

3. Biogeochemistry of nutrients and nutrient emission modelling

3.1 Biogeochemistry of nutrients

Nutrients are elements essential for an organism's growth, survival and reproduction. Nutrients include two groups: macro-nutrients (they are required in large quantities for cell development: C, H, N, O, P, S, Ca and Si) and micro – or trace nutrients (Mn, Cu, Zn, Fe and others). Nitrogen and phosphorus are two of the most important nutrients essential for the growth of aquatic and terrestrial plants. Their loadings into surface waters have increased significantly over the last 150 years (CHAPRA, 1997). Nitrogen and phosphorous compound concentrations depend on surrounding land use, season, and geological settings. They are highly dynamic because they may be utilized, stored, transformed and excreted rapidly and repeatedly by the various aquatic organisms (WETZEN and LINKENS, 2000).

3.1.1 Biogeochemistry of nitrogen

3.1.1.1 The nitrogen cycle

Nitrogen is an essential plant nutrient; it is an essential component of all amino acids and therefore proteins (CAMPBELL, 1990). In aquatic system, nitrogen occurs in organic and inorganic forms. Organic nitrogen (living form) includes N in phytoplankton and bacteria, dissolved organic N. Inorganic form (non-living form) includes nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and nitrogen gas (N_2). Nitrate (NO_3^-) and ammonium (NH_4^+) are the most popular inorganic form of nitrogen in aquatic environment. Gaseous forms of nitrogen include: nitrogen gas (N_2), nitrous oxide (N_2O), nitrogen oxides (NO_x) and ammonia (NH_3). Nitrogen serves as one of the major limiting factors that controlled the dynamics, biodiversity, and functioning of many ecosystems.

The total amount of nitrogen in atmosphere, soils and waters of the Earth is approximately 4×10^{15} tons – more than the total mass of C, P, O and S. 93.75% of nitrogen is buried in lithosphere, and 6.3% is in atmosphere (GALLOWAY et al., 2003). The Earth's atmosphere is 78% of nitrogen gas, but most plants and animals cannot use nitrogen gas directly from the air like carbon dioxide and oxygen. Instead, they have to wait for nitrogen to be “fixed” or called nitrogen fixation - the process converts gaseous nitrogen into the most biologically available forms: ammonium and nitrate (Figure 3.1). Nitrogen fixation includes natural (by biological nitrogen fixation with Cyanobacteria and lightning) and anthropogenic/industrial fixation (i.e., fertilizer and food production, energy production). In the absence of human activities, biotic fixation is the primary source of reactive nitrogen (SANHUEZA, 1982; GALLOWAY et al., 1995, 2003, 2004; VITOUSEK et al., 1997). Symbiotic nitrogen-fixing bacteria such as the Rhizobia, for instance, live and work in nodules on the roots of peas, beans, alfalfa and other legumes. These bacteria manufacture an enzyme that enables them to convert gaseous nitrogen directly into plant usable forms. Lightning may also indirectly transform atmospheric nitrogen into nitrates, which deposit onto soil in rain water (VITOUSEK et al., 1997). The amount of gaseous nitrogen being fixed at any given time by

In aquatic environment, two of the most important nitrogen transformation processes occupy: nitrification and denitrification. Nitrification is the oxidation of ammonia to nitrate, via nitrite, occupies when oxygen is present. Nitrifying bacteria are the organisms capable of converting the most reduced form of nitrogen (ammonia), to the most oxidised form (nitrate) in two steps. In the first step, bacteria of the genus *Nitrosomonas* and *Nitrosococcus* convert ammonium ion (NH_4^+) to nitrite,



In the second step is mainly done by bacteria of the genus *Nitrobacte* convert nitrite to nitrate,



The conversion from nitrite to nitrate is faster than the conversion of ammonium to nitrite. The occurrence of nitrification depends on additional factors besides the presence of ammonium: the presence of adequate numbers of nitrifying bacteria, alkaline pH level (optimally at about 8) and sufficient oxygen. As with the decomposition of carbonaceous matter, nitrification will cause a decrease of dissolved oxygen concentration in water (CHAPRA, 1997).

