# Dynamic modelling of phosphorus export at river basin scale based on Global NEWS

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This research was implemented in the framework of an internship at Alterra

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Abstract

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Phosphorus (P) is a main element contributing to large-scale coastal eutrophication. P transport from land to coastal waters is predominantly driven by watershed responses to P inputs on land, where P dynamics is a key factor, and by P transformation within the river system. Until now, global scale modeling of P export by world rivers has neglected both the dynamic behaviour of P in watersheds and P river retention. We developed a simplified dynamic approach for watershed dissolved inorganic P (DIP) export generated from anthropogenic diffuse sources in the period 1900-2050 based on Global NEWS (Nutrient Export from WaterSheds) approaches while accounting for P river retention. Results show a significant impact of P dynamics on DIP export at the watershed scale while the impact is limited at the river basin scale due to the large contribution of point sources. Watershed dynamic DIP export is calculated to be lower compared to steady state projections. Future DIP export might be increased by about 10% in 2050 compared to 2000 under dynamic conditions while large increases or decreases are observed under static conditions.

Keywords: dynamic modeling, phosphorus export, world rivers, river retention, scenario analysis.

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# Contents

# Summary


In models, which quantify P export from land to water, it is essential to considering P dynamics in soils in the catchment because of the ability of P to build up over time in the soil, affecting its transport from the watershed (land) to surface waters. The majority of examined regional scale P models in this study (2/3 out of 26 models) thus includes P dynamics in their estimations of P export is emphasizing its importance. Modelling of phosphorus export by river basins at global scale, carried out by the Global *NEWS* model, however neglects P dynamics in the catchment, since NEWS is a steady state model. The study describes a dynamic approach that was developed and applied in the Global *NEWS* model to assess the impact of P dynamics in watersheds on P export at the river basin scale. P dynamics within the river system was not included in this study, but the impact of river retention, presently neglected in Global *NEWS,* was taken into account.

The study area covered river basins of the world taken from the Global *NEWS* model, which area occupies more than four grid cells by 0.5x0.5 degree. At later stage, the study area was limited to almost 70% of their area due to methodological reasons. The developed dynamic approach applied only to DIP export at the watershed scale, which is generated from anthropogenic diffuse sources namely synthetic fertilizer and animal manure applications to land. DIP weathering over agricultural areas is also included for this purpose.
The dynamic approach was developed on the basis of main processes involved in P transformations in the soil, including P adsorption/desorption, controlled by Langmuir P adsorption.

To enable global application of the Global *NEWS* model, various assumptions were made. Watershed DIP concentrations were assumed to be in equilibrium with the reversible P pool in the soil. P accumulation in the soil was calculated for the period of 1900-2050, where P inputs to land was assumed to be equal to P outputs from land in 1900. Calculations over this period were based on four sub-periods with known Global *NEWS* values for 1970, 2000, 2030 and 2050. The fraction of P accumulation was estimated only for 2000 and assumed to be the same for future years. The P adsorption constant was estimated on the basis of basin characteristics and soil properties. Its estimation was done for the year 2000 based on inputs from the Global *NEWS* model. This constant was found to be sensitive to watershed DIP concentrations, which are increasing with increasing fractions of river retention from zero to 0.50. Under these conditions, the constant is becoming lower and more comparable to literature data, illustrating that river retention most likely takes place. Inputs for dynamic estimations were derived from the Global *NEWS* model for each river basin except for bulk density, soil thickness, content of aluminium and iron oxides and river retention. These variables were taken from the other literature sources and were subject to sensitivity analysis. All estimations were done outside of the Global *NEWS* model.

In order to identify the impact of the dynamic approach, DIP export was analysed at the watershed and river basin (DIP that is exported at the mouth of rivers) scales separately according to both steady state (the Global *NEWS* approach) and dynamic approaches. In this study DIP export was presented both in terms of DIP concentrations (mg $l^{-1}$) and DIP fluxes (yields, kg $ha^{-1}$ $year^{-1}$) for the years 2000, 2030 and 2050. Analyses for future years were based on the Global Orchestration (GO) scenario of the Millennium Ecosystem Assessment. The scenario pays particular attention on global economy rather than on the environment.

The dynamic approach has significant impact on DIP export at the watershed scale while it has limited impact on DIP export at the river basin (mouth of rivers) scale. Generally, according to the dynamic approach DIP concentrations and fluxes are lower compared to the steady state approach especially at the watershed scale. Based on minimum values of variables, which were used for sensitivity analysis in the dynamic approach, dynamic DIP concentrations at the watershed scale are 3/4 of stead state values on a global scale.

Considering maximum values of those variables, watershed dynamic DIP concentrations are only 2/4 of steady state values on the global scale.

For the future, the dynamic approach suggests lower increases in DIP export over the period of 2000-2050 than the steady state approach. At the watershed scale, dynamic based DIP concentrations might be increased over this period by about 60%, 10% or 3% depending on minimum, average and maximum values of the variables respectively while steady state concentrations are expected to increase about 80% on the global scale. Lower DIP export under the dynamic approach can be caused by P transformations in the soil via P adsorption/desorption processes leading to less DIP leaching from the soil to water bodies.

At the river basin scale, differences between both approaches are more visible for individual river basins of the world. Majority of river basins in South America might have at their mouth less DIP concentrations in the future than in the past according to the dynamic approach while more in the future than in the past according to the steady state approach. The impact of the dynamic approach on DIP export at the river basin scale depends on several factors. Large contribution of point sources to DIP export is a major factor here. Actual water discharge used to estimate DIP concentrations might also contribute to this via, for instance, dilution effect.

Results show that the dynamic approach is not considerably sensitive to used different values of input variables excluding river retention at both watershed and river basin scales. Under minimum values, future changes in DIP export are relatively higher than under average and/or maximum values. This is because the efficiency of DIP leaching to water bodies within one meter of the soil with 50 mmol per kg of aluminium and iron oxides (bind P) (minimum values) is higher than within five and/or ten meters with 100 and/or 150 mmol per kg of aluminium and iron oxides (average and/or maximum values). Values for bulk density do not vary substantially and thus this variable may contribute less than the others.

The inclusion of river retention was followed by an assumption that only watershed DIP export is influenced by this for both dynamic and steady state approaches. This was done in order to improve watershed DIP concentrations, which were found to be very low under static conditions. This directly affects estimations of P adsorption constant in the dynamic approach. The inclusion of river retention increased watershed DIP export in 2000 with higher increase for future years under the steady state approach and less increases in the future under the dynamic approach. Dynamic DIP concentrations were estimated to increase in 2030 and 2050 by about 0.5 and 6 times by including 10% and 50% of river retention (in addition to minimum and maximum values) respectively on a global scale. Steady state global DIP concentrations for these years were estimated to increase by 1 and 10 times by adding 10% and 50% of river retention respectively. This can be explained by that with increasing fractions of river retention, P pool is increasing leading to increases in DIP export. However, since P dynamics are involved, increases in DIP export are smaller under the dynamic approach. Despite of the assumption, DIP export was found to be slightly influenced by river retention at the mouth of rivers under only the dynamic approach and only for future years. However, its effect is different at this scale than at the watershed scale. Results show that with increasing fractions of river retention dynamic DIP concentrations and yields at the river mouth are slightly going down. Globally, on the basis of minimum values of the variables dynamic DIP concentrations in 2050 were reduced from 0.36 mg per L under 0% of river retention to 0.34 mg per L under 10% of river retention. On the basis of maximum values, dynamic DIP concentrations went down from 0.35 mg per L when 0% of river retention to 0.23 mg per L when 50% of river retention on a global scale for the year 2050.

Summarizing, the dynamic approach was developed with some simplifications in order to be able to apply it to the Global *NEWS* model. Results emphasize that the dynamic approach has significantly affected DIP export at the watershed scale rather than at the river basin scale. The dynamic approach, in general, suggests lower changes in DIP export than the steady state approach. DIP export was found to be considerably sensitive to the inclusion of river retention according to both approaches. To this end, this was the first attempt to include P dynamics in the Global *NEWS* model. Therefore, there are still rooms for future improvements.

# 1 Introduction

## 1.1 Phosphorus in the environment

Phosphorus (P) plays an important role in the environment. It is an essential nutrient for terrestrial and aquatic ecosystems because of its capacity to participate in transferring energy and thus, to control biological productivity (Scheffer, 2004; Filippelli, 2002; Busman et al., 2002; Harrison et al., 2010; Bouwman et al., 2009). Inversely, elevated contents of P in aquatic ecosystems generate algal growth and thus eutrophication developments. It has been reported that 0.01-0.07 mg P (reactive forms) $dm^{-3}$ in water can already stimulate algal growth in Western Europe (Del Campillo et al., 1999). Specially coastal waters suffer from eutrophication resulted from riverine transport of nutrients (Mayorga et al., 2010; Harrison et al., 2010). Phosphorus in rivers is present in particulate (PP), dissolved organic (DOP) and dissolved inorganic forms (DIP). Dissolved inorganic P is considered to be most bioavailable in rivers while dissolved organic and particulate P are almost not available for living organisms. The relative share of dissolved inorganic P in rivers is small compare to organic and particulate forms. For instance, around 10% of P transported within river systems globally as DIP in 1995 (1.5 Tg of DIP compare to 20 Tg of TP) (Harrison et al., 2010).

Since the last several decades P export has been altered due to human intervention (Filippelli, 2002; Bouwman et al., 2009; Alvarez-Cobelas et al., 2009). As a result, global dissolved P export from land to rivers has increased two times from 2-4 Tg P $year^{-1}$ to 4-6 Tg P $year^{-1}$ (Filippelli, 2002). Main sources of elevated P in the environment are human waste, detergents and P inputs in agriculture. Human waste (mainly sewage effluents) and detergents are considered to be a major sources of P pollution in rivers (Harrison et al., 2010; Grizzetti and Bouraoui, 2006; Alvarez-Cobelas et al., 2009). For instance, these sources contributed from 77% to 99% of DIP to the Thames River in the period of 1995-1999 (Harrison et al., 2010). The other main source is P lost from agricultural soils receiving P mainly via fertilizers and manure applications in order to increase crop yields (Del Campillo et al., 1999; Shoumans and Groenendijk, 2000). P in manure and fertilizer is in soluble form and thus this P is easily available for crops. However, when manure and fertilizer is applied in excess of plant needs, then phosphate can be leached to deeper soil layers and/or lost to surface waters causing eutrophication (Del Campillo et al., 1999; Harrison et al., 2010). Deforestation is the other source of P, resulting in soil erosion that leads to enhance particulate P leaching from soils to rivers. Human alterations within river systems in terms of constructed dams, water removal have also implications on P export (Ruttenberg, 2005).

Since P is a key nutrient that contributes to eutrophication, insight in its future delivery to aquatic ecosystems by modelling of P transport is very relevant (Alvarez-Cobelas et al., 2009) (for information about existing P models the reader is referred to Chapter II). Modelling P export from soils to coastal waters requires insight in P inputs to terrestrial ecosystems via manure and fertilizer applications to land and atmospheric P deposition, P export by crop and forest, accumulation of P in the soil (phosphorus retention), leaching from the soil to streams and/or direct export to streams and transport of P within the river to coastal waters (Mayorga et al., 2010; Alvarez-Cobelas et al., 2009). In this context, understanding of P transformation and its accumulation in the soil (determining P export from land to rivers) and in the river system (determining P export within the river system to coastal waters) is crucial. Those processes change over time and thus they show dynamics. Integration of dynamics in models is important in order to project appropriate P export for the future (Shoumans and Groenendijk, 2000; Keller and Schulin, 2003; Scheffer, 2004).

A short description of phosphorus in terrestrial and aquatic ecosystems is given below in order to get more insight into P transformation and its accumulation in the soil and in the river system.

**Phosphorus in terrestrial ecosystems**

The P cycle in terrestrial ecosystems includes different P forms (Figure 1). Phosphorus is added to the soil via manure and fertilizer applications in soluble forms (Busman et al., 2002). Plants take up P in dissolved inorganic form (orthophosphate, $PO_4^{3-}$). A fraction of P is retained in the soil (accumulated) in different forms (inorganic and organic), whereas the remainder is leached to deeper soil layers and/or lost to surface waters. Animals consume plants and via excrements and also via crop residues P is returned to the soil mostly in organic form (Busman et al., 2002; Bouwman et al., 2009; Del Campillo et al., 1999). Some part of this organic phosphorus is processed by microorganisms, which convert organic P into inorganic P (mineralisation process). This process depends on soil conditions, such as pH, soil moisture, temperature and soil minerals (Busman et al., 2002) (Figure 1). In natural terrestrial ecosystems, biotic mobilisation hardly plays a role in the P cycle. Phosphorus generated in these ecosystems stem mainly from P-containing rocks via their weathering (dissolution of minerals) under certain physical-chemical conditions (Bouwman et al., 2009; Ruttenberg, 2004).

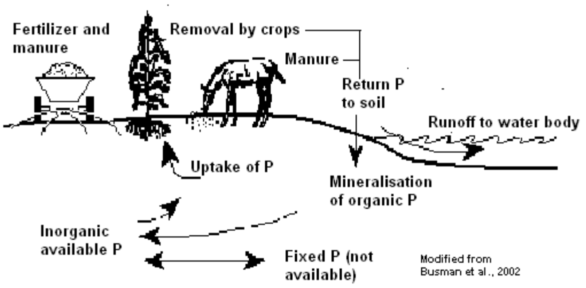
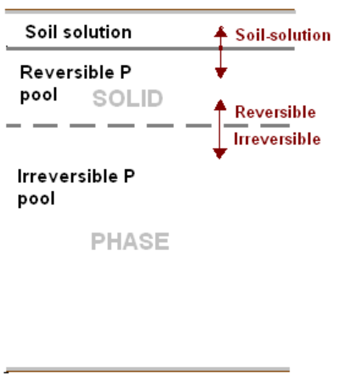



*Figure 1*
*Simplified phosphorus cycle in terrestrial ecosystems with focus on agricultural areas. (Source: Busman et al., 2002).*

Phosphorus that is retained (accumulated) in the soil is presents in different P pools (Shoumans and Groenendijk, 2000; Busman et al., 2002; Bouwman et al., 2009). In general, a distinction is made in three P pools, i.e a soil solution pool (see Busman et al., 2002), a reversible pool (or active pool according to Busman et al., 2002) and an irreversible pool (or fixed pool according to Busman et al., 2002) (Schoumans and Groenendijk, 2000) (Figure 2).

The soil solution phase contains mostly plant available P (DIP) and also a small amount of organic phosphorus that is not available for plants. However, this available P pool is relatively small compared to the other two P pools (Busman et al., 2002). The DIP in soil solution that is available to plants is mainly controlled by soil solution-soil solid phase interaction. This interaction depends on soil properties (oxalate extractable Al and Fe concentrations, pH, soil texture) as well as P concentrations in soil solution and in soil solid phase (Shoumans and Groenendijk, 2000; Busman et al., 2002). The interaction is described by a Langmuir equation (description is given in Section 3.2.1) (Schoumans and Groenendijk, 2000). P concentrations in the soil solid phase in turn are influenced by the net P input (P input minus P removal) to the soil (Bouwman et al., 2009).

The soil solid phase includes reversible (active) and irreversible pools (fixed), which are considered to be included by an oxalate extraction (Schoumans and Groenendijk, 2000; Busman et al., 2002; Bouwman et al., 2009). The ratio between these two pools are 1/3 for the reversible pool and 2/3 for the irreversible pool. This ratio is assumed to be constant (Schoumans and Groenendijk, 2000). Reversible pool is considered to be most important because of its ability to control availability of P to plants. This is because this pool has phosphorus that is available for plants: inorganic phosphorus that is attached to or adsorbed at surface of soil minerals (oxides, calcium carbonate) and organic phosphorus that is easily transformed to inorganic (mineralisation) (Busman et al., 2002). This solid phase actively interacts with soil solution phase creating soil solution - soil solid interaction. For instance, plants take up P, this leads to an decease of P concentration in soil solution, at the same time P is coming from the reversible pool to soil solution in order to sustain P concentration there. There is reaction between the reversible P pool and irreversible P pool. However, this is slow process because the irreversible P pool has phosphorus in such forms that are resistance to mineralisation and hardly are soluble (for instance, crystalline). P can be in this pool for many years (Busman et al., 2002; Schoumans and Groenendijk, 2000). Oxide iron (Fe) and aluminium (Al) usually control P availability in P pools. This is because they react with phosphorus forming insoluble forms of phosphorus (Bouwman et al., 2009).




| Fraction of P pool | P forms | Remarks |
|---|---|---|
| Very small | Dissolved inorganic<br>Dissolved organic | Available for plants<br>Not available for plants |
| 1/3 of total pool | Inorganic, Organic — associated with soil particles | P interaction via adsorption to soil particles;<br>Control P availability |
| 2/3 of total pool | Inorganic, Organic — associated with soil particles | P interaction via precipitation and dissolution;<br>Not availble for plants;<br>P forms are hardly mineralized;<br>P forms are insoluble |

*Figure 2*
*Simplified schematic representation of the P pools in the soil and their main characteristics. (Sources: Schoumans and Groenendijk, (2000); Busman et al., (2002); Bouwman et al., (2009); Del Campillo et al., (1999); Ruttenberg, (2004); Koopman et al., (2004a,b)).*

## Phosphorus in aquatic ecosystems

Phosphorus is transported from terrestrial ecosystems to aquatic ecosystems via surface and/or subsurface runoff (Reddy et al., 1999). Its transportation within river systems to coastal waters is influenced by retention within the river, constructed reservoirs and consumptive water use (Mayorga et al., 2010).

Phosphorus retention within the river generally occurs at the sediment-water interface (Scheffer, 2004). This has strong link to phosphorus cycle in aquatic ecosystems, which shows dynamics over time. Water systems usually receive P externally (external P loading) and internally (internal P loading from the sediment). External inputs of P are mainly via point (waste waters) and non-point (agriculture) sources (Scheffer, 2004; Bouwman et al., 2009). Vegetation, microorganisms (for instance, algae) and living organisms (fish, any other animals) consume phosphorus (mainly dissolved inorganic P), which then return to the system as organic matter. This organic matter is exposed to mineralisation process. This makes phosphorus available for organisms again. Under aerobic conditions (presence of oxygen) at the bottom layers of the sediment, ferric iron ($Fe^{3+}$, oxidized form) binds phosphorus (mainly inorganic P), which is no longer available for organisms. Phosphorus can be temporary retained in that pool. Aluminium and carbonate calcium are also important, but iron is dominant with respect to P. When oxygen is depleted at the bottom layers of the sediment (anoxic conditions), Fe-bound P is released from that system to the water column that leads to internal loading of P. Depletion of oxygen can occur for instance due to consumption of oxygen by bacteria needed to mineralize organic P into inorganic P (Scheffer, 2004; Filippelli, 2002; Reddy et al., 1999). Other factors, such as temperature, pH and light penetration, also contribute to P transformation. P concentration in the sediment is usually much higher than in the water column (Scheffer, 2004). For detailed information about phosphorus dynamics in shallow lakes the reader is referred to Scheffer (2004).

