surface waters and peatlands, and fluxes to estuaries in Finland*. The Science of the Total Environment Vol. 365(1-3), p. 238-259.
Lepistö, A., Kenttämies, K. and Rekolainen, S., 2001. *Modeling combined effects of forestry, agriculture and deposition on nitrogen export in a northern river basin in Finland*. AMBIO: A Journal of the Human Environment Vol. 30(6), p. 338-348.
Lischeid, G. and Langusch, J., 2004. *Comparative simulation of the nitrogen dynamics using the INCA model and a neural network analysis: implications for improved nitrogen modelling*. Hydrology and Earth System Sciences Vol. 8(4), p. 742-750.
Loos, S., Middelkoop, H., van der Perk, M. and van Beek, R., 2009. *Large scale nutrient modelling using globally available datasets: A test for the Rhine basin*. Journal of Hydrology Vol. 369(3-4), p. 403-415.
MEA, 2005. *Ecosystems and Human Well-Being: Current State and Trends*. Washington D.C. Island Press.
Meybeck, M., 1982. *Carbon, nitrogen, and phosphorus transport by world rivers*. American Journal of Science Vol. 282(40), p. 401-450
Mourad, D. S. J., 2008. *Patterns of nutrient transfer in lowland catchments. A case study from northeastern Europe.*
Mulligan, D., Bouraoui, F., Grizzetti, B., Aloe, A. and Dusart, J., 2006. *An Atlas of pan-European data for investigating the fate of agrochemicals in terrestrial ecosystems* Technical series EUR 22334. Directorate General Joint Research Centre. Institute for Environment and Sustainablility. .Ispra, Italy. Retrieves Acces Data Acces 2006
Nieder, R. and Benbi, D. K., 2008. *Carbon and nitrogen in the terrestrial environment*. Springer Verlag.
Nixon, S., 2004. *(WEU2) Nutrients in rivers - (WEU5) BOD and ammonium in rivers.* Indicator fact sheet. 2009 from http://themes.eea.europa.eu/Specific_media/water/indicators/WEU02%2C2004.05. European Envrionemental Agency, Copenhagen, Denmark.
Nixon, S., Trent, Z., Marcuello, C. and Lallana, C., 2003. *Europe's water: an indicator-based assessment. Topic report 1/2003*. European Environment Agency. 97.Copenhagen. Retrieves Acces Data Acces 2003
Oenema, O., Witzke, H. P., Klimont, Z., Lesschen, J. P. and Velthof, G. L., 2009. *Integrated assessment of promising measures to decrease nitrogen losses from agriculture in EU-27*. Agriculture, Ecosystems and Environment Vol. 133(3-4), p. 280-288.
OSPAR, 2003. *Inputs of Nutrients into the Convention area - Implementation of PARCOM Recommendations 88/2 and 89/4*. Eutrophication and Nutrients Series. Retrieves Acces Data Acces 2003
Raat, K. J., Vrugt, J. A., Bouten, W. and Tietema, A., 2004. *Towards reduced uncertainty in catchment nitrogen modelling: quantifying the effect of field observation uncertainty on model calibration*. Hydrology and Earth System Sciences Vol. 8(4), p. 751-763.
Salminen, R. and De Vos, W., 2007. *Geochemical atlas of Europe*. Geological Survey of Finland.
Saraiva, S., Pina, P., Martins, F., Santos, M., Braunschweig, F. and Neves, R., 2007. *Modelling the influence of nutrient loads on Portuguese estuaries*. Hydrobiologia Vol. 587(1), p. 5-18.
Saunders, D. L. and Kalff, J., 2001. *Nitrogen retention in wetlands, lakes and rivers*. Hydrobiologia Vol. 443(1), p. 205-212.
SCENES, 2008. *Descriptions of the Regions and the Pilot Areas.* GOCE 036822. from http://www.environment.fi/download.asp?contentid=96243&lan=en. Finnish Environment Institute, Helsinki.
Schoumans, O. F. and Silgram, M., 2003. *Review and literature evaluation of quantification tools for the assessment of nutrient losses at catchment scale*. EUROHARP report Vol. p. 1-2003.
Seitzinger, S., 2008. *Nitrogen cycle: Out of reach*. Nature Reports Climate Change Vol. p. 162-163.
Sigleo, A. C. and Frick, W. E., 2007. *Seasonal variations in river discharge and nutrient export to a Northeastern Pacific estuary*. Estuarine, Coastal and Shelf Science Vol. 73(3-4), p. 368-378.
Silgram, M., Anthony, S. G., Fawcett, L. and Stromqvist, J., 2008. *Evaluating catchment-scale models for diffuse pollution policy support: some results from the EUROHARP project*. Environmental Science and Policy Vol. 11(2), p. 153-162.
Smil, V., 1999. *Nitrogen in crop production: An account of global flows*. Global Biogeochemical Cycles Vol. 13(2), p. 647–662.
Srivastava, P., McNair, J. N. and Johnson, T. E., 2006. *Comparison of process-based and artificial neural network approaches for streamflow modeling in an agricultural watershed*. Journal of the American Water Resources Association Vol. 42(3), p. 545-563.
Stevenson, F. J., 1986. *Cycles of soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients*. New York. John Wiley.