Denitrification is the process of reducing nitrate and nitrite, into gaseous nitrogen under anaerobic conditions. The process is performed by heterotrophic bacteria. Nitrate can serve as an electron acceptor for bacteria, nitrite is formed as an intermediate, with the principal end product being free nitrogen. This free nitrogen becomes a source of atmospheric nitrogen. Denitrification represent a purging mechanism that does not occur for phosphorus (CHAPRA, 1997; MCCLAIN et al., 2001; TKALICH and SUNDARAMBAL, 2003). Therefore, the nitrogen cycle is driven by microorganisms and plants (SMIL, 2000),

3.1.1.2 Human impact on the nitrogen cycle

Due to increasing demand on food and energy, the global nitrogen cycle has been greatly altered by human activities (VITOUSEK et al., 1997; DALTON and BRAND-HARDY, 2003). Through processes such as manufacturing fertilizers, burning fossil fuels, and cultivating crops (soybeans, peas, and other crops that host symbiotic nitrogen-fixing bacteria), humans have already changed the nitrogen cycle over the last once and a half century, accelerating the rate of N fixation in landscapes and delivery of N to water bodies (VITOUSEK et al., 1997; ASNER et al., 2001; BOYER et al, 2002; BREEMEN et al., 2002; HOLLAND et al., 2005). Furthermore, human activities are also speeding up the release of nitrogen from long-term storage in soils and organic matter. More than 50% of annual global reactive N emission is related to human activities (VITOUSEK et al., 1997).

Human activities, such as agricultural fertilization and discharges of waste water, have resulted in increased nutrient levels in surface water bodies, groundwater and coastal seas all over Europe (STANNERS and BOURDEAU, 1995). Amounts of total dissolved nitrogen in rivers are also

correlated with human population density. With increasing human disturbance, a higher proportion of the nitrogen in surface waters is composed of nitrate (VITOUSEK, 1997). Nitrogen easily leaks from agricultural and urban landscapes as the very mobile inorganic nitrate ion (TURNER et al., 2003). Nitrogen concentrations in surface waters have increased as human activities have accelerated the rate of fixed nitrogen being put into circulation. Nutrient pollution has several undesirable effects related to the increased growth of phytoplankton and other aquatic plants (eutrophication). Eutrophication has effected serious changes within aquatic communities and can result to the collapse of entire aquatic ecosystems (OECD, 1982; CONLEY, 1999; de WIT, 2001).

In general, nitrogen fluxes were improved by human activities in two directions: in the form of by-product or waste product in the case of fuel combustion and the main product in the case of fertilizer production, food production (legume and rice cultivations) (GALLOWAY, 1995, 1996). Nitrogen fluxes into environment are also affected by geographical locations. Human Nr (reactive nitrogen species) creation in many temperate regions is primarily controlled by a different factor – the use of fossil energy to produce energy and fertilizer. Therefore, the latitude dependency changes first driven by solar intensity and ecosystem type and second to driven by population density and industrial productivity (GALLOWAY et al., 2004). The increase in fixed nitrogen circulating around the globe and falling to the ground as wet or dry deposition is readily detectable, even in cores drilled from the glacial ice of Greenland (VITOUSEK, 1997)

Prior to 1860, natural biological nitrogen fixation was the dominant source of nitrogen for the terrestrial environment. Between 1860 and the early 1990ies, the amount of Nr created by natural terrestrial processes decreased by 15% (120 to 107×10^9 kg Nyr⁻¹) while Nr creation by anthropogenic processes increased by 10-fold (15 to 156×10^9 kg Nyr⁻¹). Obviously, the production of reactive nitrogen species by humans has been greater than production from all natural terrestrial systems during the last few decades (COWLING et al., 2001; BOYER et al., 2002; GALLOWAY et al., 2003, 2004). Since 1940, human activity has doubled the rate of nitrogen cycling through the global atmosphere, and the rate is accelerating. By 2050, 90% of river dissolved inorganic nitrogen export can be considered anthropogenic (KROEZE and SEITZINGER, 1998).

Table 3.1: Emissions of nitrogen compounds and related human activities

| | | |
|------------------------------|--|--------|
| Sources for NO _x | Traffic | ~ 60 % |
| | Fossil fuel – fired heat and power | ~ 30 % |
| | Industry | ~ 10 % |
| Sources for NH ₃ | Agriculture | ~ 80% |
| Sources for N ₂ O | Fossil fuel – fired heat and power | ~ 30 % |
| | Forest fires, landgain | ~ 60 % |
| | Industry (e.g. adipic acid production) | ~ 10 % |

(Source: ZEVENHOVEN and KILPINEN, 2004)

3.1.2 Biogeochemistry of phosphorus

3.1.2.1 *The phosphorous cycle*

Phosphorus is an essential nutrient for all life forms as a key element in many physiological and biochemical processes. In comparison to the relatively rich supply of other major nutritional and structural components of the biota (C, N, O, S), and according to Leibig's Law of minimum, phosphorus is often the most limiting nutrient to plant growth in fresh water (STEEN, 1998; COMPTON et al., 2000; ANDERSON and DOWNING, 2006). Most of the phosphorous of fresh waters is in the particulate phase of living biota, primarily algae and higher aquatic plants (WETZEN and LINKENS, 2000; SMOL, 2002). Total phosphorus measurement has long been used widely to quantify eutrophication (CHAPRA, 1997).