The other main factor influencing P transportation within river systems is constructed reservoirs within the river. Reservoirs do not allow particulate matters to go further. This generates an obstacle for P export, leading to its sedimentation (Mayorga et al., 2010). On the other hand, reservoirs can provoke erosion. As a result, P export can be increased (Ruttenberg, 2005). Consumptive water use is another aspect stimulating reduction in P export. Water from rivers is often used for irrigation purposes, for industrial and domestic use. This implies some P losses from the water system and thus, to reduced P export to coastal waters (Mayorga et al., 2010).

## 1.2 Research objectives, study area and contents of the report

**Research objectives**

Phosphorus dynamics is a crucial aspect in modelling P export from soils to rivers, since P accumulation is a key characteristic affecting P export. This has implications for future projections of P export. For instance, P can be accumulated to the solid phase in the soil over time, and as a result P concentrations in the soil are changed and thus, P leaching from the soil to water is also changed. Following this, phosphorus export will be different because of those changes in the soil.

In this study, the Global *NEWS* (Nutrient Export from WaterSheds) model is taken as the basis for P export at a global scale. This is because the model calculates P export from land to rivers and by rivers to coastal waters, including both point sources and diffuse sources. Besides, the model considers different P forms: particulate, dissolved inorganic and organic P. In addition, the model calculates P export for the past and future. However, this model is fully based on a steady state approach rather than on a dynamic approach (Mayorga et al., 2010). This provides an opportunity to apply a dynamic approach to the model and consequently to show the importance of P dynamics in soils. P dynamics in rivers is not included in this study.

Therefore, main objectives of the study are:

1. To develop a dynamic approach for modelling P export by rivers at basin scale to be included in the Global NEWS model instead of the present steady-state approach.
2. To assess the impacts of a dynamic approach on P export at a global scale.

Application of the dynamic approach will be done only with respect to DIP because of its bioavailability and also interaction with the soil P pool (see Section 1.1). The other P forms (dissolved organic and particulate) are influenced by other factors. This is also clear from the different approach in calculating the concentrations of different P forms in the Global *NEWS* model (see Section 2.2).

In addition, this research aims to evaluate the impact of included river retention on DIP export presently neglected in the Global *NEWS* model.

**Study area**

The study area covers river basins of the world. These river basins are from the Global *NEWS* model (available at http://marine.rutgers.edu/globalnews/datasets.htm). The model estimates nutrient export for 6292 river basins, which drain to coastal waters of African, Australian, European, North and South American, North and South Asian and Oceania continents (Figure 3). However, small river basins, which areas do not cover more than four grid 0.5x0.5 degree cells, are excluded from the study. This is because the model performs better for large basins. Therefore, the study area includes only 1163 river basins covering almost 90% of the total area of the world (basin areas of the basins were taken from the Global *NEWS* model).

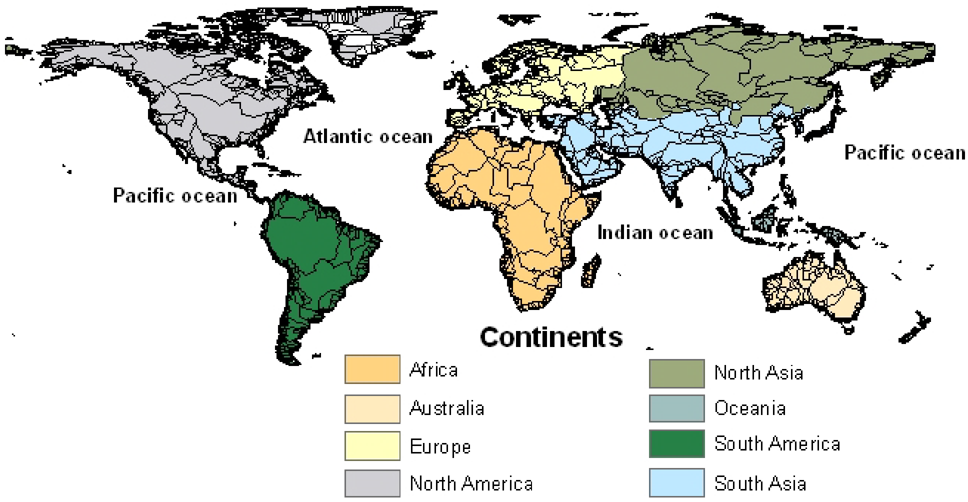



*Figure 3*

*The study area that covers river basins draining to coastal waters of eight continents in the world: African, Australian, European, North and South American, North and South Asian and Oceania. Delineation of basins is taken from the Global NEWS model (available at http://marine.rutgers.edu/globalnews/LMEworkshop.htm).*

**Contents of the report**

To get more insight into the modelling of phosphorus export, a review of existing P models is presented in the beginning of this report in Chapter II. Since the Global *NEWS* model is the basis in this study, its description is given in Chapter II as well.

An approach to include phosphorus dynamics into the Global *NEWS* model at the watershed scale is presented in Chapter III to this report. This chapter includes a short description of the dynamic approach (Section 3.1), then methodological aspects of implementing dynamics to the model are introduced (Section 3.2). And, this chapter is finished by a description of input data that are required to apply this dynamic approach (Section 3.3).

Following this, model application results are combined with sensitivity analysis results and they are discussed in chapter IV. Initially, phosphorus adsorption results are presented (Section 4.1) in this chapter. This is because the phosphorus adsorption constant (expressed as $K_P$) is a basic parameter in a dynamic approach, which considers phosphorus distribution between soil solution and soil solid phases. Besides, model application is based on its results and thus they have to be discussed at the first stage. After this, results of model application are given in Section 4.2. Finally, this report is finished by discussions (Section 5.1), conclusions (Section 5.2) and recommendations (Section 5.3) (Chapter V).

# 2 Modelling P fluxes at regional and global scale

A review of literature was done by paying attention on models that describe modelling of phosphorus export at different scales. A simplified description of the various models is provided in this chapter on the basis of the following criteria:

- Regional scale/global scale
- Abbreviation of the model
- Main purpose of the model
- Dynamic approach/steady-state approach applied in the model
- Spatial and temporal resolution of the model
- Forms of modelled phosphorus
- Pathways and processes included in the modelling phosphorus fluxes
- Main inputs and outputs of the model
- Applicability of the model

In general, two main categories of models can be distinguished, i.e models that are based on a steady state approach and models that are based on a dynamic approach.

A dynamic approach means that changes over time in nutrient processes (physical, chemical and biological) are described. Thus, this approach is often also process-based, since empirical models mostly have not a specific time dimension. Dynamic models are advantageous in situations when time dependent processes (for instance, phosphorus sorption and precipitation) play an important role. This approach, however, requires a lot of data that are not always available. In addition, this approach is rather complex compared to a steady state approach. This is because of considering a lot of processes on-going in the system (e.g. in the soil), which needs a description in a comprehensive way, and this needs integration of many formulas into the model.

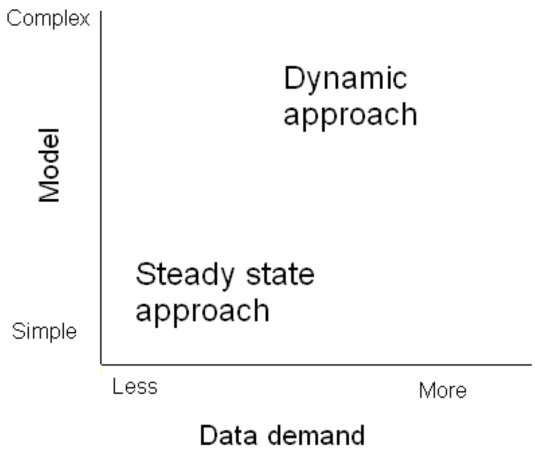



*Figure 4*
*Simplified schematic representation of relation between data demand (less data required versus more data required) and types of the model (simple versus complex) with two approaches: a steady state and dynamic.*

A steady state approach has no time component and thus considers processes of nutrient transformation at steady state conditions. This makes models more simple and easy to interpret. Models are usually based on empirical data and thus less input data are needed. However, the main disadvantage of the approach is that it does not take into consideration time dependent processes. This means that results of models can only be interpreted for that specific time when nutrient fluxes are modelled without considering changes from previous years (Arheimer and Olsson, 2010). The place of both approaches within data demand and their complexity is schematically shown in Figure 4.

Models also can be distinguished into two types: mechanistic (or physically based), where all processes are considered and empirical models, where processes are not explicitly included or described highly empirically. It is also possible to have models, which are combination of these two types. Dynamic models can be based on mathematical description of the processes (Arheimer and Olsson, 2010).

Which model approach to choose depends on the study purpose. In this study, however, since we consider phosphorus export, which has the ability to build up in the soil as well as in the river system over time, a dynamic approach is the most reasonable choice to consider rather than a steady state approach.

## 2.1 Regional scale

Modelling of phosphorus (P) export occurs more often at a regional scale than at a global scale. Here, 27 models were reviewed and almost all of them (26) are applied at a regional scale (Figure 5). This is because in many cases data are available at this scale rather than at the global scale (Alvarez-Cobelas et al., 2009).

Most of the examined models were developed starting from 1980s in United States and Europe (Table 1). This can be explained by the fact that since that time environmental problems have become an interest of scientists, particular eutrophication developments in surface waters (Alvarez-Cobelas et al., 2009). For instance, the Black Sea ecosystems have been suffered from eutrophication since 1970s (Borysova et al., 2005; BSC, 2008).

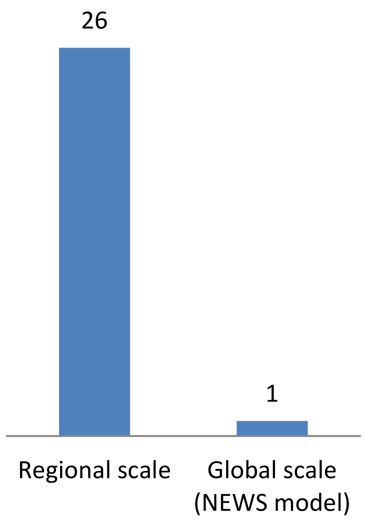



*Figure 5*
*Number of examined models that are applied at the regional and global scales.*

The examined regional P models are divided into three major categories in this study. The first category consists of the models that estimate P transport at soil/field scale (Section 2.1.1). The second category combines the models that estimate P transport only in water bodies, where nutrient sources may be considered as external loadings (Section 2.1.2). Finally, the last category includes models that estimate P export at watershed/river basin scale (Section 2.1.3). The majority of the examined models (12) are focused on modelling P export at watershed/river basin scale rather than on at soil/field scale or in water bodies (Table 2). Only five P models are linked to soil/field scale while nine P models are related to water bodies. The dominance of P models at river basin scale might be associated with their performance at larger scale covering not only P modelling from the soil to surface waters, but also within the water systems.

***Table 1***
*Time and place, where models were developed.*

| Time (years) | Regional scale | Developed in country or continent |
|---|---|---|
| Till 1980 | ANSWER | United States |
| From 1981 to 1990 | ANIMO | The Netherlands |
| | EPIC | North America |
| | GLEAMS | United States |
| | AGNRS | United States |
| | NWPCAM | United States |
| | QUAL2E | United Sates |
| | NBV-P | Sweden |
| From 1991 till now | MONERIS | Europe |
| | SWAT | America |
| | SPARROW | United Sates |
| | MACRO | Sweden |
| | ANSWER-2000 | United Sates |
| | CE-QUAL-RIV1 | United Sates |
| | DBS** | Europe |
| | PH-ALA | Italy |
| | NL-CAT | Europe |
| | LEEDS | Sweden |
| | PC-Lake | Europe |
| | TRANS | Europe |
| | BATHTUP | United States |
| | LIMNOD | Switzerland |
| | GREEN | Europe |
| | TRK system | Europe |
| | RIVERSTRAHLER | Europe |
| | PREWet | United Sates |
| | PolFlow | Europe |

* *(started from 1980s).*
** *DBS=DELWAQ-BLOOM-SWITCH.*

A dynamic approach is applied to 2/3 of reviewed models (18 out of 26 models) (Table 2). P models at soil/field scale are based only on a dynamic approach. Inversely, around 1/3 of P models focusing on P modelling in water bodies and around 2/4 of P models focusing on P modelling at river basin scale apply the steady state approach. This indicates that with increasing scale of modelling, the complexity of models and data demands are increasing as well and thus, steady state approaches are more often applied.

*Table 2*
*Reviewed models in this study. The models are divided into three main categories such as P modelling at soil/field scale, P modelling in water bodies and P modelling at watershed/river basin scale. The models are separated into models that use dynamic approach and models that use steady state approach.*

| P modelling (different scales) | | | |
|---|---|---|---|
| Model approach | At soil/field scale (Section 2.1.1) | In water bodies (river channels, lakes, streams, etc.) (Section 2.1.2) | At watershed/river basin scale (Section 2.1.3) |
| Dynamic | ANSWER<br>ANIMO<br>EPIC<br>GLEAMS<br>MACRO | CE-QUAL-RIV1<br>DBS<br>LEEDs<br>LIMNOD<br>PC-LAKE<br>PH-ALA | AGNPS<br>HBV-P<br>NL-CAT<br>RIVERSTRAHLER SWAT<br>TRK system<br>TRANS |
| Steady state | | BATHTUP<br>PREWet<br>QUAL2E | GREEN<br>MONERIS<br>NWPCAM<br>PolFlow<br>SPARROW |

### 2.1.1 P modelling at soil/field scale

P modelling at soil/field scale is associated with modelling of P export from land to surface and/or ground water excluding retention in surface waters. These investigated models, i.e. ANSWER, ANIMO, GLEAMS, EPIC and MACRO are all dynamic as it has been already mentioned above (see also Table 2). A description of their abbreviations as well as main references and internet-sources can be found in Table 3.

*Table 3*
*Abbreviations, references and internet-sources of the models that estimate phosphorus fluxes at soil/field scale*

| Model | Abbreviation | References | Internet sources |
|---|---|---|---|
| ANSWER | Aerial Nonpoint Source Watershed Environment Response Simulation | Beasley and Huggins, 1978; Dillaha et al., 1982; Parsons et al., 2004; Simon et al., 2005 | http://s1004.okstate.edu/S1004/Regional-Bulletins/Modelling-Bulletin/ModelSummaryTables.html#998197 |
| ANIMO | Original version: Agricultural NItrogen Model; Recently improved: Agricultural NutrIent Model | Schoumans et al., 2002; McGechan and Hooda, 2010; Schoumans and Silgram, 2003; Groenendijk and Kroes, 1999; Groenendijk et al., 2005; Kroes and Rijtema, 1998; Arheimer and Olsson, 2010 | http://ecobas.org/www-server/rem/mdb/animo.html |
| EPIC | Erosion Productivity Impact Calculator; Environmental Policy Impact Climate Model | Arheimer and Olsson, 2010; De Barros et al., 2001; Simon et al., 2005 | http://s1004.okstate.edu/S1004/Regional-Bulletins/Modelling-Bulletin/ModelSummaryTables.html#998197 |
| GLEAMS | Groundwater Loading Effects of Agricultural Management Systems | Arheimer and Olsson, 2010 | http://www.bae.ncsu.edu/www3/acad/Regional-Bulletins/Modelling-Bulletin/ASCE99-gleams-draft.html |
| MACRO | Water and Solute Transport in Macroporous Soil | McGechana et al., 2005; Arheimer and Olsson, 2010; | http://ecobas.org/www-server/rem/mdb/macro.html |

The ANSWER model is the oldest of the considered models. It was developed in 1970s while ANIMO, GLEAMS and EPIC were developed in 1980s (Table 1). The MACRO model is a relatively new model developed in 1990s (Table 1). Three of them (ANSWER, GLEAMS, EPIC) were originally established in America whilst ANIMO and MACRO were developed in the Netherlands and Sweden respectively (Table 1). Descriptions for each model are summarized in Table 4.

*Table 4*

*Summary of main characteristics of the models, where N is nitrogen; P is phosphorus, SW is surface water. GW is ground water. Surface pathway includes nutrient losses via runoff while subsurface pathway considers nutrient losses via their leaching through the soil.*

| Main characteristics | | Models | | | | |
|---|---|---|---|---|---|---|
| | | ANSWER** | ANIMO** | GLEAMS | EPIC | MACRO |
| Purpose | | Export of nutrients to SW | Leaching of nutrients to SW and GW | Movement of pollutants within root zone and effects of agricultural practices | N, P transport and their losses from agricultural areas; Effects of conservation practices | Main focus on water quality affected by agricultural activities; Nutrient transport |
| Modeled substances | | N and P | N and P | N, P and pesticide | N, P and pesticide | N, P, water flow |
| Main inputs | | Land use;<br>Soil properties;<br>Management practices | Land use;<br>Soil type;<br>Water fluxes | Precipitation;<br>Temperature; Watershed flow profile; Fertilizer and manure applications;<br>Pesticide inputs; Initial soil N and P; For each horizon: clay, silt, calcium carbonate, organic matter content, base saturation | Weather conditions;<br>Soil types;<br>Management systems | Initial values of N and P content in the soil;<br>Soil types;<br>Land use |
| Main outputs | | N and P losses to SW | N and P losses to GW and SW | N, P and pesticide losses to surface runoff;<br><br>N and P cycles | N, P cycles (soluble inorganic and organic) and N, P and pesticide losses from the field | Nutrient losses from farm catchments |
| Addressed main processes In the soil | | Transformation, mineralization of N and P | Retention, transport, transformation of N and P | N-related (e.g. nitrification/ denitrification, ammonifica-tion, crop uptake);<br>P-related (mineralization, immobilization, crop uptake, sediment and leaching) | N-related (denitrification, immobilization, mineraliza-tion, biological nitrogen fixation, crop uptake and fertilization); P-related (mineralization, sorption-desorption process, crop uptake and fertilization) | P-related (P sorbed onto particles; transformation and transportation via the soil) |
| Space and time scale | | Grid cells,<br><br>Estimation for different time-step | Field scale with vertical resolution of 7-15 m in the soil; Annual | Agricultural fields with vertical resolution of five soil horizons (based on user selection); Annual estimations with daily time-step | Field scale<br><br>Simulations can be done on daily basis | Field soils, farms<br><br>Simulations can be done on daily basis |
| Type of the model* | | Process-based dynamic model on the basis of mathematical description | Mechanistic dynamic model | Process-based, conceptual dynamic model | Mathematical, conceptual dynamic model | Physically-based, mechanistic dynamic model |
| Sources | Diffuse | + | + | + | + | + |
| | Point | | | | | |
| Pathway | Surface | + | | + | + | + |
| | Subsurface | | + | + | | + (via soil matrix) |
| Nutrient retention in soil | | + | + | + | + | + |
| Application | | Watersheds of Georgia, United Sates and Europe | Dutch agricultural areas | Georgia, United Sates; adopted to European conditions; applied to Poland. Finland, Russia, Denmark, Spain, | North America; adopted to Europe; applied to Denmark, United Kingdom, France | United Kingdom, Spain, Denmark |
| Additional information (if available) | | See text | See text | This model is extension of CREAMS model;<br>The model considers dissolved and organic N, P | Includes GLEAMS, integrated to NELUP modelling system | The model is involved to EU forum FOCUS and to the EU project PEGASE |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based.*

** *model is described in a text.*

\+ *= model addresses nutrient sources, processes or pathways in its estimations.*

The main purpose of the models is focused on evaluating the impact of agricultural activities on water quality via inputs of nutrients to land by estimating their transformation in the soil matrix and leaching to surface and/or ground waters (Table 4). Almost all models consider nutrient inputs only to agricultural areas. They perform estimations for nitrogen (N) and phosphorus (P). GLEAMS and EPIC models also reflect on pesticides. Retention of P as well as N in the soil is taken into account in the models via for instance sorption-desorption and mineralisation processes. The models use different time and space resolutions. For instance, ANIMO, GLEAMS, MACRO and EPIC use field/farm as unit or plot while ANSWER is applied at grid cell scale. GLEAMS performs estimations for five different soil horizons, which are defined by users. This makes the model flexible with respect to this situation. Only the ANIMO model takes into account subsurface pathways of N and P losses to ground/surface waters while the others pay attention only on surface runoff. Since the models consider only agricultural areas, diffuse sources of N and P inputs to soils are dominant in the models.