STOWA, 2008. *Uitspoeling van meststoffen uit grasland*. Talsma, M. Rijkswaterstaat. 49.Utrecht. Retrieves Acces Data Acces 2008

Sundberg, C., Svensson, G. and Söderberg, H., 2004. *Re-framing the assessment of sustainable stormwater systems*. Clean Technologies and Environmental Policy Vol. 6(2), p. 120-127.

Thieu, V., Billen, G. and Garnier, J., 2009. *Nutrient transfer in three contrasting NW European watersheds: The Seine, Somme, and Scheldt Rivers. A comparative application of the Seneque/Riverstrahler model.* Water Research Vol. 43(6), p. 1740-1754.

USGS, 2007. *Global land cover characterization* U.S. Geological Survey. Retrieves Acces Data Acces 2007 from http://edc2.usgs.gov/glcc/glcc.php

Van Breemen, N., Boyer, E. W., Goodale, C. L., Jaworski, N. A., Paustian, K., Seitzinger, S. P., Lajtha, K., Mayer, B., Van Dam, D. and Howarth, R. W., 2002. *Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA*. Biogeochemistry Vol. 57(1), p. 267-293.

Van der Perk, M., 2006. *Soil and water contamination: from molecular to catchment scale*. Leiden, The Netherlands. Taylor & Francis.

Van Deursen, W. P. A. and Wesseling, C. G., 1995. *PCRaster Software. Department of Physical Geography, University of Utrecht*. Retrieves Acces Data Acces 1995

Van Drecht, G., Bouwman, A. F., Knoop, J. M., Beusen, A. H. W. and Meinardi, C. R., 2003. *Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water*. Global Biogeochemical Cycles Vol. 17(4), p. 1115.

Van Drecht, G., Bouwman, A. F., Knoop, J. M., Meinardi, C. and Beusen, A., 2001. *Global pollution of surface waters from point and nonpoint sources of nitrogen*. The Scientific World Vol. 1(S2), p. 632-641.

Van Egmond, K., Bresser, T. and Bouwman, L., 2002. *The European nitrogen case*. AMBIO: A Journal of the Human Environment Vol. 31(2), p. 72-78.

Van Gerven, L. P. A., Smit, A. A. M. F. R., Groenendijk, P., Van der Bolt, F. J. E. and De Klein, J. J. M., 2009. *Retentieschatting van N en P in het oppervlaktewater op verschillende schaalniveau's* Alterra-rapport. Alterra. 78.Wageningen. Retrieves Acces Data Acces 2009

Van Kessel, C., Clough, T. and Van Groenigen, J. W., 2009. *Dissolved organic nitrogen: an overlooked Pathway of nitrogen loss from agricultural systems?* Journal of Environmental Quality Vol. 38p. 393 - 401.

Velthof, G. L., Oudendag, D., Witzke, H. P., Asman, W. A. H., Klimont, Z. and Oenema, O., 2009. *Integrated Assessment of Nitrogen Losses from Agriculture in EU-27 using MITERRA-EUROPE*. Journal of Environmental Quality Vol. 38(2), p. 402.

Vörösmarty, C. J., Sharma, K., Fekete, B., Copeland, A. H., Holden, J., Marble, J. and Lough, J. A., 1997. *The storage and aging of continental runoff in large reservoir systems of the world*. Ambio Vol. 26p. 210-219.

Wade, A. J., Neal, C., Butterfield, D. and Futter, M. N., 2004. *Assessing nitrogen dynamics in European ecosystems, integrating measurement and modelling: conclusions*. Hydrol. Earth Syst. Sci Vol. 8p. 846-857.

Wahlin, K. and Grimvall, A., 2008. *Uncertainty in water quality data and its implications for trend detection: lessons from Swedish environmental data*. Environmental Science and Policy Vol. 11(2), p. 115-124.

WATERBASE, 2009.

Waterbase-rivers: quality. 2009.

Whitehead, P. G., Wilson, E. J., Butterfield, D. and Seed, K., 1998. *A semi-distributed integrated flow and nitrogen model for multiple source assessment in catchments (INCA): Part II—application to large river basins in south Wales and eastern England*. Science of the Total Environment, The Vol. 210p. 559-583.

Willett, V. B., Reynolds, B. A., Stevens, P. A., Ormerod, S. J. and Jones, D. L., 2004. *Dissolved organic nitrogen regulation in freshwaters*. Journal of Environmental Quality Vol. 33(1), p. 201.

Wolfe, A. H. and Patz, J. A., 2002. *Reactive nitrogen and human health: acute and long-term implications*. AMBIO: A Journal of the Human Environment Vol. 31(2), p. 120-125.