Phosphorus plays a number of indispensable biochemical roles, but it does not have a rapid global cycle like nitrogen or carbon. The most prevalent phosphate minerals are species of the apatite family. In igneous deposits there are three species of apatite: chlorapatite, hydroxylapatite and fluorapatite. In sedimentary rocks the species are francolite (marine and freshwater deposits) and hydroxyl-fluor-carbonate (cave deposits of bird and bat droppings). Today, some 80% of the world phosphate production has origin from sedimentary deposits (GLEISBERG, 1988; STEEN, 1998; SMIL, 2001; WORTMAN, 2005). In the natural water bodies, phosphorus is supplied through the weathering and dissolution of rocks and minerals (apatite family) with very low solubility. Phosphorus is available to plants in the form of orthophosphate (PO_4^{3-}), which is also the only inorganic form in which phosphorus occurs in appreciable amounts (STEEN, 1998; COMPTON et al., 2000). Phosphorus released from decomposing organic matter reenters the aquatic ecosystem as PO_4^{3-} . At neutral or acidic pH, PO_4^{3-} is generally bonded to one or two hydrogen (H) atoms in the forms of phosphoric acids, HPO_4^{2-} and H_2PO_4^- , this PO_4^{3-} source is immediately available for reutilization and the idealized cycle is complete (Figure 3.2).

When enters streams the bioavailable phosphorus may increase or decrease depending on whether phosphorus is adsorbed or desorbed by stream sediment. There is an adsorption-desorption interaction between dissolved inorganic phosphorus and dissolved particulate matter in the water column. Phosphate tends to sorb strongly to fine-grained particles. The adsorption reactions, along with co-precipitation reactions with Fe, Ca and Al, make PO_4^{3-} biologically unavailable to organisms. The settling of these particles, along with the sedimentation of organic particles containing phosphorus, serves to remove phosphorus from water column to the bottom sediment. Sediment with a high phosphorus concentration that enter a water body can contribute bioavailable phosphorus by desorption, which is most often associated with anoxic conditions and acting as an internal source of phosphorus (Figure 3.2). Sediment-phosphorus release rates is a function of pH, the higher pH increased is, the higher the rate of phosphorus release from sediments is. The nutrient flux and death of phytoplankton produce organic nitrogen and organic phosphorus in the water column (CHAPRA, 1997; FISHER and WOOD, 2001; MCCAIN, 2001; WHITE et al., 2004).