Only two of the rest models (ANSWER and ANIMO) are described in detail below because of time limitation. Selection of those two models out of the rest was done considering different pathways of nutrients entering water bodies (surface via runoff and subsurface via leaching).

**ANSWER model**
There are two versions of the model, an initial version (ANSWER) and an updated version (ANSWER-2000). Here, most of the information here is referred to the updated model. This considers transport of nutrients (nitrogen and phosphorus) in the soil to streams. This model is specifically focused on agricultural areas. References to this model are presented in Table 2.

<u>Abbreviation:</u> Areal Non-point Source Watershed Environment Response Simulation.
<u>Purpose:</u> focus on water quality by estimating the fate of nutrients in the soil and their export to surface waters particular to streams (Beasley and Huggins, 1978; Parsons et al., 2004). The model can also be used to provide information about effects of management practices applied to agricultural areas. Consequently nutrient reduction strategies can be integrated into the model (Dillaha et al., 1982).
<u>Time scale:</u> this model is continuous and event-based. This means that all processes are described in the model during the event and these processes are simulated with different time steps. For instance, hydrological processes are simulated with 30-second time steps during the event (for instance, intensive precipitation). The period of simulation can be 20 or even more years (Parsons et al., 2004).
<u>Spatial scale:</u> this model is applied to relatively large-scale watersheds such as farms and fields (Parsons et al., 2004; Beasley and Huggins, 1978). The watersheds are divided into small grid cells (square or ha). All inputs data, simulations and outputs of the model are based on grid cells (range from 0.4 to 1ha). Vertical resolution of the model (soil thickness taken in the model), however, was not found from the examined literature.

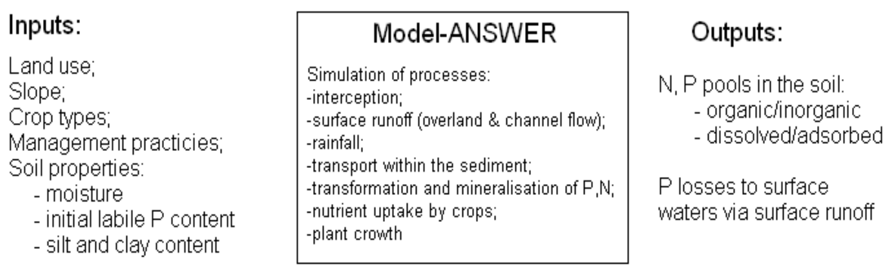



*Figure 6*
*Simplified schematic representation of ANSWER structure: inputs, main processes, which the model simulate and outputs. Source: Parsons et al., (2004).*

Approach used in the model: N and P dynamics in the soil are taken into account in the model. Nutrient pools and P losses to surface waters are expressed in concentrations.
Forms of modelled P: dissolved/adsorbed and organic/inorganic.
Model structure: this is a mathematical model, which estimates nutrient pools (N and P) in soils and P losses from watersheds via surface runoff as a function of inputs to watersheds such as soil properties and site-specific characteristics (for instance, land use, slope) and simulated processes in the soil (see Figure 6).
Applicability and historical aspects of the model: The first version of the model was developed in 1970s while current version (ANSWER-2000) was developed in the middle of 1990s in United State (see Table 1). The original model was aimed to perform simulations only towards surface runoff and main processes in the soils. Then, export of nutrients was added to the model. Strengths of the model are that effects of agricultural management strategies can be evaluated. Grid cells are small and thus more accurate information is provided. Furthermore, nutrient dynamics are taken into consideration. In addition, inputs to the model are relatively easy to obtain, for instance from land use maps. However, there are also some weaknesses. The model has not been applied to many watersheds. From the examined literature, the model was used in Indiana watersheds, in one watershed of Virginia and two watersheds of Georgia. Applications to watersheds with the other conditions like in Europe that are different from United Sates are uncertain. The model takes into account only diffuse sources of nutrients. Point sources as human wastes and detergents are not considered.

**ANIMO model**
There are two versions of the model: original and updated. This model has been used in the Netherlands specifically to evaluate P losses from agricultural areas to surface/ground water.
Abbreviation: in the original version of the model, the abbreviation stands for Agricultural Nitrogen Model. In the improved model, the abbreviation stands for Agricultural Nutrient Model because P is also included in the model.
Purpose: the model aims to estimate nutrient losses to any surface waters (ditches, canals etc.). The other purpose of the model is to assess long-term impact of different scenarios to reduce nutrient inputs to land (five scenarios available) (Schoumans et al., 2002; McGechan and Hooda, 2010; Schoumans and Silgram, 2003; Groenendijk et al., 2005).
Time scale: calculates nutrient losses annually. The time step of the model is daily.
Spatial scale: this model is applied to watersheds, polders and/or at field scale. The unit is plot up to maximum 100 km$^2$ (Schoumans and Silgram, 2003). All inputs, outputs and calculations are done at each plot (Schoumans et al., 2002). Vertical scale of the model covers around 7-15 m within the soil below the surface (Arheimer and Olsson, 2010).
Approach used in the model: this is a dynamic mechanistic model (Schoumans et al., 2002; McGechan and Hooda, 2010; Schoumans and Silgram, 2003; Groenendijk and Kroes, 1999; Groenendijk et al., 2005; Kroes and Rijtema, 1998; Arheimer and Olsson, 2010).
Forms of modelled P: particulate, dissolved organic/inorganic.

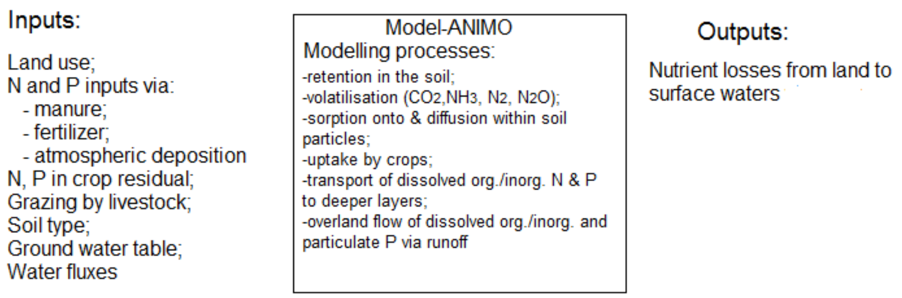



*Figure 7*
*Simplified schematic representation of ANIMO model with inputs, modelling processes and outputs. Sources: Schoumans et al., (2002); McGechan and Hooda, (2010); Groenendijk et al., (2005).*

Model structure: this model estimates nutrient (N and P) losses (in kg per ha) from agricultural areas via subsurface pathway (leaching to ground waters and surface waters). Nutrient losses are estimated as a function of nutrient inputs to land, soil properties and simulated N and P related processes in the soil, where nutrient retention, transformation and leaching to deeper layers are considered (see Figure 7). Cycling of organic matter is an important component in the model simulations (Schoumans and Silgram, 2003).
Applicability and historical aspects of the model: the model was developed in 1985 in the Netherlands and in 1991 ANIMO was updated in terms of added phosphorus (Schoumans and Silgram, 2003; Arheimer and Olsson, 2010). The model was integrated into the STONE model in order to be able to assess long-term effects of agricultural policies on N and P fluxes. In addition, the model is part of the NL-CAT model. Disadvantage of the model is its complexity and thus a lot of data are needed. Application of the model has been limited mainly to Dutch agricultural areas. The main advantage of the model is that it includes almost all important and time dependent processes of P in the soil. Hence, it gives a lot of insight in P behaviour.

### 2.1.2 P modelling in water bodies (river channels, ditches, streams, lakes)

Nine models with respect to phosphorus modelling in water bodies were reviewed, including LEEDs, DBS, PC-lake, BATHTUP, QUAL2E, LIMNOD, PH-ALA, CE-QUAL-RIV1 and PREWet. These are the models that estimate nutrient fluxes and/or transport independently from land. They consider effects of land sources (for instance, diffuse) via external nutrient loadings. These models pay more attention on internal nutrient loadings rather than on external ones. In most cases, these models are hydrological models. In contrast to P models at soil/field scale, the minority of these models are based on a steady state approach (Table 2 and Tables 6, 7 and 8). This can be explained by limited data. Furthermore some processes in the water system are difficult to model over time (over years and seasons). The model's abbreviations, main references to them as well as internet-sources are given in Table 5.

The oldest model is QUAL2E. This model was developed in 1980s while the rest was developed around 1990s (Table 1). Four models namely BATHTUP, QUAL2E, CE-QUAL-RIV1 and PREWet were originally established in the United States. PC-lake and DBS came from Europe while LEEDs, LIMNOD and PH-ALA are from Sweden, Switzerland and Italy respectively (Table 1). Detailed information for each model separately is summarized in Tables 6, 7 and 8.

Overall purpose of the models is to address water quality problems in different water bodies with particular focus on eutrophication. More specific purposes are given in Tables 6, 7 en 8. These models estimate not only phosphorus, but also nitrogen and other water quality variables (e.g. chlorophyll-a, algal biomass, biological oxygen demand: BOD etc.) except for the LEEDs model, which is particular for P. Some of the models are used only for lake waters, i.e. LEEDs, PC-lake, LIMNOD and PH-ALA (Table 6). The PreWet model performs estimations for wetlands only, whilst CE-QUAL-RIV1 and QUAL2E can be applied for both wetlands and streams (Table 7). Water quality problems in lakes as well as in rivers are addressed by the DBS and BATHTUP models (Table 8).

*Table 5*
*Abbreviations, references and internet-sources of the models that estimate phosphorus fluxes in water bodies such as river channels, lakes, ditches.*

| Model | Abbreviation | References | Internet-sources |
|---|---|---|---|
| Dynamic models | | | |
| CE-QUAL-RIV1 | - | - | http://el.erdc.usace.army.mil/elmodels/riv1info.html |
| DBS | DELWAQ-BLOOM-SWITCH | Van der Molen et al., 1994; Arheimer and Olsson, 2010 | - |
| LEEDs | Lake Eutrophication Effect Dose Sensitivity | Dahl, 2004 (thesis report); Dahl, M. and Perz, B.C. 2004 | - |
| LIMNOD | - | Arheimer and Olsson, 2010 | - |
| PC-Lake | - | Janse, 2005 (thesis); Arheimer and Olsson, 2010 | - |
| PH-ALA | - | Arheimer and Olsson, 2010 | - |
| Steady-state models | | | |
| BATHTUP | - | Kennedy, 1995 | http://www.wes.army.mil/el/elmodels/emiinfo.html |
| PREWet | - | - | http://el.erdc.usace.army.mil/elmodels/wwqinfo.html |
| QUAL2E | Enhanced Stream Water Quality Model | Arheimer and Olsson, 2010; Brown and Barnwell 1987 | http://s1004.okstate.edu/S1004/Regional-Bulletins/Modelling-Bulletin/ModelSummaryTables.html#998197 http://smig.usgs.gov/SMIC/model_pages/qual2e.html #ABSTRACT |

The vertical spatial resolution of the examined models differs among them. The LEEDs, LIMNOD and DBS models divide water into two layers, i.e the epilimnion (top layer) and hypolimnion (deeper layer) or even more layers (e.g. DBS). The PH-ALA model simulates P concentrations in water and in the sediment. Simulations can be made on a monthly (e.g. LEEDs) and on a daily (e.g. QUAL2E, DBS) basis (Table 6, 7 and 8).

Nutrient (N and P) removal in water bodies are considered in all models, but with different ways of describing the processes related to this removal (Tables 6, 7 en 8). The main processes related to P include adsorption/desorption of P in the sediment, P mineralisation and transformation in water column.

Some models address point and diffuse sources of nutrients via external loadings from land (LEEDs, PC-lake, BATHTUP, DBS) (Table 6, 7 and 8). For instance, QUAL2E model addresses only point sources of nutrients, which directly enter the water (Table 7). The descriptions of the models in the available information (Table 5) contained no data with respect to nutrient sources for the models LIMNOD, CE-QUAL-RIV1, PH-ALA and PREWet. Only one model, LEEDs, is described below (summary in Table 6). The model was chosen because of focusing specifically on different forms of P rather than on other water quality variables.

*Table 6*

*Summary of main characteristics of the models that are applied only to lake waters, where N and TN are nitrogen and total nitrogen respectively; P, TP, DIP and PP are phosphorus, total phosphorus, dissolved inorganic phosphorus and particulate phosphorus respectively; C is carbon and COD is chemical oxygen demand.*

| Main characteristics | | Models | | | |
|---|---|---|---|---|---|
| | | LEEDs** | PC-lake | LIMNOD | PH-ALA |
| Purpose | | Effects of P loads exported to lakes | Transition from clear-water state to turbid water state and vice versa | Effects of different scenarios on water quality in lakes in terms of nutrients | Long-term effects of eutrophication on water quality |
| Modeled substances | | P and suspended sediments | N, P, phytoplankton, macrophytes, | P, C | P and phytoplankton |
| Main inputs | | River flow;<br>Point sources;<br>Weather parameters;<br>Initial P values in sediment | Water flow; N, P loadings to the lake; Temperature; Light; Lake size and depth; Initial N, P content | Lake size and depth;<br>Temperature;<br>Conductivity | Temperature; Wind and water velocity; Density anomaly; Daily sunshine; Location of pollution spots |
| Main outputs | | TP, DIP, PP content;<br>Phytoplankton content;<br>COD;<br>Chlorophyll-a content | Concentrations (mg/l) of TN; TP; $PO_4$; detrital P, N; algal P,N in water and the sediment | Concentrations of dissolved and particulate P, oxygen, organic carbon | P concentrations in water and in the sediment |
| Addressed main processes In the soil | | P build-up in the sediment and its release from the sediment | Infiltration; Mineralization; Adsorption/ desorption of P; Nitrification/ denitrification; Nutrient uptake | Physical, biochemical and processes related to sedimentation | ? |
| Space and time scale | | Lake area that is divided vertically into epilimnion and hypolimnion layers;<br>Monthly | Lake area;<br>?  | Lake area divided vertically into emilimnion and hypolimnion layers<br>? | Lake area<br>? |
| Type of the model* | | Complex dynamic model that based on mass-balance approach | Mechanistic dynamic model | Mechanistic dynamic model | Mechanistic dynamic model |
| Sources | Diffuse | + | External loadings as sum of point and diffuse inflow | ? | ? |
| | Point | + | | | |
| Nutrient retention in water | | + | + | + | + |
| Application | | Swedish lake | Applied to shallow lakes in the Netherlands | Applied to lake in Switzerland | Applied to lake in Italy |
| Additional information (if available) | | See text | Describe the most important ecological interactions | | Consists of two models: hydrological model and a mass-balance model |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based.*

** *model is described in a text.*

\+ *= model addresses nutrient sources, processes or pathways in its estimations.*

? *= information was not found or uncertain.*

*Table 7*

*Summary of main characteristics of the models that are applied either to streams or wetlands, where N and TN are nitrogen and total nitrogen respectively; P and TP are phosphorus and total phosphorus respectively; OD and SOD are oxygen and sediment oxygen demands respectively; BOD is biochemical oxygen demand.*

| Main characteristics | | Models | | |
|---|---|---|---|---|
| | | CE-QUAL-RIV1 | QUAL2E | PREWet |
| Purpose | | Predict water quality variables | Impact of human activities on water quality | Removal of nutrients, chemicals by wetlands;<br>Effects of this removal on water quality |
| Modeled substances | | N,P, Oxygen, Algal, Iron | N,P, SOD, BOD, Algae, Coliforms | N, P, metals, organic chemicals, coliforms, suspended solids, OD |
| Main inputs | | Uncertain | Stream/river data: reach length. Location, latitude, longitude etc.; Inflow per reach; Temperature, wind speed etc.; Organic phosphorus settling rate; rate constant for the decay of organic phosphorus to dissolved phosphorus; Initial P content; Others | Wetland characteristics |
| Main outputs | | Hydraulic characteristics (e.g. depth, velocity); Temperature; COD; Dissolved inorganic/organic P,N; Algal; Dissolved iron; Coliform bacteria | Dissolved inorganic/organic N, P content at stream reach, SOD, BOD, Algae, Coliforms | TN, TP, metals, organic chemicals, coliforms, suspended solids, OD |
| Addressed main processes In the soil | | ? | N-related (mineralization; nitrification; uptake by the algae, regeneration from the sediment and from algal respiration); P-related (mineralization; sedimentation and uptake) | ? |
| Space and time scale | | Stream or river waters;<br>Simulations are done during the event | Stream reach<br>Daily loads | ?<br>? |
| Type of the model* | | Dynamic model | Steady state model | Steady state model |
| Sources | Diffuse | ? | | ? |
| | Point | ? | + | ? |
| Nutrient retention in water | | ? | + | ? |
| Application | | Applied to streams in United States; Can be applied to rivers | Applied to streams in United Sates | Applied to wetlands in United Sates |
| Additional information (if available) | | The model is based on hydrodynamic code and water quality code | Developed in 1987; The model can perform dynamics for algal and oxygen only, but time-step has to be determined by users | |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based.*

\+ *= model addresses nutrient sources, processes or pathways in its estimations.*

? *= information was not found or uncertain.*

*Table 8*
*Summary of main characteristics of the models that are applied to both rivers and lakes, where N and TN are nitrogen and total nitrogen respectively; P and TP are phosphorus and total phosphorus respectively; Si is silica; C is carbon*

| Main characteristics | | Models | |
|---|---|---|---|
| | | BATHTUP | DBS |
| Purpose | | Effects of eutrophication on water quality variables | Address eutrophication problems;<br>Effects of reducing external nutrient loads |
| Modeled substances | | N, P, Oxygen, chlorophyll-a | N, P, Si, C cycle, oxygen |
| Main inputs | | Watershed characteristics; N,P loads; Water inflow; Morphology of lakes, reservoirs, rivers | Inflows to the system; Outflows to the system; Loadings of nutrients to the system; Irrigation; Water temperature; Grazing rate |
| Main outputs | | TP, TN content; Chlorophyll-a; Transparency; Oxygen depletion | Nutrient content, oxygen |
| Addressed main processes in the soil | | Processes that are related to N, P transport and sedimentation | Mineralization; Sedimentation; Resuspension; Adsorption/desorption (for P only); Uptake by plants in waters |
| Space and time scale | | Water body<br><br>? | For instance, lake with several segments; Outputs are provided daily |
| Type of the model* | | Steady state model | Process-based, mechanistic dynamic model |
| Sources | Diffuse | + ( via water inflow) | + (via external loadings of nutrients) |
| | Point | | |
| Nutrient retention in water | | + | + |
| Application | | Applied to rivers, lakes, reservoirs in United Sates | Applied to lakes in the Netherlands and other countries, which belong to Danube river basin; Applied for the assessment of the Black Sea |
| Additional information (if available) | | Usually applied to situation, where data is limited | Developed in 1994 by Institute for Inland Water Management and Waste Water Treatment;<br>The model can be applied to rivers, estuaries, oceans |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based.*
\+ *= model addresses nutrient sources, processes or pathways in its estimations.*
? *= information was not found or uncertain.*

**LEEDS model**
Abbreviation: Lake Eutrophication Effect Dose Sensitivity
Purpose: this is the model that specifically was developed for modelling phosphorus content and suspended sediments in lake waters. Thus the main purpose is to evaluate effects of phosphorus loads to lakes (deep and shallow) resulting from external inflow, point sources and climate forcings (precipitation, temperature, wind).
Time scale: inputs data and estimations are on monthly resolution.
Spatial scale: there are distinguished horizontal and vertical resolutions. The horizontal resolution of the model is area of the lake. The area can be divided into several sub-areas, but this depends on the total area of the lake. The vertical resolution covers epilimnion (top) and hypolimnion (deeper) layers of the lake water. Therefore, phosphorus content can be estimated in surface water, in deep water and in the sediment layer. The model covers all important time-dependent processes of P retention and transformation in lake waters.