Zumft, W. G. and Cardenas, J., 1979. *The inorganic biochemistry of nitrogen bioenergetic processes*. Naturwissenschaften Vol. 66(2), p. 81-88.

APPENDICES

Appendix 1 - Global Nitrogen stock

RESERVOIRS			10^{16} kg	% OF TOTAL
Biosphere	**Total Biosphere**		**0.028**	**0.0002**
	plants [1		0.0015	0.000009
	animals [1		0,00002	< 0.000001
	humans [1		0,0000009	<< 0.000001
	microbial biomass		0.0006	0.000004
Hydrosphere	**Total Hydrosphere**		**2.3**	**0.014**
Atmosphere	**Total Atmosphere**		**390**	**2.3**
	N2		390	2.3
	N2O		0.00014	< 0.000001
Geosphere	**Total Geosphere**		**16400**	**96.5**
	Soils and Sediments	soils and sed. total	35 - 400	0.2 -2.4
		soil organic matter[2	0.015	0.00009
		coal	0.007	0.00004
	Crust		130 -1400	0.78-8.4
	Mantle and Core		16000	94.1
Reservoirs Total			**17000**	**100**

Modified from: (Stevenson, 1986; Krug and Winstanley, 2002; ISWS, 2009)

(1 source: (Jenkinson, 2001)

Appendix 2 – Literature overview on estimations of catchment scale retention fractions: soil-groundwater, instream and overall catchment retention.

River basin	Average instream retention %	Aquifer retention %	Overall catchment N retention %	comments	source
Po	26				Palmeri et al., 2005
Vantaanjoki					Grizetti et al.,2003
Seine, Somme, Scheldt		20 – 50		Most retention took place in riparian zone	Thieu et al., 2009
Basins in northeastern Germany	18				Behrendt et al, 1999
Basins in Finland	22			Range of in-stream retention: 0 – 68 %	Lepistö et al., 2006
Rhine river basin	21				De Wit, 1999
Elbe river basin	42				De Wit, 1999
Ahja River	10			In June July, Nret-instream is 70%, May –Septermber no N retention	Mourad, 2008
Global	50				Galloway et al 2004
Global	18			''loss' of N dependent on residence time and temperature	Green et al. 2004
Global	30		9		Bouwman et al, 2003
Various basins Europe	9 -27				Grizzetti and Bouraoui, 2006
16 basins in USA			40 -60		Seiztinger et al., 2002
Global	11	34			Van Breemen et al., 2002

Appendix 3 – Specifications of geographical projection of gridded data in the TN concentration model

GCS WGS 1984	
Angular Unit:	Degree (0.0174532925199433299)
Prime Meridian:	Greenwich (0.000000000000000000)
Datum:	D_WGS_1984
Spheroid:	WGS_1984
Semimajor Axis:	6378137.000000000000000000
Semiminor Axis:	6356752.314245179300000000
Inverse Flattening:	298.257223563000030000
Columns and Rows:	1000, 641
Cell size X, Y:	0.083333, 0.083333

Appendix 4. – Detailed description of the TN concentration model for European river basins.

- **Atmospheric deposition: direct**

The direct component of atmospheric deposition is the deposition of N on surface waters, while N deposition on urban, agricultural and natural areas are considered as indirect N emissions (fig (A-1.2).

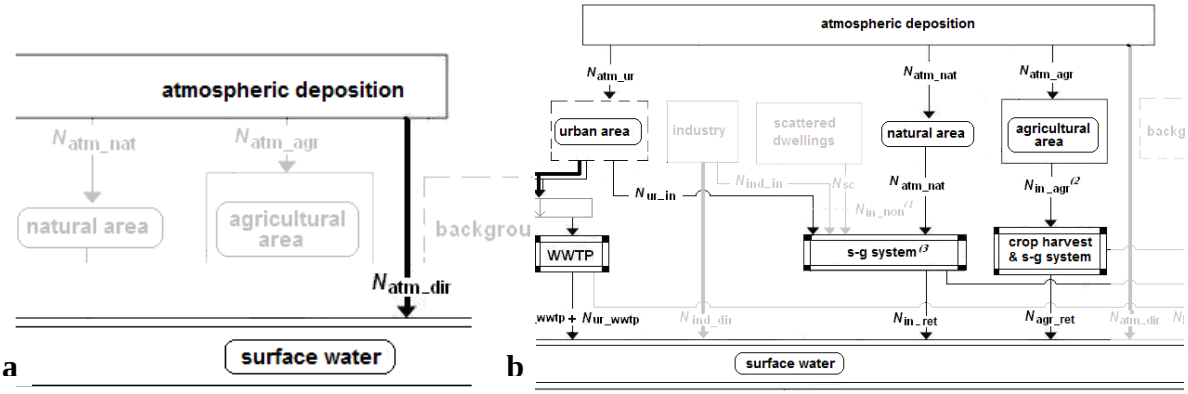


Fig. A-1 Schematic representation of direct (a.) and indirect (b) atmospheric N emissions to surface waters