3. Biogeochemistry of nutrients and nutrient emission modelling

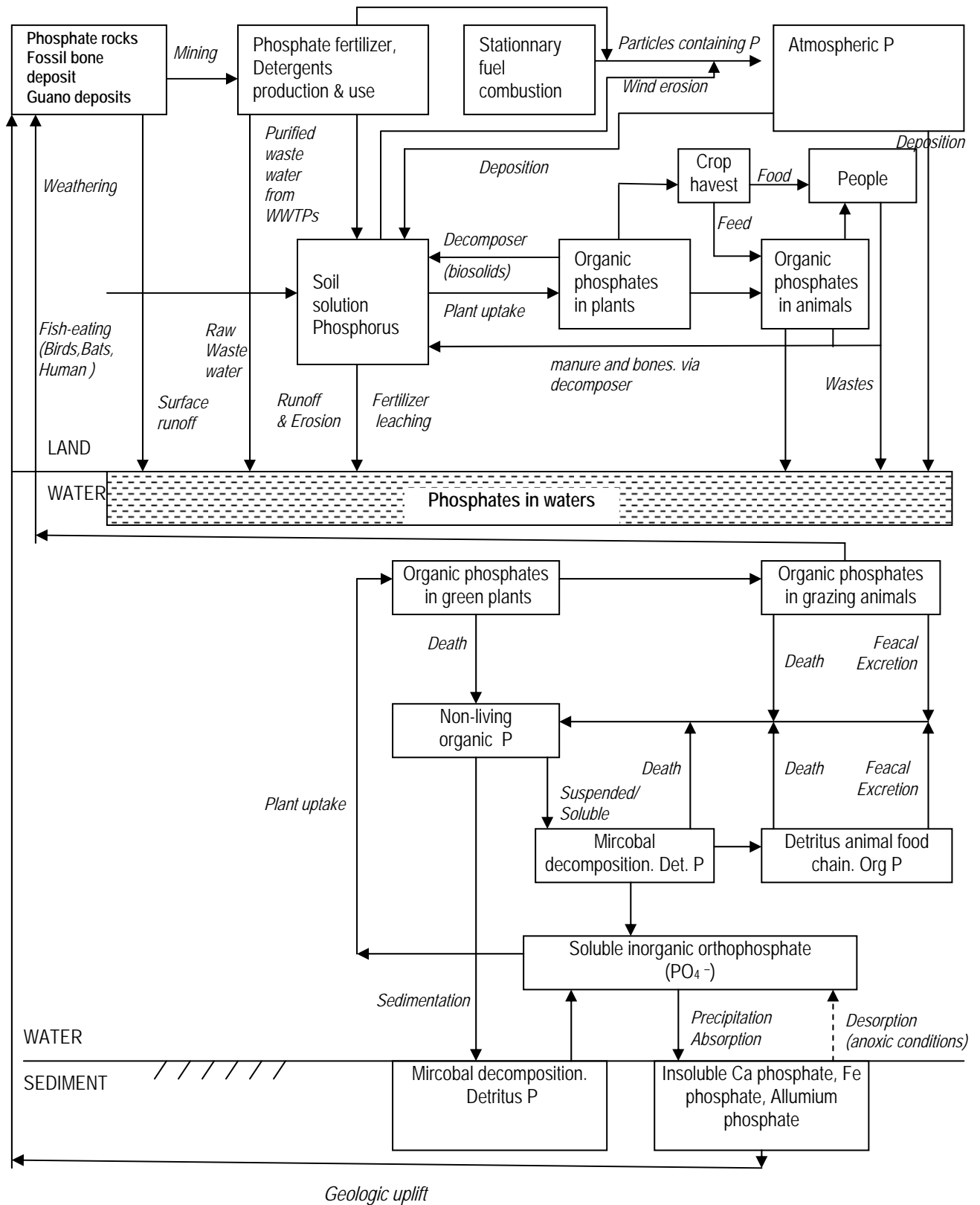


Figure 3.2: The phosphorus cycle
(based on MILLER, 1985; TACON, 1988; SML, 2001; TKALICH and SUNDARAMBAL, 2003)

Major sources of particulate P in the atmosphere are soil particles containing both naturally occurring and fertilizer derived, P on sea-salt particles, P from industrial sources. The major sources of industrial P emissions are the phosphate industry, and stationary combustion sources (GRAHAM and DUCE, 1979; ANDERSON and DOWNING, 2006).

Phosphorus is much more vulnerable to extreme climatic events than nitrogen due to being mobilized and delivered in substantial quantities from erosion processes and linked hydrological pathways (soil erosion, preferential flow in soils and bank erosion). The total phosphorus concentration increases with increasing river flow rate during storm events for many rivers (VERHOFF et al., 1982; KRONVANG et al., 2003). Through calculating the total nutrient loads in 100 different river basins in Europe, BEHRENDT (2000) found that the load-weighted retention of phosphorus is controlled practically only by the specific runoff of the basin. The load-weighted retention of nitrogen is further dependent on the proportion of the basin area occupied by surface water, the basin size itself and the mean annual nitrogen concentration at a specific monitoring station (BEHRENDT and OPITZ, 2000).

3.1.2.2 Human impact on the phosphorus cycle

Anthropogenic sources of phosphorus compounds in water are WWTPs effluent, agriculture, urban developments (particularly from detergents), and industrial effluents. The major human impacts on the P cycle belong to four major categories:

- *Accelerated erosion, runoff and leaching*

Grasslands and forests have negligible soil erosion rates compared to the land planted with annual crops. Accelerated erosion and runoff owing to the conversion of forests and grasslands have been going on for millennia, but the process has intensified since the mid-nineteenth century with the expansion of cropping and with advancing urbanization (SMIL, 2000). In the agricultural sector, the major sources of phosphorus emission are the leaching of fertilizer nutrients applied to crops and manures produced by livestock rearing with the main mechanism by runoff and soil erosion (STENN, 1998). This loss occurs either as dissolved phosphorus (soluble) or as particulate phosphorus (attached to the sediment particles). The loss of soluble phosphorus occurs in surface water runoff or leaching and is comprised mostly of orthophosphate, which is immediately bioavailable for algae uptake. Particulate phosphorus is associated with eroded soil and organic matter particles (SCHUMAN et al., 1973; SHARPHEY et al., 1993).