Approach used in the model: this is a dynamic complex model based on a mass-balance approach. Complexity is related to a lot of variables and parameters used by the model.
Forms of modelled P: PP, dissolved inorganic P ($PO_4$) and total P (TP).

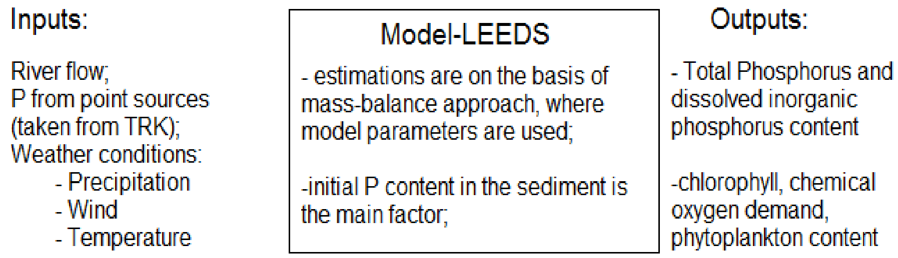



*Figure 8*
*Simplified schematic representation of LEEDs model with its inputs and outputs. Sources: Dahl, (2004); Dahl. M. and Perz. B.C. (2004).*

Model structure: this is an independent model in terms of modelling P only in lakes without touching processes at soil scale. The model inputs are weather conditions as wind, temperature, rainfall and point sources. Point sources of P are taken from TRK system (the systems that includes two dynamic simulation models, SOILNDB and HBV-N). Diffuse sources are considered via external loadings to water. The model calculates TP, PP and DIP ($PO_4$) content on the basis of a mass-balance approach. Initial content of P in the sediment is assumed to be the main factor that affects significantly final results (Figure 8).

Application and historical aspects of the model: the model has been recently developed and applied to a Swedish lake. Inclusion of sediment-water interaction to the model makes it more efficient among the other dynamic P models. This is because the inclusion gives possibility to estimate build-up of P in the sediment and release from the sediment over time. In addition, relationship between the sediment and water column has been known as the main source of internal P in waters and hence became main concern of water managers (Scheffer, 2004). However, complexity of the model does not allow easily to apply the model to other conditions (not only in Sweden).

### 2.1.3 P modelling at watershed/river basin scale

These are the models that perform modelling of P export at watershed/river basin scale covering not only P processes in the river system, but also in the soil. In some cases, these models combine hydrological models with models that estimate nutrient export from land to water bodies. In addition, some models provide riverine nutrient export to coastal waters.

In this section, twelve models are reviewed and they are AGNPS, SWAT, NL-CAT, TRK system, HBV-P, TRANS, RIVERSTRAHLER, MONERIS, GREEN, SPARROW, PolFlow and NWPCAM. Their abbreviations, main references and internet-resources used in this study are provided in Table 9. More than half of the models are based on a dynamic approach. These models are AGNPS, SWAT, NL-CAT, TRK system, HBV-P, TRANS, RIVERSTRAHLER. Estimations of P export in the other models are done on the basis of steady state approach (Table 2 and 9).

Most of the models were developed starting from 1991 except for AGNPS, HBV-P and NWPCAM, which were developed between 1981 and 1990 (Table 1). The majority of the examined models (eight out of twelve models) were established in Europe while the rest (four models) was developed in United Sates namely SWAT, AGNPS, NWPCAM and SPARROW models (Table 1). Information about the models is summarized in Table 10.

*Table 9*

*Abbreviations, references and internet-sources of the models that estimate phosphorus export at watershed/river basin scale*

| Name of the model | Abbreviation | Main reference | Internet sources |
|---|---|---|---|
| Dynamic models | | | |
| AGNPS | AGricultural Non-Point Source pollution model or AGricultural NonPoint Source | Arheimer and Olsson, 2010; Young et al., 1986; Simon et al., 2005 | - |
| HBV-P | - | Andersson et al., 2003; Andersson et al., 2005; Dahl, M. and Perz, B.C., 2004 | http://harmoniqua.wau.nl/public/Papers/DifPol_04_hqua_hbvnp_paper_v4.pdf |
| NL-CAT | - | Schoumans and Silgram, 2003 | - |
| RIVERSTRAHLER | - | Garnier et al., 2005; Andersson et al., 2005 | - |
| SWAT | Soil and Water Assessment Tool | Neitsch et al., 2010; Grizzetti et al., 2003; Gassman et al., 2007; Arheimer and Olsson, 2010; Andersson et al., 2005 | http://www.brc.tamus.edu/swat/ |
| TRK system | - | Dahl M. and Perz B. C. 2004; Schoumans and Silgram, 2003 | - |
| TRANS | Transport, Removal and Accumulation of Nutrients in waterSheds | Kronvang et al., 1999; Andersson et al., 2005 | - |
| Steady state models | | | |
| GREEN | Geographic Regression Equation for European Nutrient losses | Grizzetti and Bouraoui, 2006 | |
| MONERIS | The Modelling Nutrient Emissions in River Systems | Behrendt et al., 2007 (Manual); Venohr et al., 2009 (Manual); Schoumans and Silgram, 2003 | http://www.iia.cnr.it/rende/big_file/EUROCAT/publications/EUROCAT%20WD22.pdf |
| NWPCAM | the National Water Pollution Control Assessment Model | USEPA, 2000 | - |
| PoLFlow | Pollutant Flow | De Wit and Pebesma, 2001; De Wit, 2001; Andersson et al., 2005 | - |
| SPARROW | SPAtially Referenced Regressions On Watershed attribute | Grizzetti and Bouraoui, 2006; Smith et al., 1997; Smith et al., 2005 | http://water.usgs.gov/nawqa/sparrow/FAQs/faq.html#1 |

*Table 10*

*Summary of main characteristics of the models that are applied at watershed/river basin scale, where N and TN are nitrogen and total nitrogen respectively; P and TP are phosphorus and total phosphorus respectively.*

| Main characteristics | | Models | | | |
|---|---|---|---|---|---|
| | | SWAT | TRANS | AGNPS | TRK system |
| Purpose | | Environmental problems of watersheds resulted from non-point sources | Nutrient losses from watersheds | Nutrients and pesticide loadings that are resulted from non-point sources | Nutrient transport to seas, their sources and retention within the basin; Effects of mitigation policies |
| Modeled substances | | Nutrients | N, P | N, P | N, P |
| Main inputs | | Hydrology; Soil properties; Humidity, wind, precipitation; Crops; Fertilizer and manure inputs | Soil type; Land use; Hydrology (from MIKE-11); Others | Land use; Slope; Soil characteristics; Information about point source; Others | Crops; Soil types; Land use; Climate variables; Fertilizer regime |
| Main outputs | | Diffuse N,P emissions at sub-watershed outlet; Removal of N, P in the basin (e.g. via retention) | N, P losses from diffuse sources; TN, TP fluxes in water and sediment | N, P loadings | N, P loads; Source contribution |
| Addressed main processes<br>In the soil | | Evapotranspiration Infiltration; Nutrient losses within the e.g. river channel (e.g. retention) | Denitrification; Deposition | ? | Processes that are associated with three models: SOILNDB, ICECREAM and HBV-NP |
| Space and time scale | | Sub-watersheds, watershed, basin with vertical resolution of 1m in the soil (ten layers); Area in a range of 0.01-100km$^2$; Daily time-step for simulations | Watershed<br><br>Annual | Watershed, calculations are done at grid-cell resolution with size between 0.4-16 ha Simulations of nutrient transport are done during the event (event-based) and can be daily | Sub-watersheds within 1m of soil depth;<br>Annual and for simulations - daily |
| Type of the model* | | Physically-based, complex conceptual dynamic model | Dynamic model | Dynamic conceptual model, with focus on mathematic approach to describe processes | Dynamic model |
| Sources | Diffuse | + | + | + | + |
| | Point | | + | + | + |
| Pathway | Surface | + | + | + | + |
| | Subsurface | + | + (via coefficient) | | + (via leaching through the soil) |
| Nutrient retention in soil | | + (expressed by a parameter) | | ? | + |
| Nutrient retention in water | | In ponds, wetlands, rivers (expressed by a parameter) | + | ? | + |
| Application | | Applied to large rivers, where dominant land use is agriculture | Applied to Gjern river basin during the period of 1994 - 1995;<br>Mainly applied to rural areas | Applied almost to all European countries: Austria, Belgium, Switzerland. Denmark, Finland, France, the Netherlands, Poland, Russia | Applied to Sweden: nutrient export from Sweden to the sea |
| Additional information (if available) | | P associated with sediment processes is based on CREAMS model; The model is based on SWIM model | It is recently developed; It is based on hydrodynamic model MIKE-11, which simulates water flow | Originally developed in 1987 in United States; adopted to European watersheds; consider urban and agricultural areas; diffuse source are taken into account via erosion from agricultural areas; uses CREAMS model to predict nutrient export | Include GIS;<br>Based on SOILNDB, ICECREAM and HBV-NP models, which are dynamic; |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based.*
\+ *= the model addresses nutrient sources, processes or pathways in its estimations.*
? *= information was not found.*

*Table 10 (Continued)*
*Summary of main characteristics of the models that are applied at watershed/river basin scale, where N and TN are nitrogen and total nitrogen respectively; P and TP are phosphorus and total phosphorus respectively.*

| Main characteristics | | Models | | | |
|---|---|---|---|---|---|
| | | RIVERSTRAHLER | NL-CAT | HBV-P** | GREEN** |
| Purpose | | Nutrient transport and budgets | Evaluation of pollution and effects of management strategies | Riverine P transport from watersheds; Scenario analyses | Define watersheds that have high level nutrient inputs |
| Modeled substances | | N, P | N, P | P | N, P |
| Main inputs | | Ground water;<br>Land use;<br>Water flow;<br>Point sources: industrial, municipal, wastewaters; | Atmospheric deposition;<br>Fertilizer and manure;<br>Plant uptake;<br>Management practices;<br>N fixation;<br>Point sources;<br>Water flow | Atmospheric deposition; Rural households; Industries; Wastewater treatment plants; Temperature; Precipitation; Surface runoff | Basin characteristics; Diffuse and point sources |
| Main outputs | | Dissolved and particulate N, P budgets;<br><br>Dissolved and particulate N, P fluxes at the outlet of the river basin (coastal zones) | In-stream retention in streams and rivers;<br>Loads/concentrations from land to water bodies (excluding retention in water):<br>Soluble inorganic P;<br>Dissolved organic N/P;<br>Particulate organic N/P;<br>TP; Nitrate; Ammonium;<br>Dissolved inorganic N | P fluxes at watershed outlets | N, P loads at river outlets |
| Addressed main processes In the soil | | Denitrification;<br>Rock weathering;<br>P exchange between particulate and dissolved parts;<br>Biological, physic-chemical in-stream processes | N, P mineralization;<br>C cycle; P sorption/ desorption; P precipitation;<br>Nitrification/denitrification<br>Volatilization; Erosion (gross/net) | P-related processes to its transformation and export within the soil and in water bodies | Retention processes in the soil and water |
| Space and time scale | | River basin that can be divided into sub-basins;<br><br>Annual | Watersheds, with vertical resolution of 1m in the soil;<br>Outputs are calculated daily | Watersheds,<br><br>Monthly and/or seasons | River basin<br><br>Annually |
| Type of the model* | | Dynamic model | Process-based, dynamic model | Dynamic model | Steady state model |
| Sources | Diffuse | + | + | + | + |
| | Point | + | + | + | + |
| Pathway | Surface | + | + | | + |
| | Subsurface | + (via coefficient) | + | + | |
| Nutrient retention in soil | | Uncertain | + | Uncertain | + (via parameter) |
| Nutrient retention in water | | Uncertain | + | + | + (via parameter) |
| Application | | Applied to Seine river basin, Mosel, Scheldt, Danube; Can be applied to other European rivers. | European watersheds | Swedish watersheds | European river basins |
| Additional information (if available) | | Budgets are calculated as a function of diffuse and point sources; Retention within the drainage network and reservoirs are provided as difference between N,P budgets and N,P fluxes at the outlets; Diffuse sources are taken into account via constant concentration of nutrients in water flow from the watershed; This model was improved for P dynamics | Consider agricultural and natural areas;<br>The model consists of several models: ANIMO, which is responsible for N,P losses from the soil to water, SWAP, SWQN and SWQL models are responsible for modelling nutrient retention in surface waters | See text | See text |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based;*
** *model is described in a text;*
\+ *= model addresses nutrient sources, processes or pathways in its estimations.*

*Table 10 (Continued)*

*Summary of main characteristics of the models that are applied at watershed/river basin scale, where N and TN are nitrogen and total nitrogen respectively; P and TP are phosphorus and total phosphorus respectively.*

| Main characteristics | | Models | | | |
|---|---|---|---|---|---|
| | | NWPCAM | PolFlow | MONERIS | SPARROW |
| Purpose | | To control water quality;<br>To evaluate economic benefits from water management policies | Nutrient export via rivers to coastal waters;<br>Effects of management strategies | Identification of main nutrient sources;<br>Assessment of nutrient export and nutrient retention in river systems | Riverine export of nutrients to coastal waters |
| Modeled substances | | N, P | N, P | N, P | N, P |
| Main inputs | | Point sources<br>Non-point sources;<br>Discharge data;<br>Land use;<br>Hydrological data;<br>AFO/CAFOs (animal feeding operations; C-concentrated) data | Soil type;<br>Aquifer type;<br>Nutrient sources (e.g. agriculture and industry);<br>Runoff;<br>Lithology | Land cover; Slope; Soil texture; Livestock density; Manure and fertilizer applications; Runoff;<br>Precipitation;<br>N deposition;<br>Population density, Sewage plants; Plant uptake;<br>Management practices | Fertilizer,<br>Manure.<br>Atmospheric deposition;<br>Channel characteristics, e.g. size;<br>Others |
| Main outputs | | WTB (Willing To Pay to improve water quality);<br>TN, TP loadings to agricultural cells and subset of rivers/streams | 5-year average N, P fluxes at the river outlet | Emissions from land to water bodies:<br>- TP and suspended solids concentrations/loads;<br>- DIN and TN concentrations/ loads; Retention of nutrients in water systems and below the root zone | TN, TP at river basin outlets |
| Addressed main processes<br>In the soil | | Processes related to nutrient transport from land to river network and their transport in-streams | Loss of nutrients in the river network and in the soil-groundwater system are described by parameters | Denitification;<br>Sediment delivery function;<br>Enrichment ratio | Main equation does not describe physical process of N, P cycles |
| Space and time scale | | National scale (states) with focus on river networks<br><br>Annually | River basin with spatial resolution of 1km$^2$;<br>5 year time step, run can be performed for 5-50 years | Watersheds within the river basin, where root zone is considered;<br><br>Annually | River basin<br><br>Annual loads (in kg/year) |
| Type of the model* | | Steady state | Process-based, steady state | Conceptual, steady state | Mechanistic, steady state |
| Sources | Diffuse | + | + | + | + |
| | Point | + | + | + | + |
| Pathway | Surface | + | + | + | + |
| | Subsurface | | Uncertain | + | |
| Nutrient retention in soil | | | + (parameter) | + | Uncertain |
| Nutrient retention in water | | + | + (parameter) | + | Uncertain |
| Application | | In United Sates | Europe, particular applied to Elbe and Rhine river basins | Applied to Danube river basin, | Applied in United Sates; used in many models as the basis |
| Additional information (if available) | | Retention in water is considered via described kinetics;<br>Modelling nutrient transport is based on SPARROW model | GIS system is a part of the model; Leaching from the soil is considered, but not explicitly described; Dynamic function is considered for nutrient delay traveling from the soil to surface water | GIS is included in the model; Considers agricultural and natural areas | Simplified illustration of nutrient losses within the river system and pathways of nutrient transport; The model is based on mass-balance approach;<br>Regression analysis is used |

* *model type is classified as dynamic/steady state, mechanistic/conceptual, physically-based, process-based;*

\+ *= model addresses nutrient sources, processes or pathways in its estimations.*

Five main purposes of the reviewed models can be distinguished such as (see also Table 10):
1. To analyze environmental problems caused by non-point sources: AGNPS and SWAT models;
2. To estimate nutrient losses from watersheds: TRANS, HBV-P, NL-CAT and MONERIS models;
3. To estimate nutrient export to river outlets: TRK system, RIVERSTRAHLER, GREEN, PolFlow and SPARROW models;
4. To assess effects of management strategies applied to watersheds: PolFlow, NWPCAM, HBV-P, NL-CAT and TRK system;
5. To identify dominant sources of nutrients: MONERIS and TRK system.

Almost all models perform their estimations for nutrients namely N and P, except for HBV-P model, which addresses only P export (Table 10).

The examined models in this study are based on different scales (Table 10). Some models are based on watershed scale (or watershed is divided into sub-watershed). These are SWAT (area in a range of 0.01 to 100 km$^2$), AGNPS (grid cells in a range of 0.4 to 16 ha), TRK system, TRANS, HBV-P, NL-CAT and MONERIS models. Few models have river basin scale namely RIVERSTRAHLER, GREEN, PolFlow (area of 1 km$^2$) and SPARROW models. And one model, NWPCAM, is based on national scale. Vertical resolution also differs between the models. For instance, estimations of nutrient fluxes are performed within the root zone in the MONERIS while within 1m of soil thickness in the NL-CAT, SWAT and TRK system.