Quantification of direct N deposition on surface waters is done according to the following principle:

$N_{atm\_dir} = (L_{atm} * A_{sw})$

Where N_{atm_dir} is N input from atmospheric deposition onto surface waters (kg), L_{atm} is the atmospheric N deposition per unit area (kg km^{-2}), and A_{sw} is the water surface (km^2),

Indirect atmospheric N deposition on urban areas follows the pathways as described under 'urban runoff' explained in below. Before atmospheric deposition on natural areas enters surface waters in the model, it is reduced with the retention factor for indirect emissions onto non-agricultural areas (f_{sg}), while atmospheric deposition on agricultural areas is reduced with the retention factors for indirect emissions onto agricultural areas (f_{agr}) as described is section 3.6.2 of this report.

- **Urban runoff**

The amount of N that can potentially runoff from urban areas is quantified by calculating the atmospheric deposition on and the amount of N litter in urban areas which is assumed to be 4 kg ha^{-1} yr^{-1} (Behrendt et al., 2002). The atmospheric deposition data is derived from the atmospheric N deposition map for the year 2000 available from the *EMEP-website*. The data on location and size of urban areas in catchments is derived from a map of built-up areas which was available within the SCENES project, from the CESR.
It is assumed that 50% of N in urban runoff enters the soil - groundwater system, 50 % goes into the sewage of which half is treated and half flows into surface waters untreated as depicted bellow.

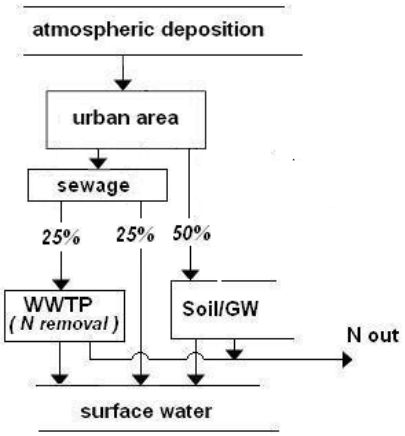


Fig. A-2 Pathways of emissions from urban runoff to surface waters

The overall N removal efficiency of N from surface waters can be calculated as follows:

$$R_{tot\_X} = R_1 * f_1 + R_2 \cdot f_2 + R_3 * f_3$$

With:

- R_{tot_X} : overall N removal efficiency per country (X)
- R_1, R_2, R_3 : N removal efficiency per treatment type *(primary =1, secondary=2, tertiary =3)*
- f_1, f_2, f_3 : fraction of the waste water entering sewage systems that is treated per treatment type *(primary =1, secondary=2, tertiary =3)* per country

The distribution of the N load from urban runoff is calculated as follows:

50% of N in urban runoff enters the soil – groundwater system:

$$N_{ur} * 0.5 = N_{ur\_in}$$

25% flows directly into surface waters:

$$N_{ur} * 0.25 = N_{ur\_dir}$$

25% is treated in a WWTP plant:

$$N_{ur} * 0.25 * (1- R_{tot\_X}) = N_{ur\_wwtp}$$

With:

- N_{ur}: total N emission from urban runoff
- N_{ur_in} : indirect N emission from urban runoff
- N_{ur_dir} : direct N emissions from urban runoff
- N_{ur_wwtp}: direct N emission from urban runoff after treatment in WWTP

- **Households**

In this section the quantification methods of N output from households connected to sewage systems is described. In this model concept the term 'household' will only refer to households connected to a sewage system, while scattered dwellings (3.6.4) is used to refer to unconnected households and is quantified separately under 'scattered dwellings'. N emissions from households is either treated in waste water treatment plant (WWTP's) or released to surface waters untreated. The fraction of the N emission that is treated, as well as the N removal efficiency during treatment differs per country.

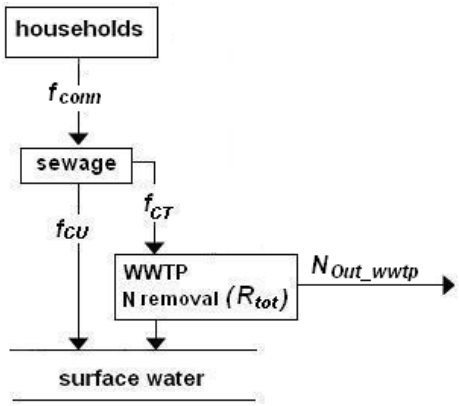


Fig. A-3 Pathways of household N emissions to surface waters

First the treated and untreated fraction of household N emission is calculated, then the *effective* N emission per capita for those connected to WWTP is determined. With this information and data on population numbers the overall household N emission can be calculated per catchment.