- *Recycling of organic wastes*

Human and animal wastes contain substantial amounts of phosphorus with average daily excretion of 98% of the ingested P. The P emission per inhabitant via excrement is between 1.2 and 1.4 g P per day. Most manure P is in inorganic forms (50-95%), such as calcium phosphates and dissolved orthophosphate. The proportion of manure P soluble in water varies greatly

depending on the animal species, age, and diet, and can vary from trace amounts to more than 80% of the total P. Dairy manures generally have the lowest, and poultry wastes have the highest P content (CHAPRA, 1997; SMIL, 2000; WORTMAN, 2005). The importance of recycling organic manures to maintain crop production has been recognised by farmers for thousands of years and the practice remains a desirable component of modern farming (SMIL, 2000). But with an increasing demand on foods from increasing population, the natural source of phosphorus is no longer enough for improving and maintaining the soil fertility in an intensive agriculture. The mining of phosphate deposits and increased availability of phosphate fertilisers were made the compensation for the shortage of phosphorus supply (STEEN, 1998).

- *Untreated human wastes*

Around 50% of the phosphorus in municipal waste water originates from urine. Whereas phosphorus in waste water is present in low concentrations of around 8 mg P/l, the concentration in undiluted urine is around 800 mg P/l (WILSENAC, 2001). The application of water closets, centralized waste water treatment along with urbanization process during the last 150 years shifted the human wastes from land to the water bodies (GLEISBERG, 1988). In urban and populated areas, the significant sources of phosphorus emissions are mainly from human excrement and from the using of P-content detergents. In addition to 1.2 g P (dietary)/capita discharged daily from food, the P emission per capita must be added 1.3–1.8 g P from other non-dietary sources: industrial and household detergents (SMIL, 2000). Since the 1970ies, detergent phosphates have been labeled as the major cause of eutrophication in lakes and other freshwater bodies, and legislation has been introduced in many countries to prevent their use in detergent formulations. In rural localities where there is no sewerage collection system, these phosphate loadings are still discharged back into the environment via septic tanks (CHAPRA, 1997; PHOSPHORUS & POTASSIUM, 1998; STENN, 1998). The emission source of phosphorus from human excrements has an increasing significant. According to GLEISBERG (1998), the annual phosphorus freight from human excrements (0,55kg P/inh.a) rose from 0.69 million tons of phosphorus in 1850 to 3.58 million tons in the year 2000.

- *Applications of inorganic fertilizers*

World fertilizer consumption has increased tenfold since 1930. However, the global fertilizer consumption growth rate has leveled out, the peak year being 1988 with a total consumption of 37.7 million tons P₂O₅. Overall, mineral fertilizers account for approximately 80% of phosphates used worldwide with the balance divided between detergents (12%), animal feeds (5%) and specialty applications (3%), for example, food grade, metal treatment etc (PHOSPHORUS & POTASSIUM, 1998; STEEN, 1998).

3.2 Nutrient emission modelling

3.2.1 Major trends of nutrient emission modelling

The behaviour (transport, retention and loss) of nutrients in the soil, groundwater and river network is a very complex function of numerous biological, physical and chemical processes. In addition, monitoring all sources of pollution to assess the loads contributed by various sources is difficult and/or impossible and expensive and also subjected to analytical errors. Therefore, modeling (simplified representations of the real system) is relatively cheaper and less time consuming, it can estimate the loadings that could not be directly monitored (DE WIT, 2001; CHANDRA SEKHA and SREENIVASULU, 2003). Estimation of nutrient loadings is crucial to environmental management and planning. Models addressing excessive nutrient loading in the environment originated over 50 years ago, especially in 1970ies when the principal water quality problem was eutrophication. Since then, they have improved due to progress in modeling techniques and technology as well as enhancements in scientific knowledge (CHAPRA, 1997; RECKHOW and CHAPRA, 1999; ZHANG and JORGENSEN, 2005).