Some of the models estimate nutrient export on annual basis. These models are TRANS, TRK system, GREEN, NWPCAM, MONERIS, SPARROW and RIVERSTRAHLER (Table 10). NL-CAT provides outputs on daily basis while AGNPS provides during the event. Internal time steps can be involved in the models. For instance, the AGNPS model simulates every day, but gives outputs for each event.

P retained either in the soil system or in the water system is expressed via certain processes of P transformation in these systems, for instance P desorption/adsorption. Retention processes of P are taken into account in 2/3 of examined models (Table 10). For the other models, information with respect to these processes was uncertain. The SWAT, TRK system, NL-CAT, GREEN, PolFlow and MONERIS models address P retention in the soil system as well as in the water system. Only river retention of P is considered in the TRANS, NWPCAM and HBV-P models (in the soil is uncertain). Retention processes can be described by parameters/coefficients. This is often done for steady sate models. For example, the GREEN and PolFlow models describe retention processes of P in the soil and in water by parameters.

Models at these scales (large watersheds, river basins) often combine several models together. NL-CAT model includes four other models such as the ANIMO, which is responsible for nutrient losses from the soil, the SWAP, SWQN and SWQL models, which are responsible for modelling nutrients within the river system. The TRK system is the other example. This combines the SOILNDB, ICECREAM and HBV-NP models into one framework. The TRANS model is partly based on the MIKE-11 model, which simulates water flow. The AGNPS uses the CREAMS model in order to predict nutrient export. In the NWPCAM model, nutrient transport is based on the SPARROW model.

Two models were selected to be described below in more detail. These are the models that represent a dynamic approaches (HBV-P) and a steady state approach (GREEN). In addition, HBV-P model is particular focused on P modelling.

**HBV-P model**
Abbreviation: not available.
Purpose: is to evaluate riverine P transport for watersheds. The model can be suitable also for scenario analyses as well as for assessing management strategies regarding P inputs to watersheds (Andersson et al., 2005).
Time scale: the model provides outputs on monthly basis. Outputs can be given also for seasons (Andersson et al., 2003).
Spatial scale: watersheds, which do not have horizontal and vertical differences (Andersson et al., 2005).
Approach used in the model: this is a dynamic mass-balance model (Andersson et al., 2005; Andersson et al., 2003). The model is rather simple compare to other models applied to watersheds (for instance, LEEDs model).
Forms of P modelled: particulate and dissolved inorganic (soluble reactive) phosphorus (Andersson et al., 2005; Andersson et al., 2003).

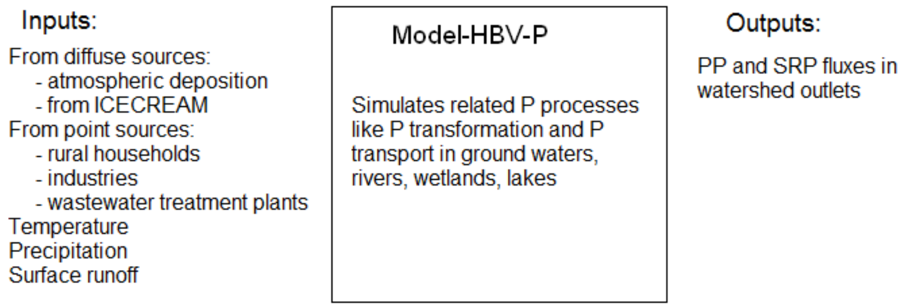



*Figure 9*
*Simplified schematic representation of HBV-P model with its inputs and outputs. Sources: Andersson et al., (2003); Andersson et al., (2005); Dahl M. and Perz B. C. (2004).*

Model structure: a hydrological model (HBV) is the main part of the model. This model accounts P transformation and retention in water systems (rivers, lakes and wetlands). Sedimentation and resuspention processes of P within the rivers are incorporated into the model as well. HBV has two zones, upper and lower with different transit time. For detailed information the reader is referred to a paper of Andersson et al., (2005) and Andersson et al., (2003). Inputs of P to watersheds are taken from the ICECREAM model. These are management practices applied within watersheds, land use, soil prosperities and vegetation types. The model estimates P transport resulting from point and diffuse sources. Temperature and precipitation are inputs to the model and they are provided on a daily basis (Andersson et al., 2003) (Figure 9).

Applicability and historical aspects of the model: the model was developed for Swedish watersheds between the end of 1980s and beginning of 1990s under VASTRA programme (Swedish Water Management Research Programme) (Andersson et al., 2005; Andersson et al., 2003). The model was successfully applied for three lakes in Sweden (Dahl, M. and Perz, B.C., 2004).

**GREEN model**
Abbreviation: Geographic Regression Equation for European Nutrient losses.
Purpose: the model has been developed to assess nutrient (N and P) losses from diffuse and point sources at a European scale. The other objective is to define watersheds that have high level of nutrient inputs and losses.
Time scale: river loads of N and P are calculated annually.

Spatial scale: the model is used at a river basin scale. The river basin can be divided into sub-basins depending on its area size.
Approach used in the model: this is a simplified empirical model that is based on a steady state approach.
Forms of modelled P: in most cases N and P loads are referred to TN and TP respectively. However, with respect to N and P inputs to watersheds from diffuse sources, the model mostly refers to dissolved forms of N (nitrate) and P (SRP: soluble reactive phosphorus).
Model structure: the GREEN model estimates river loads of N and P (in ton per year) at the outlet of the river basin or at the outlet of the sub-basin as a function of nutrient inputs from diffuse and point sources, basin characteristics (rainfall, river length) and retention processes in the soil as well as in the river system (Figure 10). Nutrient sources and retention processes are described statistically in the model. Retention processes in the soil and in the river are depicted by a basin reducing factor and a river reducing factor respectively. Retention in the soil is estimated on the basis of basin attributes such as rainfall and river length. Denitrification and volatilization processes as well as soil storage and plant uptake of nutrients are lumped via a basin reducing factor. Retention in the river is also calculated on the basis of basin characteristics, but there denitrification, volatilization, uptake by plants and net sedimentation are considered.
Application and historical aspects of the model: The GREEN model has been developed by Institute for Environment and Sustainability in 2006 to assess the response to environmental changes in ecosystems. In 2006 the FATE project was organized with the aim to develop quantitative tools which assess nutrient losses from river basins at a European scale. The GREEN model was one of the models developed during that project. This model is based on the SPARROW model, which was established for United State river basins. The SPARROW model was adjusted to the European scale and simplified in order to be able to implement. The advantage of the GREEN model is that the model is rather simple and, hence can be applied to situations with scare data. In addition, it accounts for N and P retention in the soil as well as in the river system. The model considers point and non-point (diffuse) sources of nutrients.

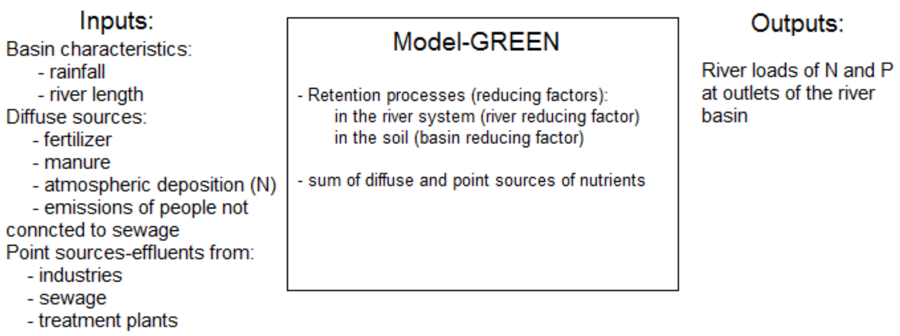



*Figure 10*
*Simplified schematic representation of GREEN model with its inputs and outputs. Sources: Grizzetti and Bouraoui, (2006).*

To conclude, the main massage of this model review (Section 2.1) was to get insight into existing P models applied at different scales (soil/field, in water bodies and watershed/river basin), their characteristics and used approach (dynamic or steady state). Here, twenty six models have been examined. Less than 1/3 of the models are focused on P export estimated for an individual unit on a soil/field scale, over 1/3 of the models in water bodies and 2/4 of the models on a watershed/river basin scale. An analysis of these models shows that the majority of them (18) are based on a dynamic approach rather than on a steady state approach. In contrast, dynamic models are more complex than steady state models due to including a lot of processes. Only a few models (HBV-P and LEEDs) out of the rest were developed with focus particular on P export.

## 2.2 Global scale: *NEWS* steady state P model

The *NEWS* model is the most well-known example of a global-scale nutrient export model (Mayorga et al., 2010; Seitzinger et al., 2010).

Since the *NEWS* model is the basis for this study, more detailed information is provided in this section compare to the other models discussed in previous section (Section 2.1). First, background information is presented. Next, key formulas to estimate riverine P export are mentioned (Section 2.2.2.).

### 2.2.1 Background information

Abbreviation: *NEWS* model is Nutrient Export from WaterSheds.
Purpose: the *NEWS* model is developed to estimate riverine export of nutrients. Additional purposes of the model are to assess the impacts of human activities on nutrient export to coastal waters and their potential to cause eutrophication (Mayorga et al., 2010; Seitzinger et al., 2010). The later purpose has been recently added to the model in terms of the ICEP indicator (an Indicator for Coastal Eutrophication Potential). This indicator was proposed by Billen and Garnier (2007). It is based on the Redfield ratio: C:N:P:Si (106:16:1:20). The ICEP accounts presence of dissolved SI (silica) over N and P. Excess of dissolved Si over N and P recommends a little risk for coastal eutrophication and vice versa (Garnier et al., 2010).
Time scale: *NEWS* provides annual nutrient inputs at the mouth of the river for 1970, 2000, 2030 and 2050 (Mayorga et al., 2010).
Spatial scale: the model calculates nutrient export at a river basin scale on the basis of 0.5x0.5 degree cell resolution (Mayorga et al., 2010).
Approach used in the model: the *NEWS* model is based on a steady state approach. The model includes empirical and mechanistic (process based) process formulations in its estimations (Mayorga et al., 2010).
Forms of modelled nutrients: the model estimates particulate (PN, PP, PC), dissolved inorganic (DIN, DIP) and organic (DON, DOP, DOC) forms of nitrogen, phosphorus and carbon. Recently, dissolved silica (DSi) has been added in the model.

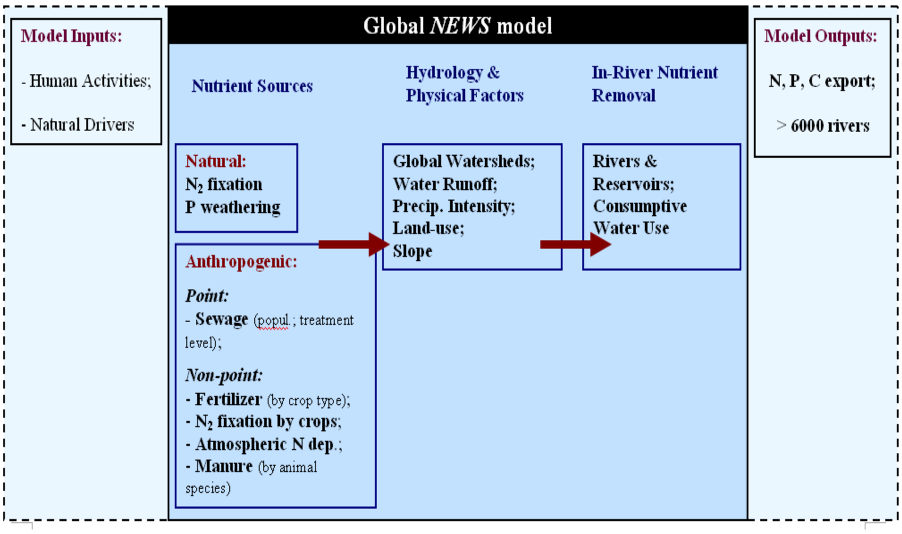



*Figure 11*
*Schematic representation of the Global NEWS structure: inputs, main components in the model and outputs. Sources: Mayorga et al., (2010); Seitzinger et al., (2010).*

Model structure: the *NEWS* model calculates nutrient export for over 6.000 rivers as a function of human activities (i.e. manure and fertilizer applications in agriculture and sewage effluents) and natural drivers (i.e. precipitation intensity and runoff) (Figure 11). Natural and anthropogenic sources of nutrients to land and to the river and nutrient removal within the catchment are included on the basis of external datasets, while river retention is related to river basin characteristics (see Figure 11). Particulate forms of N, P, C are calculated based on regression analysis while dissolved forms of nutrients are calculated based on a mass-balance approach (Mayorga et al., 2010; Beusen et al., 2005). Future riverine export of nutrients is based on Millennium Ecosystem Assessment (MEA) scenarios such as Adaptive Mosaic (AM), Global Orchestration (GO), Order from Straight (OS) and Technogarden (TG). These scenarios incorporate different storylines how the world might be developed (regionalized or globalized world) and management approaches to deal with environmental problems (reactive or proactive) in the future. The AM and OS share regionalized world view with proactive and reactive management approaches respectively. The GO and TG are globalized scenarios with reactive and proactive approaches respectively (Seitzinger et al., 2010; Alcamo et al., 2006). Main components incorporated to the model from the scenarios are hydrology (Fekete et al., 2010), sewage (Van Drecht et al., 2009) and agricultural trends (Bouwman et al., 2009).

Application and historical aspects of the model: the Global *NEWS* model (*NEWS-1*) was developed in 2002 by UNESCO Intergovernmental Oceanographic Commission (IOC). In 2009 the model was updated and improved (*NEWS-2*) (Mayorga et al., 2010). The model is applied at the global scale. Various studies have used the model to assess nutrient export to coastal waters. Some examples are global riverine export of dissolved inorganic nitrogen (Dumont et al., 2005) and phosphorus (Harrison et al., 2010), dissolved organic nutrient forms (Harrison et al., 2005), particulate forms (Beusen et al., 2005) and dissolved silica (Beusen et al., 2009) to coastal waters. In addition, this model has also been used to analyse nutrient transport to coastal waters at regional scales (Yan et al., 2010; Van der Struijk and Kroeze, 2010; Yasin et al., 2010; Thieu et al., 2010).

### 2.2.2 Estimation of riverine P export

P export via rivers to coastal waters in the Global *NEWS* model is estimated for three P forms, i.e. dissolved inorganic (DIP), dissolved organic (DOP) and particulate (PP) phosphorus. In this study, only DIP is considered since this form is highly bioavailable compared to DOP and PP. Therefore, descriptions of formulas used to calculate riverine P export are given with respect to DIP. For detailed information regarding estimations of riverine export of the other P forms the reader is referred to Mayorga et al., (2010).

River export of DIP in the Global *NEWS* model is associated with its export from watersheds (land) to the river system and along the river to the river mouth (Figure 12).

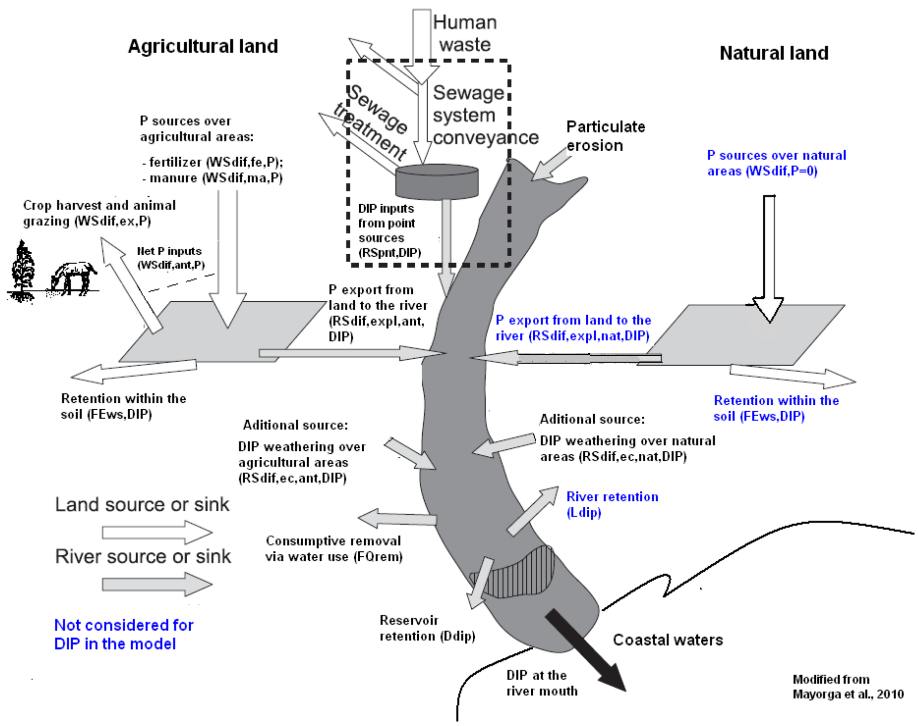



*Figure 12*

*DIP sources and sinks from land (WaterShed sources denoted as WS), sources to the river (River Sources indicated as RS) and DIP export to the river mouth. Terms of land sources and river sources as well as terms of DIP removal within the river system are given according to Mayorga et al., (2010), where dif and pnt are diffuse and point sources respectively; ant and nat are anthropogenic and natural sources respectively; expl means that DIP is originated from explicit sources while ec means that DIP sources are described by using an export-coefficient approach; FE is an export fraction. Source: Mayorga et al., (2010).*

### Export of DIP from watersheds to the river system

Export of DIP from watersheds to the river system is driven by anthropogenic and natural sources. Anthropogenic sources of P (indicated as ant) are divided into diffuse (denoted as dif) and point (denoted as pnt) sources. Diffuse sources include fertilizer ($WSdif_{fe,P}$) and manure ($WSdif_{ma,P}$) applications into agricultural areas (or watersheds, indicated as WS) and DIP weathering over agricultural areas ($RSdif_{,ec,ant,DIP}$). DIP export from land to the river ($RSdif_{expl,ant,DIP}$) is estimated as a function of net P inputs to the soil ($WSdif_{ant,P}$) and P retention within the soil ($FEws_{DIP}$) according to formulas 1 and 2 (Mayorga et al., 2010):

$$WSdif_{ant,P} = WSdif_{fe,P} + WSdif_{ma,P} - WSdif_{ex,P} \quad (\text{kg km}^{-2}\text{ year}^{-1}) \qquad (1)$$

$$RSdif_{expl,ant,DIP} = WSdif_{P} \cdot FEws_{DIP} \quad (\text{kg km}^{-2}\text{ year}^{-1}) \qquad (2)$$

where,

$WSdif_{fe,P}$ and $WSdif_{ma,P}$ - diffuse anthropogenic sources of P to watersheds (land) from fertilizer and manure use respectively in kg km$^{-2}$ year$^{-1}$.

$WSdif_{ex,P}$ - export of P via grazing and harvesting in kg km$^{-2}$ year$^{-1}$;

$FEws_{DIP}$ - is a watershed export fraction, ranged from 0 to 1. This fraction represents P retention within the soil. It is calculated empirically on the basis of mean annual runoff ($R_{nat}$, m year$^{-1}$) from land to streams (Mayorga et al., 2010).

In natural systems, anthropogenic P inputs are negligible (Mayorga et al., 2010).