The fraction of household N emission that is treated or untreated is calculated as follows:

$$f_{CT(countryx)} = (P_C - P_{CU}) / 100$$
$$f_{CU(countryx)} = P_{CU} / 100$$

With:
- f_{CT_X} : fraction of household waste water that is *treated* per country (X)
- f_{CU_X} : fraction of household waste water that is *untreated* per country (X)
- P_C : percentage of households connected to a sewage system
- P_{CU} : percentage of households connected to sewage, of which waste water is not treated.

The effective N emission per capita for those connected (treated) to a WWTP in country x, is derived as follows:

$$N_{cap} * (1 – R_{tot\_X}) = N_{cap\_CT\_X}$$

With:
- $N_{cap\_CT\_X}$: effective N emission per capita for those connected (treated) to a WWTP per country (X)
- N_{cap}, : N output per capita (g N day^{-1} cap^{-1})
- R_{tot_X} : N removal per capita per country (X)

Quantification of total effective household N output of both sewage (untreated) and WWTP's (treated) per country lying within a certain catchment:

$$(PopNo \cdot (f_{CT} \cdot N_{cap\_CT} + f_{CU} * Ncap)) = N_{hh\_tot}$$

With:
N_{hh_tot} : total N emission to surface waters, from households connected to the sewage system (treated + untreated) (kg).
PopNo: Population number (-)
f_{CT} : fraction of people connected(treated) per country (≤ 1)
f_{CU} : fraction of people connected(untreated) per country (≤ 1)
N_{cap_CT} : effective N output per capita for households connected to WWTP, per country (kg yr^{-1}).

N emissions per river basins are calculated by adding up all household emissions for all grid cells lying in a river basin. River basins are are defined by a map that has unique ID numbers for all grid cells lying in a certain basin.

- **Scattered dwellings**

It is assumed that all waste water originating from scattered dwellings enters the soil/groundwater system.

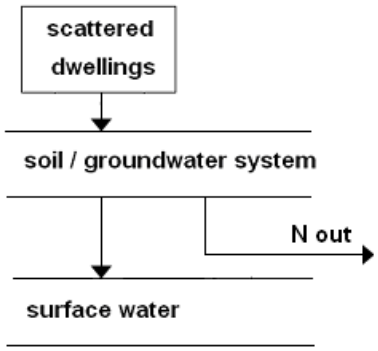


Fig. A-4 Pathway of N emissions from scattered dwellings to surface waters

Total N emissions from scattered dwelling (N_{sc}) is quantified as follows:

$$PopNo * N_{cap} * (1- P_c) = N_{sc}$$

Where N_{sc} is N emissions from scattered dwelling (kg), PopNo is the population number in a catchment, N_{cap} is the N emission per capita (kg yr^{-1}), and Pc is the fraction of the people connected to a sewage system.

- Industry

For estimation of induatrial emissions the EPER dataset was used. In this dataset all factories are spatially referenced by coordinates that can be allocated to corresponding grid cells. Two pathways from industrial facility to surface waters are distinguished: direct emissions or indirect emissions via the soil and groundwater system. These two pathways are highlighted in figure A-5. In this model it is assumed that emissions as registered in EPER are one-seventh of the 'true' emissions, and therefore EPER emission loads (kg) are multiplied with 7.

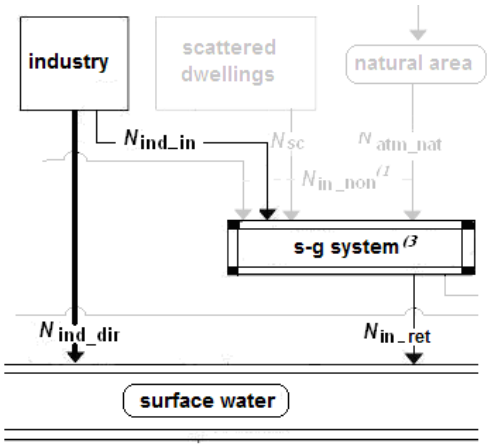


Fig. A-5 Direct input from industrial N emissions to surface waters

- Agriculture

Agricultural N emissions are estimated from maps on mineral fertilizer and manure application from Mulligans et al (JRC, 2009). If on the land cover map, a grid cell is classified as agriculutural land, then the N emission is calculated from the N application rate (manure + fertilizer) and the surface area the grid cell represents.