Several nutrient load models to river basins have been developed during the last decades. These quantification tools were developed for different goals and scopes, such as

- RIVERSTRAHLER (BILLEN et al., 1994; GARNIER et al., 1995; LANCELOT et al., 2006).
- TRK-The Swedish system, HBV, HBV-N (BERGSTRÖM, 1995; SWEDISH EPA, 1997; PETTERSSON, 2001; EUROHARP, 2001; FOGELBERG, 2003).
- EvnFlow (ANTHONY et al., 1996; DE WIT, 2001; EUROHARP, 2001).
- WEKU - A GIS supported stochastic model of ground water residence times in the upper aquifers for the supraregional ground water management (KUNKEL & WENDLAND, 1997).
- The WBLMER nitrogen loading model (VALIELA et al., 1997) first estimates inputs by atmospheric deposition, fertilizer use, and wastewater to surfaces of the major types of land use (natural vegetation, turf, agricultural land, residential areas, and impervious surfaces) within the landscape.
- Nitrate Leaching Estimator N-LES CAT (SIMMELSGAARD and DJURHUUS, 1998; SIMMELSGAARD et al., 2000; EUROHARP, 2001).
- Réalta - The Irish Phosphorus Model (MAGETTE, 1998; DALY et al., 2002; EUROHARP, 2001).
- GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) Management model: to test the effect of different agricultural management practices on losses of different elements (water, N, P, sediments and pesticides) from fields (KNISEL et al., 1999; BLOMBÄCK and DJODJIC, 2003).

- Source Apportionment (OSPAR 00/9/2, 2000).
- SWAT (ARNOLD et al., 1998; ARNOLD and FOHRER, 2005; NEITSCH et al., 2005; GASSMAN et al., 2007).
- Lakeshore Capacity Model – LCM (REAVI et al., 2002).
- MODEST (Model of Diffuse Nitrogen Entries via Subsurface Trails into the Surface Water Bodies at the Regional Scale – Dynamic & the spatially distributed mechanistic approach model (DANNOWSKI et al., 2003).
- MIRO (LANCELOT et al., 2005).

These nutrient emission models have been developed with different respect to complexity, structure and input data demands. They are different in their assumptions on the sources and losses, the way that they simulate the processes in the environment, their processes are included in the model and the complexity of their formulations. These nutrient load models typically follow one of two approaches: dynamic or static models.

The deterministic/dynamic models

The dynamic models seek to describe an environmental process and generally imply that variables and formulations have some physical meanings (AHLGREN et al., 1988; SMITH and ALEXANDER, 2000; SCHALLENBERG and BURNS, 2001). The dynamic models provide a fundamental understanding of a physical process. The simple dynamic models include a simple accounting of the inputs (e.g., fertilizer application, livestock waste, atmospheric deposition, and point sources) and outputs (e.g., river export, crop removal) of nutrients. The mass balance is estimated by comparing those major sources and the total losses are to be assumed to volatilization, soil adsorption, sedimentation, groundwater storage and denitrification processes. More complex dynamic models describe transport and loss processes in more detail and incorporate terms for spatial and temporal variations in sources and sinks. Therefore, they often require large amounts of input data at a very detailed temporal and spatial scale. In this model, the catchments will be divided into unique combinations of land use, level of nutrient input, slope, soil type, hydrological situation/drainage system, and then consider them as homogeneous plots. The dynamics of the fate of nutrient inputs are modelled in a two or three-dimensional way, often on a daily basis. All major biological and chemical processes that occur in soil and water are taken into account (e.g. mineralisation/immobilisation, (de)nitrification and phosphorus (de)sorption). Nutrient concentrations are calculated based on the representation of system processes (PETER, 1986; SMITH and ALEXANDER, 2000; ASNER, 2001; EUROHARP, 2001; DALY, 2002; BIEGEL, 2004). Dynamic nutrient models may be excellent tools for the evaluation of different water bodies management strategies, but require more data and qualified scientists for their proper use (AHLGREN et al., 1988).