DIP weathering over agricultural areas ($RSdif_{,ec,ant,DIP}$) introduces an additional diffuse anthropogenic source of DIP to the river. This is calculated in the model using an export-coefficient approach according to:

$$RSdif_{ec,ant,DIP} = \int_{DIP}(R_{nat}) \cdot EC_{DIP} \text{ (kg km}^{-2}\text{ year}^{-1}\text{)} \quad (3)$$

where,
$R_{nat}$ - is mean annual runoff from land to streams (m $year^{-1}$);
$EC_{DIP}$ - is a calibrated export coefficient that represents weathering of P minerals over agricultural areas. This constant is the same for natural areas (Mayorga et al., 2010).

Point sources of P include human waste and detergent that directly discharge into the river as sewage effluents. These sources are called as river sources and denoted by *RS* in the Global *NEWS* model (Mayorga et al., 2010; Harrison et al., 2010). DIP export from point sources to rivers is estimated as:

$$RSpnt_P = (1 - hw_{frem,P}) \cdot I \cdot WShw_P \text{ (kg km}^{-2}\text{ year}^{-1}\text{)} \quad (4)$$

$$RSpnt_{DIP} = FEpnt_{DIP} \cdot RSpnt_P \text{ (kg km}^{-2}\text{ year}^{-1}\text{)} \quad (5)$$

where,
$RSpnt_P$ - is point source emissions of P (as element) to streams in kg $km^{-2}$ $year^{-1}$;
$RSpnt_{DIP}$ - is point source emissions of DIP to streams in kg $km^{-2}$ $year^{-1}$;
$FEpnt_{DIP}$ - is a fraction of $RSpnt_P$ exported as DIP. $FEpnt_{DIP} = 1$ for DIP;
$hw_{frem,P}$ - is a fraction of P removed through sewage treatment;
I - is a fraction of population density connected to a sewage system. When the fraction is zero, it means that no emissions from point source is input to streams, since emissions are lost within watersheds as a diffuse source;
$WShw_P$ - is human waste (excrement) and detergents from sewage systems to watersheds in kg $km^{-2}$ $year^{-1}$. They are given in the model as inputs and calculated as a function of population density and gross-domestic product (GDP) within the watershed (Mayorga et al., 2010).
Natural diffuse sources for DIP export from land to the river are not considered in the model. Only DIP weathering over natural areas as additional source is accounted via an export-coefficient approach ($RSdif_{,ec,nat,DIP}$) (see also Figure 12). DIP weathering over natural areas is estimated according to formula 3 (Mayorga et al., 2010; Harrison et al., 2010).

**Export of DIP at the river mouth**
DIP export at the river mouth includes DIP fluxes resulting from both anthropogenic and natural sources (their descriptions are given above) while accounting for DIP removal within the river system (see also Figure 12).

DIP removal within the river system is determined by consumptive water use (FQrem), for instance for irrigation purposes, and by reservoir retention (Ddip). DIP retention (Ldip) in the river is neglected in the model (Mayorga et al., 2010). DIP that is removed along the river system is accounted by a fraction term in the model as $FEriv_{DIP}$. The main formula used to calculate river-system export fraction for DIP is:

$$FE_{riv,DIP} = (1 - D_{dip}) \cdot (1 - FQrem) \quad (6)$$

where,
Ddip - is a fraction of DIP that is retained within reservoirs. Derivation of this fraction is based on literature data. DIP retention at each reservoir is estimated empirically on the basis of annual change in water residence time. DIP retention for the basin is estimated on the basis of calculated retention for each reservoir (discharge-weighted average of the retention);

FQrem - is a fraction of DIP that is removed from the water via its extraction for different purposes like irrigation, industrial and domestic use. It is estimated according to formula:

$$FQrem = (Qnat - Qact) / Qnat \qquad (7)$$

where,
Qnat - is total river discharge before water is consumed, $km^3$ $year^{-1}$;
Qact - is total river discharge after water is consumed, $km^3$ $year^{-1}$.

DIP export at the river mouth is calculated as:

$$Yld_{DIP} = FE_{riv,DIP} \cdot (RSdif_{expl,ant,DIP} + RSdif_{ec,ant,DIP} + RSdif_{ec,nat,DIP} + RSpnt_{DIP}) \qquad (8)$$

where,
$Yld_{DIP}$ - is DIP yield at the river mouth, kg $km^{-2}$ $year^{-1}$. DIP loads at the mouth are calculated by multiplying DIP yields with the basin area. DIP loads are expressed in the model in Mg $year^{-1}$.

Note, that all formulas mentioned above are adjusted to DIP export while Mayora et al., (2010) provides formulas for all nutrient forms. Harrison et al., (2010) gives a central formula to calculate DIP flux at the river mouth. However, in this section (Section 2.2.2) estimations of DIP fluxes to the river system from watersheds and along the river system are provided separately. Detailed information regarding calculations is provided in the supplementary material of Mayorga et al. (2010).

P inputs from manure and fertilizer applications in agriculture and P export via crop harvest and animal grazing are inputs to the *NEWS* model and they were derived from the IMAGE model. Land cover, monthly precipitation, temperature and hydropower production were taken also from IMAGE and they are inputs to the Water Balance Model ($WBM_{plus}$). This model provides inputs to the *NEWS* model regarding dam construction, consumptive water removal and river discharge. Based on those inputs, the model estimates P fluxes (Seitzinger et al., 2010).

# 3 Chapter III. Inclusion of P dynamic to the Global NEWS model (methodology and input data)

In this study, we investigated the impacts of dynamics on DIP fluxes and concentrations at the watershed scale and the river mouth in response to diffuse P inputs. The dynamics in river retention is not included but the impact of river retention (at presently completely neglected in Global *NEWS)* is evaluated. Effects of watershed retention on the dynamics in DOP and PP are neglected as they are assumed to be negligible.

This chapter first presents information regarding a dynamic approach for calculating P export from watersheds (Section 3.1), followed by methodological aspects of implementing P dynamics to the Global *NEWS* model (Section 3.2) and a description of data needed to run the dynamic Global *NEWS* - P model (Section 3.3).

## 3.1 Description of a dynamic approach

In this study inclusion of P dynamics is limited to the watershed scale (land), where anthropogenic diffuse sources of P play an important role.

The Global *NEWS* model distinguishes anthropogenic diffuse sources of DIP export as fertilizer and manure use in agriculture. Weathering of P contained minerals over agricultural areas forms additional diffuse source.

The P content (P pool) in the top layers of the soil within the watershed depends on P accumulation, and the related change in watershed P concentrations. This accumulation and changes are assumed to occur completely in an oxalate extractable P pool in the soil (descriptions of P pools are given in Chapter 1). The approach assumes that 2/3 of the amount of oxalate extractable P ($P_{ox}$), that is accumulated via diffusion and/or precipitation, is irreversible, whereas 1/3 of the amount of $P_{ox}$ , that is accumulated via adsorption is reversible. The reversible P pool is dominated by soluble forms (inorganic and organic).

The annual accumulation (or depletion) of P in the soil within the watershed ($P_{ac}$) is calculated from the total annual input to the soil ($P_{in}$) minus annual uptake ($P_{up}$) and annual total P leaching from the topsoil ($P_{le}$) to surface waters according to (all fluxes in kg $ha^{-1}$ $year^{-1}$):

$$P_{ac} = P_{in} - P_{up} - P_{le} \quad (9)$$

P input includes the input by fertilizers, manure, weathering, atmospheric deposition and the P emissions from human waste excrements not connected to sewage systems. The latter two inputs are not accounted in Global *NEWS* and thus these are neglected in this study. P uptake equals net crop removal including grass harvesting and animal grazing that is also provided by Global *NEWS*. P leaching equals the leaching of DOP and DIP to surface waters. In general, total P leaching from watersheds is equal the sum of DIP and DOP leaching as PP is negligible, according to:

$$P_{le} = Q_{le} \cdot ([DIP] + [DOP]) / 1000 \quad (10)$$

$P_{le}$ - is total P leaching rate from the watershed (kg $ha^{-1}$ $year^{-1}$);
$Q_{le}$ - is water flux leaving the watershed ($m^3$ $ha^{-1}$ $year^{-1}$);
[DIP] and [DOP] - is dissolved inorganic and organic P concentrations (g $m^{-3}$ or mg $l^{-1}$);
The value of 1000 is needed to convert units from g $ha^{-1}$ $year^{-1}$ to kg $ha^{-1}$ $year^{-1}$.

Because of changes in P accumulation and, thus in P release as well as in P concentrations over time, oxalate extractable P pool changes over time too. This can be described by simple formula:

$$P_{ox}(t) = P_{ox}(t-1) + \frac{P_{ac}(t-1)}{\rho \cdot T \cdot 10} \quad (11)$$

$P_{ox}$(t) and $P_{ox}$(t-1) - is the oxalate extractable P concentration in soil at year t and t-1 (g $kg^{-1}$);
$P_{ac}$(t-1) - is the total P accumulation during a one year time step from (t-1) to (t) (kg $ha^{-1}$);
p - is bulk density of the soil (kg $m^{-3}$);
T - is soil thickness (m). The considered soil thickness is related for the soil depth where P interacts with water draining to surface water and is tentatively set equal to the depth to bedrock.

The value of 10 is needed to convert units. Actually, 10.ρ.T is the weight of the soil (tonnes $ha^{-1}$) which is exploited by the roots and which is mixed by cultivation.

There are two oxalate extractable P pools, the reversible and irreversible as it has been already mentioned above (descriptions are given in Chapter 1.1). The interest is on the reversible P pool because this P pool mainly controls P availability and thus, this pool reflects the soil P status. The amount of readily available (adsorbed) P in the soil ($P_{s,re}$) is assumed to be in equilibrium with the DIP concentration in the watershed according to a Langmuir equation (Van der Zee, 1988; Schoumans, 1995; Schoumans and Groenendijk, 2000):

$$P_{s,re} = \frac{K_P \cdot P_{s,re,\max} \cdot [DIP]}{1 + K_P \cdot [DIP]} \quad (12)$$

$P_{s,re}$ - is the actual amount of readily available (adsorbed) P in the soil (mmol $kg^{-1}$)
$K_P$ - is Langmuir adsorption constant ($m^3 g^{-1}$ P);
$P_{s,re,max}$ - is the maximum amount of readily available (adsorbed) P in the soil (mmol $kg^{-1}$).

The DIP concentration can be calculated from equation (12) as:

$$[DIP] = \frac{P_{s,re} / P_{s,re,\max}}{(1 - P_{s,re} / P_{s,re,\max}) \cdot K_P} \quad (13)$$

The actual amount of readily available P ($P_{s,re}$, mmol $kg^{-1}$) can be calculated from the known amount of total oxalate extractable P pool (reversible plus irreversible) according to (Schoumans and Groenendijk, 2000):

$$P_{s.re} = 1/3 \cdot P_{ox} \quad (14)$$

The maximum amount of readily available P (Ps,re,max, mmol kg-1) can be calculated on the basis of oxalate extractable aluminium (Alox) and iron (Feox) oxides, which both strongly react with P according to (Schoumans and Groenendijk, 2000):

$$P_{s.re,\max} = 0.5 \cdot 1/3 \cdot (Al_{ox} + Fe_{ox}) \quad (15)$$

P dynamics is often described by also including a time dependent P release from the irreversible pool (Schoumans and Groenendijk, 2000), but this aspect is not included in this approach.

## 3.2 Adaptation of the Global *NEWS* model to the dynamic approach

This section gives detailed information towards implementing P dynamics to the Global *NEWS* model considering also P retention within the river. First, the derivation of the P adsorption constant ($K_p$) is described since this is a key parameter for the next calculations (Section 3.2.1). Next, P fluxes and concentrations at the watershed scale and river mouth (Section 3.2.2) are described.

### 3.2.1 P adsorption constant ($K_p$)

In principle $K_P$ values could be derived from literature, but the disadvantage of this approach is that values range widely, depending on soil properties. The P adsorption constant is determined by soil properties such as soil bulk density and content of Al and Fe oxides ($Al_{ox}$+$Fe_{ox}$) within certain thickness of the soil and by oxalate extractable soil P pool ($P_{ox,pool}$). Furthermore, a watershed average value is needed and it is not clear whether literature values, that are mostly related to top soils also apply at larger soil depth. Furthermore, Kp values derived from adsorption-desorption differ strongly from those derived from in situ measurements of P in soil and soil solution.

Consequently, we estimated $K_P$ values using DIP concentrations calculated by the Global *NEWS* for each watershed in the year 2000 because calibrations of parameters in the Global *NEWS* model were done on the basis of data for the period of 1995-2000. All calculations are done by using an excel programme.
The formula to calculate $K_p$ is derived from equations 11, 12 and 14 as:

$$K_P = \frac{P_{ox,pool,2000}}{(0.93 \cdot \rho \cdot T \cdot P_{s,re,\max} - P_{ox,pool,2000})} \cdot \frac{1}{[DIP]} \qquad (16)$$

$K_P$ - is Langmuir adsorption constant ($m^3\ g^{-1}$ P);
$P_{ox,pool,2000}$ - is the oxalate extractable P pool (kg $ha^{-1}$); 0.93 – the value that combines values of 10 (from equation 11), 0.031 (conversion factor from mmol $kg^{-1}$ to g $kg^{-1}$) and 3 (from equation 14);
p - is bulk density of the soil (kg $m^{-3}$);
T - is soil thickness (m);
$P_{s,re,max}$ - is the maximum amount of readily available (adsorbed) P in the soil (mmol $kg^{-1}$);
[DIP] - is averaged dissolved inorganic P concentration at the watershed scale (g $m^{-3}$ or mg $L^{-1}$) (description of its estimation is given below).

In this study P adsorption constant is estimated when river retention is excluded (Ldip=0) and when river retention is included (Ldip≠0).

The $P_{s,re,max}$ pool was derived for given ranges in $Al_{ox}$ and $Fe_{ox}$ on the basis of equation (15). The $P_{ox,pool}$ in 2000 was based on an assumed background in 1900 and the net P input from 1900 to 2000 as described further.

**$K_P$ estimation without considering P river retention (Ldip=0)**
$K_P$ is estimated according to eq.(16), where $P_{ox,pool,2000}$ and [DIP] have to be calculated while the other variables are known. Schematic representation of variables, which have to be calculated and input data is illustrated in Figure 13. Detailed information on input data is given in Section 3.3.

**Estimation of $P_{ox,pool,2000}$**

The Oxalate extractable P pool ($P_{ox,pool,2000}$) in 2000 is estimated on the basis of initial concentration of oxalate extractable P in 1900 plus the amount of P accumulated over the period of 1900-2000 (in kg ha$^{-1}$) up to a given soil thickness as:

$$P_{ox,pool,2000} = \rho \cdot T \cdot 10 \cdot P_{ox,1900} + frP_{ac} \cdot \sum_{1900-2000} (P_{in,t} - P_{up,t}) \tag{17}$$

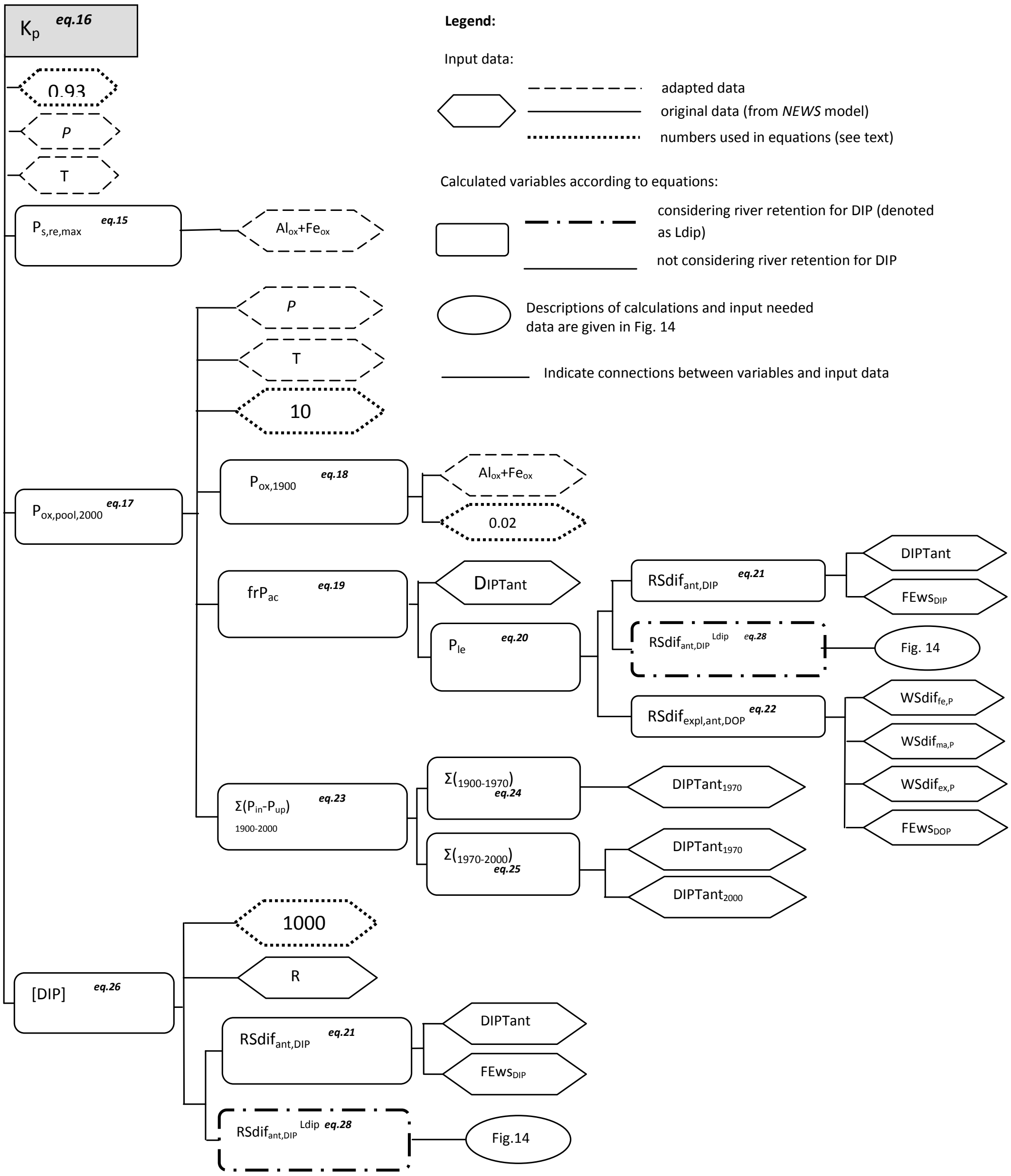



*Figure 13*

*Schematic illustration of variables and input data that are needed in order to derive P adsorption constant (Kp) according to the structure of Kp calculation. Definitions of variables and input data are given in a text. Equation that is used to estimate certain variable is mentioned in a box as eq.#. All equations can be found in Section 3.2.1. Adapted data means that data are derived from elsewhere while original data are derived from the Global NEWS model (see Section 3.3).*

1). $P_{ox,1900}$ - is oxalate extractable P concentration in 1900 year (g $kg^{-1}$). This is background value or initial P pool, which is derived from content of aluminium and iron oxides ($AL_{ox}+Fe_{ox}$) according to:

$$P_{ox,1900} = 0.02 \cdot (Al_{ox} + Fe_{ox}) \qquad (18)$$

A value of 0.02 is assumed to be an initial P concentration in agricultural top soils (see Section 3.3.2). $Al_{ox}+Fe_{ox}$ content is usually given in mmol $kg^{-1}$, thus the value of $P_{ox,1900}$ has to be converted to g $kg^{-1}$ by multiplying it by 0.031 (31/1000), where 1 mol equals 31 g of P and 1000 is needed to convert from mmol to mol.