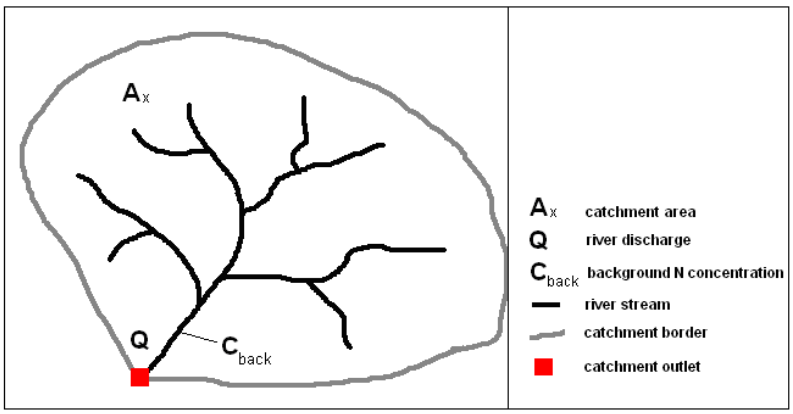
$^{1}N_{agr} = A_x * L_{agr}$

Where N_{agr} is the total N emission on a certain grid cell (kg), A_x is the surface area of a grid cell x (km^2), and L_{agr} is the N application rate from manure and fertilizer which has a separate value per river basin (kg km^2 yr^{-1}), To calculate agricultural emissions per river basin, a summation is done of all grid cell values per river basin for N_{agr}.

- Background N loss

Background loss of N is defined as N emissions resulting from biological N_2 fixation and rock weathering. These N emissions are estimated from a fixed N emission rate per surface area that is classified as agricultural or natural land. This emission rate is estimated from following three factors: N concentration in major unpolluted rivers, the annual discharge of a certain river, and the size of the upstream catchment area of that river. According to Meybeck 1993 (as in Loos et al. 2009) the global maximum of N concentration in unpolluted major river is 0.2 mg/l.

[1] $N_{agr} = N_{fert} + N_{man}$; as in fig 9. in the report

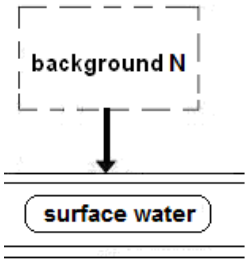


A -6. Schematic picture to demonstrate the qualification method for background emissions.

The following function was used to estimate background N emission rate per unit area:

L_{back} = ((Q * 1000 * 365 * 24 * 3600) * (C_{back} / 10^6))/ A_{rhine}

Where L_{back} as the N emission rate from natural land in kg N km^{-2} yr^{-1}, Q as the river discharge (m^3 s^{-1}), C_{back} as the estimated background TN concentration in European rivers mg l^{-1}, and A_{rhine} as the size of the Rhine river basin upstream of Lobith (km^2).



A-7. Pathway of background N emissions as represented in the model

Background N emissions are indirect N emissions in the 'real' world, but are treated as direct emissions in the model, as the background N emissions are estimated as N emissions per unit area ***to water***.

Grid cells classified as to be covered by natural or agricultural land, background N emissions are assumed to occur at a fixed rate per unit area is the same for the entire model area. The total N load from background N emissions can then be calculated as follows:

$N_{back} = A_x * L_{back}$

Where N_{back} is the background emissions that reaches surface waters from a certain grid cell (kg), A_x is the surface area represented by grid cell x (km2) that is classified as agricultural or natural area (except for natural areas covered by ice or snow, or classified as barren area), and L_{back} is the background N emission rate to water per surface area (kg km^{-2} yr^{-1})

Appendix 5 – Metadata of input, calibration and validation data used for the model

Table 6 - Overview of model input data

Data Type	Dataset	description	Year(s), which data refers to	comments	Region	unit	Spatial resolution	Source
base data	River basin boundaries	boundaries of river basins	2000	same as in WaterGap3	pan-Europe	-	Polygons	CESR
base data	Country borders of Europe	unique grid cell ID appointed to all grid cells located in a certain country	2000	same as in WaterGap3	pan-Europe	-	Polygons	CESR
base data	Map combined from CLC and GLCC maps	Dominating land cover type per grid cell, with distinction between on natural land cover classes and cropland.	2000	same as in WaterGap3	pan-Europe	classes	5 x 5 arcmin.	CESR
Base data	Built-up area	Percentage of built-up area per grid cell	2000	same as in WaterGap3	Pan-Europe	%	5 x 5 arcmin.	CESR
base data	Global Wetland Database	lakes, rivers, reservoir surface, % per grid cell	< 2004	available from the WWF website	pan-Europe	%	5 x 5 arcmin.	(Lehner and Döll, 2004)
drivers	Water availability	water quantity: model results from WaterGap for baseline scenario year 2000.	2000	output from WaterGap2[1]	major river basins	m^3/ month	5 x 5 arcmin	CESR
drivers	Population density	population density	2000	-	pan-Europe	no./ha	30 x 30 arcmin	CESR
drivers	Total N application on agricultural land	total N application per AA*	1997	estimated from Mulligan et al 2006	EU -27	kg N ha^{-1} yr^{-1} per AA	Estimated per catchment	JRC
drivers	Industrial emissions	dataset with quantity and location of industrial N emissions	2000 - 2004	Only includes industry with N emissions larger than 50 metric tons a year.	EU-15	metric tons per yr	point data; locations specified with coordinates	EPER-website (EPER_dataset_15-08-2008)
drivers	Atmospheric deposition	Atmospheric deposition of reduced and oxidized N per grid cell	2000	modeled data	EU-25	kg km^{-2} yr^{-1}	50 x 50 km grid	EMEP-website
drivers	Waste water treatment efficiency and connectivity to WWTP's	efficiencies for primary, secondary and tertiary treatment, per country	1995 - 2007	for some countries based on estimation	EU - 25	%	per country	WHO, UNICEF, EUROSTAT, OECD, national statistics
parameters	Retention factors	Terrestrial and instream retention factors	-	No fixed number, but ranges derived from literature	-	%	catchment scale	Various authors (see 3.6.4)
calibration data	N concentration	average annual TN concentrations measured near catchments outlets	1995 - 2007	measured data	Europe	mg TN L^{-1}	point data; locations specified with coordinates	(WATERBASE, 2009)
validation data	N concentration	average annual TN concentrations measured near catchments outlets	1995 - 2005	measured data	Europe	mg TN L^{-1}	point data; locations specified with coordinates	(WATERBASE, 2009)literature; various authors [2]