The static/empirical models

In contrast, the static models - empirical equations seek the simplest relationships between variables derived from statistical treatment of data, they treat the system as a "black box", with internal variables and relationships having little or no physical interpretation (AHLGREN et al., 1988; SMITH and ALEXANDER, 2000). The empirical models establish relationships between stream nutrient measurements and watershed sources and landscape properties. They do not attempt a comprehensive representation of all individual system processes. Instead, they simulate losses by using a series of simpler empirical, semi-empirical or statistical functions. These tools may include parameters such as nutrient surplus, nutrient status of the soil, soil type, land cover, precipitation or net precipitation surplus and slope. Simple static models consider sources and sinks to be homogeneously distributed in space, do not separate terrestrial from in-stream loss processes, and rarely account for the interactions between sources and watershed processes. While, more complex empirical models indicate that knowledge of spatial variations in watershed properties that influence nutrient attenuation can significantly improve the accuracy of estimates of export and source contributions at larger watershed and regional scales. An advantage of the empirical approach is the ability to quantify errors in model parameters and predictions (SMITH and ALEXANDER, 2000; EUROHARP, 2001; DALY, 2002; KRONVANG, 2003). The empirical models are useful especially when low data are available (CHANDRA SEKHA and SREENIVASULU, 2003).

The model for the reconstruction of past nutrient levels

The developing models to reconstruct past nutrient levels have long been focused. Due to the absence of long-term monitoring of surface water chemistry, there is a need for reliable estimates of previous nutrient concentrations in water bodies. In theory, the concentrations of phosphorous and nitrogen would be provided from geochemical records and then the history of past loading can be easily reconstructed. But there are some difficulties, due to many problems and challenges in using sedimentary phosphorous concentrations as a proxy of past water nutrient concentrations. The main reason is the phosphorous retention in sediment is strongly controlled by sorption onto iron oxides, and so variations in both iron content and redox condition may change phosphorous accumulation in sediment independent of its concentration in the overlaying water. Determining past nitrogen levels directly from geochemical data is also difficult. Therefore, with more indirect - secondary data approach, the diatom records - biological-based proxy methods (diatom-inferred nutrient concentrations) are primary used to infer past nutrient levels (SCHINDER, 1987; LOTTER, 1998; BEHRENT and OPITZ, 2001; BENNION et al., 2001; BRADSHAW and ANDERSON, 2001; SMOL, 2002; REAVI et al., 2002; SCHÖNERFELD, 2002, 2004).

Another method to evaluate historical changes in nutrient loading is proportioning method. In these models, nutrient inputs were partitioned into various sources. The nutrient emission sources can be the point sources or diffuse sources: the atmosphere, from surface runoff,

groundwater, soil erosion, from direct inputs from anthropogenic activities and from upstream sources. Historical simulations are generated from long-term records of land-use, fertilizer application, and livestock census data from the catchment and compares favorably with present measurements. These models have been successfully applied in different temporal and spatial resolutions, e.g. in Michigan Lakes (USA), the river Seine and the river Scheldt (France), coastal lakes in southwestern England and some catchments in Germany (CHAPRA, 1977; SMIL, 2000; CONLEY, 2004; KOVACS, 2004; BEHRENDT, 2005; VAN JILS, 2005; BILLEN et al., 2005; LANCELOT et al., 2007).

3.2.2 Source of emissions, pathways and riverine budgets of nutrients in models

Nitrogen and phosphorus enter the aquatic ecosystems via several hydrological, geological, and biological flow paths. Nutrient loads are mostly dependent on land use, fertilizer application and population density (VITOUSEK, 1997; GALLOWAY, 2004). Natural and anthropogenic disturbances disrupt nutrient cycles by altering the nature of controlling processes (i.e., hydrologic regime, temperature, and biological community) (MCCLAIN et al., 2001).

Natural emission sources of nitrogen and phosphorus include:

- fresh water that runs over geologic formations rich in phosphate or nitrate (for example: guano deposits on arid islands and evaporite nitrate deposits),
- decomposing organic matter and wildlife waste, and
- the extraction of nitrogen gas from the atmosphere by some bacteria and blue-green algae (biological nitrogen fixation).

Major anthropogenic emission sources of nitrogen and phosphorus are:

- via atmospheric deposition: fossil fuel combustion for energy and transportation as wet or dry precipitation;
- into surface water: point and non-point source discharges, effluent from WWTPs, industrial discharges, urban storm-water runoff, agricultural runoff, livestock wastes.
- into groundwater: sources are primarily underwater seepage from agricultural fields and failing septic systems.

In the term of the location of emission sources, the nutrient emissions into surface water could be divided into the external and internal loads. External load includes nutrient loading from the upstream tributaries; the point and diffuse source emissions that directly enter the surface water bodies and the nutrient emission from atmospheric depositions. Internal load refers to the nutrient to be re-enter water bodies from the sediments.