2). $frP_{ac}$ - is the fraction of added P that is accumulated in the soil in 2000. The assumption is made that this fraction remained constant during the period 1900-2000. This fraction can be estimated from the difference between net P inputs and P outputs:

$$frP_{ac} = (P_{in,2000} - P_{up,2000} - P_{le,2000}) / (P_{in,2000} - P_{up,2000}) \qquad (19)$$

$P_{in}$ - is P inputs to the watershed (land) from fertilizer and manure use in agriculture and weathering over agricultural areas (kg $ha^{-1}$ $year^{-1}$);
$P_{up}$ - is P uptake by plants (kg $ha^{-1}$ $year^{-1}$).

According to the Global *NEWS* model, $P_{in}$-$P_{up}$ is expressed by a DIPTant term, which includes net total P diffuse anthropogenic sources to land from fertilizer, manure and weathering only for DIP (see documents available at http://marine.rutgers.edu/globalnews/data/GNE.htm).

$P_{le}$ - is P leaching from land to surface waters (kg $ha^{-1}$ $year^{-1}$). Here, $P_{le}$ is the sum of DIP and DOP that is exported from land to rivers. PP is not considered since there is no link between dissolved P forms and particulate P in the Global *NEWS* model (see Section 2.2).

Based on calculated DIP (eq.21) and DOP (eq.22) fluxes that enter rivers, $P_{le}$ can be determined as:

$$P_{le} = RSdif_{ant,DIP} + RSdif_{expl,ant,DOP} \qquad (20)$$

In this study DIP export from land to rivers resulting from fertilizer, manure and weathering is denoted as $RSdif_{ant,DIP}$, where *dif* and *ant* indicate diffuse, anthropogenic sources of DIP and *RS* means river sources. According to the Global *NEWS* model, DIP export to the river that is resulted only from fertilizer and manure sources is indicated as $RSdif_{expl,ant,DIP}$ while DIP export to the river that is resulted only from weathering over agricultural areas is expressed as $RSdif_{ec,ant,DIP}$ (Mayorga et al., 2010). These diffuse sources of DIP export are combined into one term, which is $RSdif_{ant,DIP}$. Net total P inputs from these diffuse sources into the watershed over agricultural areas (DIPTant) are given directly by the model (see documents available at http://marine.rutgers.edu/globalnews/data/GNE.htm). Thus, in order to determine $RSdif_{ant,DIP}$, DIPTant has to be multiplied by the watershed export fraction for DIP ($FEws_{DIP}$). This fraction is responsible for DIP export via watersheds to surface waters. The fraction is provided by the model too. Therefore, the equation to estimate $RSdif_{ant,DIP}$ is (the Global *NEWS* source code):

$$RSdif_{ant,DIP} = DIPTant \cdot FEws_{DIP} \qquad (21)$$

DIPTant - is net total P diffuse inputs into watersheds (land) including synthetic fertilizer, animal manure and DIP weathering over agricultural areas, kg $km^{-2}$ $year^{-1}$.

$FEws_{DIP}$ - is the export fraction of P that is exported as DIP from the watershed to rivers Values of $RSdif_{ant,DIP}$ are in kg $km^{-2}$ $year^{-1}$ and thus, values have to be converted to kg $ha^{-1}$ $year^{-1}$ since this unit is used in the other equations (see also Section 3.3).

DOP export from land to rivers that is resulting only from fertilizer and manure applications to land is expressed as $RSdif_{expl,ant,DOP}$ in the Global *NEWS* model (Mayorga et al., 2010; see also Section 2.2). This term is used in this study too. This is estimated similarly to the equation (2) provided in Section 2.2.2 (Mayorga et al., 2010; the Global *NEWS* source code):

$$RSdif_{\exp l,ant,DOP} = WSdif_P \cdot FEws_{DOP} \tag{22}$$

$WSdif_P$ - is net total P diffuse inputs to the watershed (land), kg $km^{-2}$ $year^{-1}$. This is estimated according to the equation (1).

$FEws_{DOP}$ - is the export fraction of P that is exported as DOP from the watershed to river. Here, values of $RSdif_{expl,ant,DOP}$ are in kg $km^{-2}$ $year^{-1}$ and thus, values have to be converted to kg $ha^{-1}$ $year^{-1}$ since this unit is used in the other equations (see also Section 3.3).

3). $\sum_{1900-2000}(P_{in,t} - P_{up,t})$ - is the accumulated amount of P in the period 1900-2000. Since in this study $P_{in}$-$P_{up}$ equals to values of DIPTant for DIP export according to the model (see above). Note, that values of DIPTant have to be in kg $ha^{-1}$ $year^{-1}$. Accumulated amount of P is calculated according to:

$$\sum_{1900-2000}(P_{in,t} - P_{up,t}) = \sum_{1900-1970}(P_{in,t} - P_{up,t}) + \sum_{1970-2000}(P_{in,t} - P_{up,t}) \tag{23}$$

The accumulation in the period 1900-1970 is based on assumption that the P surplus ($P_{in}$-$P_{up}$) increases linearly from 0 to the Global *NEWS* value in 1970. Thus, accumulation of P in this period is calculated as:

$$\sum_{1900-1970}(P_{in,t} - P_{up,t}) = \frac{(P_{in} - P_{up})_{1900} + (P_{in} - P_{up})_{1970}}{2} \cdot 70 \text{ , where } (P_{in} - P_{up})_{1900} = 0 \tag{24}$$

70 - is the period of P accumulation over 70 years (from 1900 to 1970).

The accumulation in the period 1970-2000 is also assumed to change linearly from the known values in 1970 and 2000. Thus, P accumulation over the period 1970-2000 is estimated similarly to the equation (21) as:

$$\sum_{1970-2000}(P_{in,t} - P_{up,t}) = \frac{(P_{in} - P_{up})_{1970} + (P_{in} - P_{up})_{2000}}{2} \cdot 30 \tag{25}$$

30 – is the period of P accumulation over 30 years (from 1970 to 2000).

**Estimation of [DIP] at a watershed scale**

DIP concentration ([DIP], g $m^{-3}$) is calculated from equation (10), where $P_{le}$ equals $RSdif_{ant,DIP}$ and $Q_{le}$ equals R in this case. These abbreviations were adjusted to abbreviations used in the Global *NEWS* model. The equation to calculate [DIP] is:

$$[DIP] = \frac{1000 \cdot RSdif_{ant,DIP}}{R} \tag{26}$$

1000 - is needed to convert units from g $ha^{-1}$ $year^{-1}$ to kg $ha^{-1}$ $year^{-1}$;
R - is mean annual runoff from land to the river, $m^3$ $ha^{-1}$ $year^{-1}$.
$RSdif_{ant,DIP}$ - is DIP export from the watershed (land) to the river (RS=river sources) resulting from diffuse (dif) anthropogenic (ant) as well as DIP weathering over agricultural areas, kg $ha^{-1}$ $year^{-1}$. Its estimation is described above and is done according to equation (21).

**$K_P$ as a function of river retention (Ldip≠0)**
The main formula to calculate $K_P$ stays the same (eq. 16), where only $P_{ox,pool}$ and [DIP] results are affected by adding P retention within the river (see also Figure 13). Note that DIP river retention is into consideration in the Global *NEWS* model, however, only via consumptive water use and reservoirs, but not in the river system itself (Ldip=0 in the model) (Mayorga et al., 2010).

The oxalate extractable P pool for 2000 ($P_{ox,pool,2000}$) is estimated according to equation (17), where all parameters stay without changes except for the fraction of P that is accumulated in the soil ($frP_{ac}$). This is because $RSdif_{ant,DIP}$ is calculated differently (see also Figure 14). Values of newly calculated $RSdif_{ant.DIP}^{Ldip}$ ($L_{dip}$ indicate that river retention is included) are used instead of $RSdif_{ant.DIP}$ to estimate $P_{le}$ (eq.20), which results then are needed to estimate $frP_{ac}$ (eq.19). Afterwards, $P_{ox,pool,2000}$ can be derived according to eq. (17) (see also Figure13).

In addition, calculated $RSdif_{ant.DIP}^{Ldip}$ is also used instead of $RSdif_{ant.DIP}$ in eq. (26) in order to derive DIP concentrations, which consider river retention (see also Figures 13 and 14). This DIP concentration can be also denoted as $[DIP]^{Ldip}$ that indicates inclusion of river retention in calculations.

**Estimation of $RSdif_{ant.DIP}^{Ldip}$ (Fig. 14)**
According to a procedure used in calculations of Global *NEWS* model, when river retention is included, this will directly affect only results of DIP yields at the river mouth. This is because river retention is included in the estimation of $FE_{riv,F}$, which is directly then used to calculate DIP at the mouth (Mayorga et al., 2010; see also eq. (8) presented in Chapter 2).

However, the assumption was made that inclusion of river retention for DIP affects only the DIP flux exported from land to the river ($RSdif_{ant,DIP}$) while the DIP flux at the river mouth is not changed. This was done because the DIP fluxes at the river mouth were calibrated on available data by Global *NEWS,* implying that these data are in line with measurements. Thus, for the year of calibration (2000) values of DIP flux at the mouth without river retention (that is according to the model) equal to the DIP flux at the mouth with river retention. By using eq. (8) this assumption can be expressed as:

$$(RSdif_{ant,DIP}{}^{L_{dip}} + RSdif_{ec.nat.DIP} + RSpnt_{DIP}) \cdot FEriv_{DIP} \cdot (1 - L_{dip}) = (RSdif_{ant,DIP} + RSdif_{ec.nat.DIP} + RSpnt_{DIP}) \cdot FEriv_{DIP} \quad (27)$$

$RSdif_{ant.DIP}$, $RSdif_{ec.nat.DIP}$ and $RSpnt_{DIP}$ - are DIP fluxes exported to rivers and resulted from diffuse sources ($RSdif_{ant.DIP}$: fertilizer. Manure, DIP weathering over agricultural areas), DIP weathering ober natural areas ($RSdif_{ec.nat.DIP}$) and point sources ($RSpnt_{DIP}$), kg $ha^{-1}$ $year^{-1}$. Note, that here $RSdif_{ant.DIP}$ combines $RSdif_{ec,ant,DIP}$ (DIP weathering over agricultural areas) and $RSdif_{expl,ant,DIP}$ (net P inputs from manure and fertilizer) (see also eq. (8)).
$FE_{riv,DIP}$ - is an export fraction of DIP that is exported at the mouth of rivers via the river system.
$FE_{riv,DIP}$*(1-$L_{dip}$) - is an export fraction of DIP that is exported at the mouth of rivers via the river system. This fraction includes not only DIP retention via water consumption and reservoir retention within the river, but also DIP retention with the river system itself ($L_{dip}$).
$L_{dip}$ - is a fraction of DIP that is retained within the river system itself (for instance, retention via P accumulation in the sediments by iron when oxygen is available enough).

The, DIP flux that incorporates river retention, defined as $RSdif_{ant,DIP}^{Ldip}$ (kg ha$^{-1}$ year$^{-1}$), is calculated from eq. (27), according to (see also Figure14):

$$RSdif_{ant,DIP}^{L_{dip}} = \frac{RSdif_{ant,DIP} + (RSdif_{ec.nat.DIP} + RSpnt_{DIP}) \cdot L_{dip}}{(1 - L_{dip})} \tag{28}$$

$RSdif_{ant.DIP}$ is calculated according to eq. (21) that is presented above. Estimation of $RSpnt_{DIP}$ is done according to eq. (5) that is provided in Chapter 2, Section 2.2.

$RSdif_{ec,nat,DIP}$ is estimated as (according to the Global *NEWS* source code):

$$RSdif_{ec,nat,DIP} = DIPTnat \cdot FEws_{DIP} \tag{29}$$

DIPTnat - is net total P diffuse inputs into watershed (land) over natural areas, this term is particular for DIP and represents weathering of DIP over natural areas, kg ha$^{-1}$ year$^{-1}$. Note, that calculation of $RSdif_{ec,nat,DIP}$ is different in the paper of Mayorga et al., (2010). This is because the model does not directly provide input data to estimate $RSdif_{ec,nat,DIP}$ according to eq. (3). However, the model provides DIPTnat that gives possibility to estimate $RSdif_{ec,nat,DIP}$ by hand. Since net P inputs over natural areas (DIPTnat) are known, DIP flux entering the river system can be derived in a way of multiplying DIPTnat by a watershed export fraction for DIP ($FEws_{DIP}$).

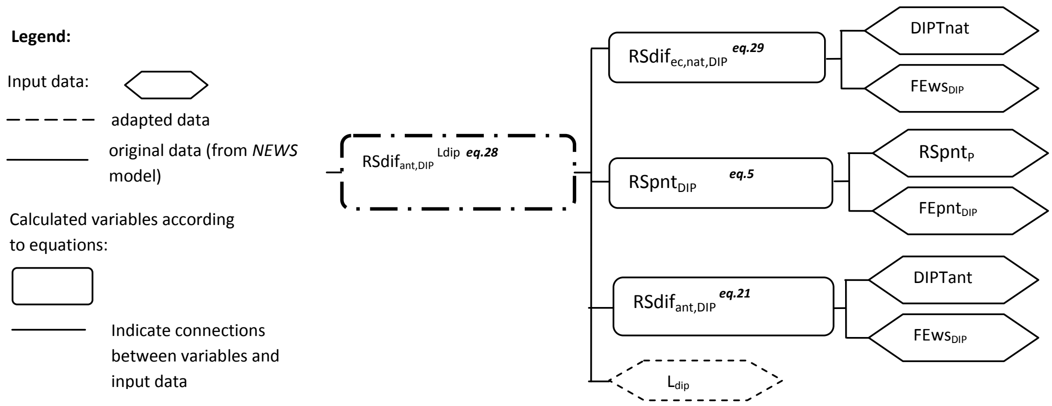



*Figure 14*

*Schematic illustration of variables and input data that are needed in order to derive $RSdif_{ant,DIP}^{Ldip}$. Definitions of variables and input data are given in a text. Equation that is used to estimate certain variable is mentioned in a box as eq.#. All equations can be found in Section 3.2.1. Adapted data means that data are derived from elsewhere while original data are derived from the Global NEWS model (see Section 3.3).*

### 3.2.2 P concentrations and fluxes

In this study estimations are performed for DIP fluxes (or yields) and concentrations at the watershed scale and the river mouth. DIP calculations are done excluding river retention (denoted as Ldip=0) and including river retention (Ldip≠0). All calculations are done outside the Global *NEWS* model by using an excel programme.

At the watershed, scale DIP fluxes and concentrations that generated only from diffuse sources (synthetic fertilizer, animal manure and DIP weathering over agricultural areas) are considered. In this study they are indicated as $RSdif_{ant,DIP}$ while DIP concentrations are denoted as [DIP] when $L_{dip}$ equals zero. When $L_{dip}$ does not equal zero, DIP flux is indicated as $RSdif_{ant,DIP}^{Ldip}$ while DIP concentration as $[DIP]^{Ldip}$ (Table 11).

At the river mouth, DIP fluxes and concentrations that generated not only from diffuse sources, but also from DIP weathering over natural areas and point sources are considered. Point sources are represented by human wastes and detergents as these are in the model. They are indicated as $RSpnt_{DIP}$. DIP weathering over natural areas is denoted as $RSdif_{ec,nat,DIP}$ as it is according to the model too. DIP fluxes at the mouth are indicated as $Yld_{DIP}$ while DIP concentrations as $[DIP]_m$, where *m* indicates mouth of the river and when $L_{dip}$ is excluded from calculations. When $L_{dip}$ is included, then DIP flux is indicated as $Yld_{DIP}^{Ldip}$ and DIP concentration as $[DIP]_m^{Ldip}$ (see Table 11).

In this study DIP fluxes and concentrations are calculated for 2000, 2030 and 2050 (Table 11). The Global *NEWS* model incorporates storylines of four MEA scenarios for future analyses of nutrient export (see Chapter 2, Section 2.2). In this study, the GO scenario of the MEA was selected for future calculations (2030, 2050). This is because the GO represents the worst case of future world developments regarding the environment. This considers a globalized world with particular attention on economic developments rather than on the environment. Additionally, the scenario takes a reactive approach to manage environmental problems (Chapter 2, Section 2.2; Seitzinger et al., 2010).

***Table 11***
*Major variables that are used to calculate DIP flux and concentration at the watershed scale as well as at the river mouth by excluding and including river retention for DIP.*

| Output variables | Estimations for the years | River retention is not included (Ldip=0) | River retention is included (Ldip≠0) |
|---|---|---|---|
| | | Abbreviation | Abbreviation |
| Watershed scale | | | |
| DIP flux | 2000<br>2030<br>2050 | $RSdif_{ant,DIP}$ | $RSdif_{ant,DIP}^{Ldip}$ |
| DIP concentration | 2000<br>2030<br>2050 | [DIP] | $[DIP]^{Ldip}$ |
| River mouth | | | |
| DIP flux | 2000<br>2030<br>2050 | $Yld_{DIP}$ | $Yld_{DIP}^{Ldip}$ |
| DIP concentration | 2000<br>2030<br>2050 | $[DIP]_m$ | $[DIP]_m^{Ldip}$ |

Calculations of DIP fluxes and concentrations at the watershed scale and at the river mouth are presented below, separately for the steady state and dynamic approaches. It is important to mention that abbreviations of DIP fluxes and concentrations at the watershed scale and river mouth do not differ between the steady state and dynamic approaches.

**Calculations under steady state conditions (Figure 15)**

– At the watershed scale
  Steady state calculations of DIP concentrations ([DIP] and $[DIP]^{Ldip}$ in g $m^{-3}$ or mg $L^{-1}$) and fluxes ($RSdif_{ant,DIP}$ and $RSdif_{ant,DIP}^{Ldip}$ in kg $ha^{-1}$ $year^{-1}$) at the watershed scale are discussed earlier in Section 3.2.1. A summary of equations is provided in Figure 15. Additionally Figures 13 and 14 (given in Section 3.2.1) provide insight into variables and input data that are required in order to calculate $RSdif_{ant,DIP}$ and $RSdif_{ant,DIP}^{Ldip}$ as well as [DIP] and $[DIP]^{Ldip}$. To estimate DIP concentrations eq. (26) is used for both without (Ldip=0) and with (Ldip≠0) river retention. The difference is that in estimation of $[DIP]^{Ldip}$ calculated $RSdif_{ant,DIP}^{Ldip}$ is used instead of $RSdif_{ant,DIP}$. $RSdif_{ant,DIP}$ is derived according to eq. (21). $RSdif_{ant,DIP}^{Ldip}$ is estimated by using eq. (28). For more explanations regarding calculations, the reader is referred to Section 3.2.1. Note that calculations in Section 3.2.1 are done for the year 2000. Here, DIP fluxes and concentrations are derived not only for 2000, but also for 2030 and 2050. Thus, input data (original or adapted, Section 3.3) have to be taken for these years too.