**AA = agricultural area*

[1] *It is expected that the output from WaterGap 3, with a spatial resolution of 5 x 5 arcmin and water availability adjusted for water consumption will be used in future versions of the model*

[2] *Po: Salvetti. et al 2006 – Göta: Helcom 1998 – Scheldt: http://www.scheldeschorren.be/natuurtalent/p9.html*

Appendix 6 - National statistics on connectivity to sewage, WWTP's, and treatment type (primary, secondary or tertiary). This data was used for quantification of N emissions from households. Source: SCENES (unpublished)

	CESR POP 2000				Connectivity (%)								
COUNTRY	Tot_Rur	Tot_Urb	Rur/Tot	Urb/Tot	Prim.	Second.	Tert.	Untreated	Connectivity	Source	Year	Rural (%)	Urban (%)
Albania	1803800	1306201	58	42	0.0	0.0	0.0	61.0	61.0	WHO/UNICEF/UNECE	2000/2002	38	93
Algeria	12551058	17266809	42	58	0.0	10.0	0.0	58.0	68.0	WHO/UNICEF/MRE	2000	45	84
Austria	2770196	5329799	34	66	0.0	17.0	64.0	4.0	85.0	EUROSTAT	1998	56	100
Belarus	3029079	7000939	30	70	0.0	46.0	0.0	21.0	67.0	WHO/UNICEF/EEA	2000/2003	22	86
Belgium	297247	9952751	3	97	0.0	22.0	16.0	44.0	82.0	EUROSTAT	1998	0	84
Bosnia and Herzegovina	2268600	1711401	57	43	0.0	5.0	0.0	51.0	56.0	WHO/UNICEF/UNECE	2000/2004	38	80
Bulgaria	2527205	5572797	31	69	1.0	36.0	0.0	30.0	67.0	EUROSTAT	2000	0	97
Croatia	1882352	2567650	42	58	17.0	4.0	0.0	52.0	73.0	WHO/UNICEF/UNECE	2000/1999	50	90
Cyprus	243359	536641	31	69	0.0	9.0	26.0	7.0	42.0	WHO/UNICEF/MEDAWARE	2000	13	55
Czech Republic	2659932	7610072	26	74	0.0	62.0	9.0	8.0	79.0	EUROSTAT	1999	19	100
Denmark	792683	4527318	15	85	2.0	3.0	84.0	0.0	89.0	EUROSTAT	1998	26	100
Egypt	39244064	28534943	58	42	2.0	9.0	0.0	20.0	31.0	WHO/UNICEF/WHO EMRO	2000/2005	10	60
Eritrea	34692	0	100	0	0.0	0.0	0.0	0.0	0.0			0	0
Estonia	419222	950779	31	69	1.0	28.0	40.0	1.0	70.0	EUROSTAT	2000	2	100
Ethiopia	4591035	5015	100	0	0.0	0.0	0.0	0.0	0.0	WHO/UNICEF/ WHO AFRO	2000	0	2
Faroe Islands	0	0	0	0	0.0	0.0	0.0	0.0	0.0			0	0
Finland	2015023	3164979	39	61	0.0	0.0	80.0	0.0	80.0	EUROSTAT	2000	49	100
France	14409871	44890098	24	76	2.0	51.0	27.0	2.0	82.0	EUROSTAT	2001	26	100
Georgia	1003442	1065735	48	52	1.0	0.0	0.0	40.0	41.0	WHO/UNICEF/UNECE	2000/2003	7	73
Germany	10284985	71994991	12	88	0.0	5.0	88.0	2.0	95.0	EUROSTAT	2001	60	100
Greece	4349096	6550897	40	60	32.0	14.0	10.0	11.0	67.0	EUROSTAT	1997	17	100
Hungary	3603586	6406398	36	64	16.0	24.0	6.0	5.0	51.0	EUROSTAT	2000	0	80
Iceland	21275	258720	8	92	33.0	0.0	0.0	57.0	90.0	EUROSTAT	2000	0	97
Iraq	3386867	2862181	54	46	2.0	5.0	0.0	50.0	57.0	WHO EMRO	2005	21	100
Ireland	1562382	2257619	41	59	40.0	21.0	5.0	27.0	93.0	EUROSTAT	1999	83	100