Nutrient concentrations are always in flux, responding to changes in:

In the natural context:

- precipitation and amount of runoff
- water temperature,
- biological activity in water bodies; and/or
- the status of other water quality parameters

In the human side:

- fertilizer and manure application rates,
- living standards,
- waste water collection system and treatment technologies, and
- regulations related to nutrient emission controls (e.g. P-free detergent, fertilizer utilization)

Nutrient concentrations are usually greatest during spring and early summer, when fertilizer use and water flow from tributaries and irrigation activities are high. High nutrient concentrations also occurred during seasonal low-flow conditions. Nutrient levels downstream from urban areas may also be high during low-flow periods. At these times, contributions from point sources can be greater relative to stream flow, and dilution is less. Natural features (e.g., geology and soils) and land management practices (e.g., drainage and irrigation) can affect the movement of nitrogen and phosphorus over land, creating local and regional effects on water quality (MCCLAIN et al., 2001).

3.2.3 MONERIS model and its applications

The nutrient emission model MONERIS (MOdelling Nutrient Emissions in RIver Systems) (BEHRENDT et al., 2000; BEHRENDT et al., 2002) is a conceptual, quasi static model developed to estimate the nitrogen and phosphorus inputs into river basins on a sub-catchment scale, from point sources and various diffuse pathways. The model estimates annual load from seven different pathways: point sources, direct atmospheric deposition, erosion, surface runoff, tile drainage, groundwater and urban systems. Each pathway has its own Excel file where the calculations are made and these files are further linked to one input data file and one output data file. MONERIS produces estimates of annual load through each of the point and diffuse pathways and it estimates nutrient retention within the river system (lakes and rivers). This model was developed and applied for medium to large scaled catchments (BEHRENDT et al., 2000; BEHRENDT et al., 2002, BEHRENDT et al., 2004; ZESSNER et al., 2005), but has also be shown to

deliver reliable results in catchments down to 50 km² (VENOHR, 2003). MONERIS utilizes both GIS analyses and data from statistical reports.

On the nutrient load reconstruction aspect, MONERIS has been tested its capability to reconstruct the nutrient loads and sources of nutrient emissions to the river system of the past (the Odra river system for the time period from the 1960s to 2000s) (KOVACS, 2004; VAN GILS et al., 2005; BEHRENDT et al., 2005).

MONERIS model has been developed in German conditions and it has been also successfully applied in more than 300 German river basins (the Elbe, Rhine and Danube, and the Weser in the period of 1983-1987, 1993-1997 and 1998-2000, the Havel, the Spree and the Dahme for the year 2000, the Lower Havel for the period of 1978-1999) (BEHRENDT et al., 1999; BEHRENDT et al., 2002; BEHRENDT et al., 2003; SCHREIBER et al., 2003; BEHRENDT et al., 2004; ZESSNER et al., 2005) and in other Europe countries like Odra River: 1960-2000; Po basin, the Ybbs, the Wulka in Austrian regions, Axios, Daugava, Vistula (DE WIT and BEHRENDT, 2002), Asia and America (BEHRENDT et al., 2003; BEHRENDT et al., 2005). MONERIS has become an important component of EUROHARP Project – European Harmonized Procedures for Quantification of Nutrient Losses from Diffuse Sources supplying the implementation of the Water Framework Directive (EUROHARP, 2001).

MONERIS has been applied in parallel to other nutrient load models (e.g. MODEST, NIIRS, HBV-N, SWAT 2000, DIFGA, GREAT-ER ...) in some projects (HAPRO, 2001; BEHRENDT et al., 2002; FOGELBERG, 2003; SCHILLING et al., 2003; KOVACS, 2004; FOGELBERG et al., 2005; BERLEKAMP et al., 2005; ZESSNER et al., 2005). The results shown that the same estimations have been achieved from detailed mechanistic approaches and a conceptual model MONERIS. In compare to other applied models and monitored data of the 388 catchments covering the whole Danube river basin for the time period 1998-2000, the MONERIS approach produced the best agreement. On the side of data requirement, the availability of data being used for MONERIS is also convincing due to they are easily available in comparison to the other model input data (higher parameterization and spatial resolution) (ZESSNER et al., 2005). MONERIS can be sufficiently adapted to the local conditions to produce accurate predictions in compare to other models (BEHRENDT and DANNOWSKI, 2002).