Israel	513400	5526601	8	92	22.0	33.0	28.0	13.0	96.0	Israel Ministry of Environment	unknown	53	100
Italy	18873111	38666861	33	67	3.0	36.0	24.0	0.0	63.0	EUROSTAT	1995	0	94
Jordan	1073519	3966482	21	79	0.0	20.0	0.0	39.0	59.0	WHO/UNICEF/WHO EMRO	2000/2005	6	73
Latvia	786838	1583162	33	67	2.0	26.0	36.0	3.0	67.0	EUROSTAT	2004	1	100
Lebanon	466320	3013681	13	87	3.0	0.0	0.0	87.0	90.0	WHO/UNICEF/WHO EMRO	2000/2005	22	100
Libyan Arab Jamahiriya	532337	4388883	11	89	0.0	8.0	0.0	46.0	54.0	WHO/UNICEF	2000	55	54
Lithuania	1154995	2345003	33	67	33.0	6.0	18.0	11.0	68.0	EUROSTAT	2002	3	100
Luxembourg	39600	400400	9	91	19.0	57.0	11.0	0.0	87.0	EUROSTAT	1995	0	96
Macedonia, former yugoslav republic	820120	1199881	41	59	5.0	5.0	0.0	90.0	100.0	EUROSTAT	2000	100	100
Malta	35491	354510	9	91	0.0	0.0	13.0	87.0	100.0	EUROSTAT	2000	100	100
Moldova, republic of	2319759	1960241	54	46	0.0	18.0	0.0	38.0	56.0	OECD/UNECE	1998/2005	19	100
Morocco	12953962	16156027	45	55	0.0	5.0	0.0	36.0	41.0	WHO/UNICEF/WHO EMRO	2000/2005	4	70
Netherlands	5676299	10223701	36	64	0.0	17.0	82.0	0.0	99.0	EUROSTAT	2000	97	100
Norway	1081748	3388262	24	76	22.0	1.0	50.0	7.0	80.0	EUROSTAT	2000	17	100
Poland	14810598	23859381	38	62	3.0	29.0	23.0	7.0	62.0	EUROSTAT	2001	1	100
Portugal	4709401	5310600	47	53	14.0	26.0	2.0	23.0	65.0	EUROSTAT	1998	26	100
Romania	10205932	12274071	45	55	27.0	17.0	0.0	13.0	57.0	EUROSTAT	2004	5	100
Russian Federation	11226991	51575015	18	82	2.0	54.0	1.0	18.0	75.0	WHO/UNICEF/EEA	2000/2003	30	85
Saudi Arabia	553289	1070942	34	66	0.0	19.0	9.0	0.0	28.0	WHO/UNICEF/WHO EMRO	2000/2005	0	43
Slovakia	2328481	3061520	43	57	9.0	61.0	0.0	0.0	70.0	WHO/UNICEF/Slovakia	2000	55	82
Slovenia	979078	1010920	49	51	9.0	5.0	5.0	23.0	42.0	EUROSTAT	2000	0	83
Spain	9657736	31092243	24	76	8.0	65.0	15.0	12.0	100.0	EUROSTAT	2000	100	100
Sudan	3119639	1822495	63	37	0.0	0.7	0.0	0.0	0.7	WHO/UNICEF/WHO EMRO	2000/2005	0	2
Sweden	1479628	7380380	17	83	0.0	5.0	81.0	0.0	86.0	EUROSTAT	2000	16	100
Switzerland	2323078	4846919	32	68	0.0	22.0	74.0	0.0	96.0	EUROSTAT	1999	88	100
Syrian Arab Republic	8263433	8296565	50	50	0.0	16.0	0.0	53.0	69.0	WHO/UNICEF/WHO EMRO	2000/2005	41	96
Tunisia	3541441	5978561	37	63	0.0	47.0	0.0	2.0	49.0	WHO/UNICEF/WHO EMRO	2000/2005	10	72
Turkey	21721349	42289632	34	66	10.0	13.0	3.0	32.0	58.0	WHO/UNICEF/MEDAWARE	2000	10	82
Ukraine	16348023	33342016	33	67	2.0	50.0	0.0	5.0	57.0	WHO/UNICEF/Derzhbud	2000/2002	21	74
United Kingdom	6530139	52299876	11	89	9.0	64.0	14.0	11.0	98.0	EUROSTAT	2000	82	100
Western Sahara	645	0	100	0	0.0	1.0	0.0	3.0	4.0	id morocco		4	0
Yougoslavia/Serbia and Motenegro	5111041	5448959	48	52	4.0	11.0	0.0	34.0	49.0	WHO/UNICEF/UNECE	2000/2007	16	80