– At the river mouth
  DIP fluxes (in kg $ha^{-1}$ $year^{-1}$) for both without ($Yld_{DIP}$, Ldip=0) and with ($Yld_{DIP}^{Ldip}$, Ldip≠0) river retention are estimated for 2000, 2030 and 2050 according to the approach used by the Global *NEWS* model (this is modification of eq. (8), where $RSdif_{ant,DIP}$ is combination of $RSdif_{ec,ant,DIP}$ and $RSdif_{expl,ant,DIP}$) as:

$$Yld_{DIP.2000} = (RSdif_{ant,DIP.2000} + RSdif_{ec.nat.DIP.2000} + RSpnt_{DIP.2000}) \cdot FEriv_{DIP.2000} \quad (30.a)$$

$$Yld_{DIP.2030} = (RSdif_{ant,DIP.2030} + RSdif_{ec.nat.DIP.2030} + RSpnt_{DIP.2030}) \cdot FEriv_{DIP.2030} \quad (30.b)$$

$$Yld_{DIP.2050} = (RSdif_{ant,DIP.2050} + RSdif_{ec.nat.DIP.2050} + RSpnt_{DIP.2050}) \cdot FEriv_{DIP.2050} \quad (30.c)$$

  $RSdif_{ant.DIP}$, $RSdif_{ec.nat.DIP}$ and $RSpnt_{DIP}$ - are DIP fluxes exported to rivers from diffuse sources ($RSdif_{ant.DIP}$), DIP weathering over natural areas ($RSdif_{ec.nat.DIP}$) and point sources ($RSpnt_{DIP}$), kg $ha^{-1}$ $year^{-1}$. 2000, 2030 and 2050 indicate year for which estimations are done. Note, that according to the steady state approach $RSdif_{ant,DIP}$ is estimated by using eq. (21) when Ldip is zero and eq. (28) when Ldip is included. $RSdif_{ec.nat,DIP}$ and $RSpnt_{DIP}$ are estimated by using eq. (29) and eq. (5) respectively. In this study an assumption was made that DIP fluxes at the river mouth are not affected by an addition of river retention to the model. DIP fluxes are affected only at the watershed scale that are generated only from diffuse sources. Thus, in this case, $Yld_{DIP}^{Ldip}$ equals $Yld_{DIP}$ (see Fig. 15). Since $Yld_{DIP}$ is directly available from the Global *NEWS* model, it can be taken without estimations.

| $L_{dip}$=0 | **Steady State Approach** | $L_{dip}\neq 0$ |
|---|---|---|

**Watershed** | **Scale**

$$[DIP] = \frac{1000 \cdot RSdif_{ant,DIP}}{R} \qquad eq.26$$

R – original data (Section 3.3.1)

$$RSdif_{ant,DIP} = DIPTant \cdot FEws_{DIP} \qquad eq.21$$

DIPTant (=$P_{in}$-$P_{up}$) – original data (Section 3.3.1)
$FEws_{DIP}$ – original data (Section 3.3.1)

$$[DIP]^{Ldip} = \frac{1000 \cdot RSdif_{ant,DIP}^{Ldip}}{R} \qquad eq.26$$

R – original data (Section 3.3.1)

$$RSdif_{ant,DIP}^{L_{dip}} = \frac{RSdif_{ant,DIP} + (RSdif_{ec.nat.DIP} + RSpnt_{DIP}) \cdot L_{dip}}{(1 - L_{dip})} \qquad eq.28$$

$RSdif_{ant,DIP}$ – eq.21
$RSdif_{ec,nat,DIP}$ – eq.29 (Section 3.2.1)
$RSpnt_{DIP}$ – eq.5 (Section 2.2.2)
$L_{dip}$ – adapted data (Section 3.3.2)

**River** | **Mouth**

$$Yld_{DIP} = (RSdif_{ant.DIP} + RSdif_{ec,nat,DIP} + RSpnt_{DIP}) \cdot FEriv_{DIP} \qquad eq.30$$

$FEriv_{DIP}$ – original data (Section 3.3.1)
$RSdif_{ec,nat,DIP}$ – eq.29 (Section 3.2.1)
$RSpnt_{DIP}$ – eq.5 (Section 2.2.2)

$Yld_{DIP}$ = Global *NEWS* value

$$[DIP]_m = \frac{1000 \cdot Yld_{DIP}}{Qact} \qquad eq.32$$

Qact – original data (Section 3.3.1)

$$Yld_{DIP}^{L_{dip}} = (RSdif_{ant.DIP}^{L_{dip}} + RSdif_{ec,nat,DIP} + RSpnt_{DIP}) \cdot FEriv_{DIP}^{L_{dip}} \qquad eq.30$$

$$FE_{riv,DIP}^{Ldip} = FE_{riv,DIP} \cdot (1 - L_{dip}) \qquad eq.31$$

$FEriv_{DIP}$ – original data (Section 3.3.1)
$L_{dip}$ – adapted data (Section 3.3.2)
$RSdif_{ec,nat,DIP}$ – eq.29 (Section 3.2.1)
$RSpnt_{DIP}$ – eq.5 (Section 2.2.2)

$Yld_{DIP}^{Ldip}$ = $Yld_{DIP}$ (an assumption that $Yld_{DIP}$ does not change by the addition of DIP resulted from river retention)

$$[DIP]_m^{L_{dip}} = \frac{1000 \cdot Yld_{DIP}^{L_{dip}}}{Qact} \qquad eq.32$$

Qact – original data (Section 3.3.1)

$[DIP]_m^{Ldip}$ = $[DIP]_m$

*Figure 15*
*Summarized equations that are used to estimate DIP fluxes and concentrations under the steady state approach when Ldip equals zero ($L_{dip}$=0) and does not equal zero ($L_{dip}\neq 0$). Section 3.2.1 is the main source for their calculations at the watershed scale. Definitions of variables are provided in this section and also in Section 3.2.1. Definitions of input data that are needed to calculate these variables are given in Section 3.3 corresponding to original data (Section 3.3.1) and adapted data (Section 3.3.2)*

$FE_{riv,DIP}$ - is an export fraction of DIP that is exported at river mouth via the river system (from 0 to 1), where DIP retention is considered via water consumption and reservoirs (see also previous section). The fraction is derived according to *NEWS* approach (eq. (6)). This fraction is directly available from the model. Thus, there is no need to estimate it. When DIP retention within the river system itself (e.g. P sedimentation) is included, this fraction is estimated as (modified from the formula presented in a paper of Mayorga et al., (2010), Section 3.2):

$$FEriv_{DIP}^{L_{dip}} = FEriv_{DIP} \cdot (1 - L_{dip}) \tag{31}$$

Ldip - is fraction of DIP that is retained in the river system itself (from 0 to 1) (see previous section).
DIP concentrations (in g $m^{-3}$ or mg $L^{-1}$) for both without ($[DIP]_m$ Ldip=0) and with ($(DIP]_m^{Ldip}$, Ldip≠0) river retention for the year 2000, 2030 and 2050 can be derived from $Yld_{DIP}$ similarly to eq. (26) as:

$$[DIP]_{m,2000} = \frac{1000 \cdot Yld_{DIP,2000}}{Qact_{2000}} \tag{32.a}$$

$$[DIP]_{m,2030} = \frac{1000 \cdot Yld_{DIP,2030}}{Qact_{2030}} \tag{32.b}$$

$$[DIP]_{m,2050} = \frac{1000 \cdot Yld_{DIP,2050}}{Qact_{2050}} \tag{32.c}$$

$Qact_{2000}$, $Qact_{2030}$ and $Qact_{2050}$ - are total river discharge (actual) corrected for water consumptive use for 2000, 2030 and 2050 respectively ($m^3$ $ha^{-1}$ $year^{-1}$). $Yld_{DIP,2000}$, $Yld_{DIP,2030}$ and $Yld_{DIP,2050}$ – are DIP flux (or yield) that is exported at the river mouth for 2000, 2030 and 2050 respectively (kg $ha^{-1}$ $year^{-1}$). These values are different for when Ldip≠0. However, because of that assumption these values are the same with those, where Ldip is zero. Following this, $[DIP]_m^{Ldip}$ also equals $[DIP]_m$ (see Figure 15).

**Calculations under dynamic conditions (Fig. 16)**

– At the watershed scale

Estimation of DIP concentrations (g $m^{-3}$ or mg $L^{-1}$) for both without ([DIP], Ldip=0) and with ($[DIP]^{Ldip}$, Ldip≠0) river retention at the watershed scale is derived mathematically from eq.(16) as (see also Figure 16):

$$[DIP]_{2000} = \frac{P_{ox,pool,2000} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max}}{[1 - (P_{ox,pool,2000} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max})] \cdot K_p} \tag{33.a}$$

$$[DIP]_{2030} = \frac{P_{ox,pool,2030} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max}}{[1 - (P_{ox,pool,2030} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max})] \cdot K_p} \tag{33.b}$$

$$[DIP]_{2050} = \frac{P_{ox,pool,2050} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max}}{[1 - (P_{ox,pool,2050} / 0.93 \cdot \rho \cdot T \cdot P_{s,re,\max})] \cdot K_p} \tag{33.c}$$

$[DIP]_{2000}$, $[DIP]_{2030}$ and $[DIP]_{2050}$ - are dynamic based averaged dissolved inorganic P concentration at watershed scale (g $m^{-3}$ or mg $L^{-1}$) calculated for 2000, 2030 and 2050 respectively;
$K_P$ - is Langmuir adsorption constant ($m^3$ $g^{-1}$ P) calculated for 2000 according to eq.(16) (see Section 3.2.1). Values of calculated Kp are used the same as for 2000 for further calculations;
0.93 - the value that combines values of 10 (from Equation 11), 0.031 (conversion factor from mmol $kg^{-1}$ to g $kg^{-1}$) and 3 (from equation 14) (see also previous Section);
ρ - is bulk density of the soil (kg $m^{-3}$). Values of bulk density are used the same for 2000, 2030 and 2050;
T - is soil thickness (m). Here this is related to watershed depth. It is also used the same for 2000, 2030 and 2050; $P_{s,re,max}$ - is the maximum amount of readily available (adsorbed) P in the soil (mmol $kg^{-1}$). $P_{s,re,max}$ is derived from the $Al_{ox}$+$Fe_{ox}$ content according to equation (15) and is expressed in mmol $kg^{-1}$. This value does not have to be converted to g $kg^{-1}$ because the conversion factor (0.031) is already incorporated in eq. (16). Values of $P_{s,re,max}$ are the same for 2000, 2030 and 2050;
$P_{ox,pool,2000}$ - is the oxalate extractable P pool (kg $ha^{-1}$) calculated for 2000 according to eq. (17) (see Section 3.2.1);

$P_{ox,pool,2030}$ – is the oxalate extractable P pool (kg ha$^{-1}$) calculated for 2030 based on $P_{ox,pool,2000}$ according to:

$$P_{ox,pool,2030} = P_{ox,pool,2000} + frP_{ac} \cdot \sum_{2000-2030}(P_{in,t} - P_{up,t}) \quad (34)$$

$frP_{ac}$ – is the fraction of P that is accumulated in the soil in 2000. The assumption is made that this fraction remained constant during the period 2000 and 2030 and is estimated according to eq. (19) (see Section 3.2.1);

$\sum_{2000-2030}(P_{in,t} - P_{up,t})$ - is the accumulated amount of P in the period 2000 and 2030 (kg ha$^{-1}$ year$^{-1}$).

$P_{in}$-$P_{up}$ equals to values of DIPTant, which can be taken directly from the model (for more explanation see Section 3.2.1 and Section 3.3 regarding input data). The P accumulation over the period 2000-2030 is based on an assumption that the P surplus ($P_{in}$-$P_{up}$) increases linearly from values of the Global *NEWS* model in 2000 to its values in 2030. Thus, accumulation of P in this period is calculated as:

$$\sum_{2000-2030}(P_{in,t} - P_{up,t}) = \frac{(P_{in} - P_{up})_{2000} + (P_{in} - P_{up})_{2030}}{2} \cdot 30 \quad (35)$$

30 – is the period of P accumulation over 30 years (from 2000 to 2030).
$P_{ox,pool,2050}$ – is the oxalate extractable P pool (kg ha$^{-1}$) calculated for 2050 based on $P_{ox,pool,2000}$ according to:

$$P_{ox,pool,2050} = P_{ox,pool,2000} + frP_{ac} \cdot \sum_{2000-2050}(P_{in,t} - P_{up,t}) \quad (36)$$

Here, $frP_{ac}$ is the same as in eq. (34). Estimation of P that is accumulated over the period 2000-2050 is divided into two periods namely P accumulated over 2000-2030 and over 2030-2050. This is because the Global *NEWS* model performs future estimation of nutrient export for 2030 and 2050. Timeframe between 2000 and 2030 as well as between 2030 and 2050 is different. Thus, in order to avoid any mistakes, accumulated amount of P is estimated as the sum of P accumulated over these two periods as:

$$\sum_{2000-2050}(P_{in,t} - P_{up,t}) = \sum_{2000-2030}(P_{in,t} - P_{up,t}) + \sum_{2030-2050}(P_{in,t} - P_{up,t}) \quad (37)$$

The P accumulation over the period 2000-2030 is derived according to eq. (35). The P accumulation over the period 2030-2050 is also assumed to change linearly from the known values in 2030 and 2050. Thus P accumulation over this period is estimated similarly to equation (35) as:

$$\sum_{2030-2050}(P_{in,t} - P_{up,t}) = \frac{(P_{in} - P_{up})_{2030} + (P_{in} - P_{up})_{2050}}{2} \cdot 20 \quad (38)$$

20 - is the period of P accumulation over 20 years (from 2030-2050).

DIP concentrations as a function of river retention ($[DIP]^{Ldip}$, Ldip≠0) are calculated according to eq. (33.a) for 2000, eq. (33.b) for 2030 and eq. (33.c) for 2050 as it was mentioned above. However, $P_{ox,pool}$ and $K_p$ used in these equations are derived based on $RSdif_{ant,DIP}^{Ldip}$ values instead of $RSdif_{ant,DIP}$ values. Hence, these variables are indicated as $P_{ox,pool}^{Ldip}$ and $K_p^{Ldip}$ (see Figure 16). A procedure to calculate this $RSdif_{ant,DIP}^{Ldip}$ for this case is revised in Section 3.2.1 and is presented in Figure14. Its estimation is done on the basis of eq. (28) (see previous Section). Note, that this $RSdif_{ant,DIP}^{Ldip}$ is estimated based on the steady sate approach rather than on the dynamic one because it is used in $P_{ox,pool}$ and $K_p$ estimations (see Figure14). $K_p$ values are derived from eq.

(16) for 2000 (see Section 3.2.1). $P_{ox,pool,2000}$ is estimated according to eq. (17) while $P_{ox,pool,2030}$ and $P_{ox,pool,2050}$ are done based on eq. (34) and eq. (36) respectively, where $frP_{ac}$ is estimated for 2000 according to eq. (19) using also $RSdif_{ant,DIP}^{Ldip}$ values estimated similarly as for $P_{ox,pool}^{Ldip}$ and $K_p^{Ldip}$.

**$L_{dip}$=0** **Dynamic Approach** **$L_{dip}$≠0**

| $L_{dip}=0$ | $L_{dip}\neq 0$ |
|---|---|
| **Watershed** | **Scale** |
| $[DIP] = \frac{P_{ox,pool}/0.93\cdot\rho\cdot T\cdot P_{s,re,\max}}{[1-(P_{ox,pool}/0.93\cdot\rho\cdot T\cdot P_{s,re,\max})]\cdot K_p}$ *eq.33* | $[DIP]^{Ldip} = \frac{P_{ox,pool}^{Ldip}/0.93\cdot\rho\cdot T\cdot P_{s,re,\max}}{[1-(P_{ox,pool}^{L_{dip}}/0.93\cdot\rho\cdot T\cdot P_{s,re,\max})]\cdot K_p^{Ldip}}$ |
| $K_P^{Ldip}$ – eq.16 (Section 3.2.1) | $K_P^{Ldip}$ – eq.16 (Section 3.2.1) |
| ρ & T – adapted data (Section 3.3.2) | ρ & T – adapted data (Section 3.3.2) |
| $P_{s.re,\max} = 0.5\cdot 1/3\cdot(Al_{ox}+Fe_{ox})$ *eq.15* | $P_{s.re,\max} = 0.5\cdot 1/3\cdot(Al_{ox}+Fe_{ox})$ *eq.15* |
| $(Al_{ox}+Fe_{ox})$ - adapted data (Section 3.3.2) | $(Al_{ox}+Fe_{ox})$ - adapted data (Section 3.3.2) |
| $P_{ox,pool}^{Ldip}$ for 2000 – eq.17 (Section 3.2.1)<br>for 2030 – eq.34 (Section 3.2.2)<br>for 2050 – eq.36 (Section 3.2.2) | $P_{ox,pool}^{Ldip}$ for 2000 – eq.17 (Section 3.2.1)<br>for 2030 – eq.34 (Section 3.2.2)<br>for 2050 – eq.36 (Section 3.2.2) |
| $RSdif_{ant,DIP} = \frac{R\cdot[DIP]}{1000}$ *eq.39* | $RSdif_{ant,DIP}^{Ldip} = \frac{R\cdot[DIP]^{Ldip}}{1000}$ *eq.39* |
| R – original data (Section 3.3.1) | R – original data (Section 3.3.1) |
| **River** | **Mouth** |
| $Yld_{DIP} = (RSdif_{ant.DIP} + RSdif_{ec,nat,DIP} + RSpnt_{DIP})\cdot FEriv_{DIP}$ *eq. 30* | $Yld_{DIP}^{Ldip} = (RSdif_{ant.DIP}^{Ldip} + RSdif_{ec,nat,DIP} + RSpnt_{DIP})\cdot FEriv_{DIP}^{Ldip}$ *eq. 30* |
| | $FE_{riv,DIP}^{Ldip} = FE_{riv,DIP}\cdot(1-L_{dip})$ *eq.31* |
| $FEriv_{DIP}$ – original data (Section 3.3.1)<br>$RSdif_{ec,nat,DIP}$ – eq.29 (Section 3.2.1)<br>$RSpnt_{DIP}$ – eq.5 (Section 2.2.2) | $FEriv_{DIP}$ – original data (Section 3.3.1)<br>$L_{dip}$ – adapted data (Section 3.3.2)<br>$RSdif_{ec,nat,DIP}$ – eq.29 (Section 3.2.1)<br>$RSpnt_{DIP}$ – eq.5 (Section 2.2.2) |
| $[DIP]_m = \frac{1000\cdot Yld_{DIP}}{Qact}$ *eq.40* | $[DIP]_m^{Ldip} = \frac{1000\cdot Yld_{DIP}^{Ldip}}{Qact}$ *eq.40* |
| Qact – original data (Section 3.3.1) | Qact – original data (Section 3.3.1) |

*Figure 16*

*Summarized equations that are used to estimate DIP fluxes and concentrations under the dynamic approach when Ldip equals zero ($L_{dip}$=0) and does not equal zero ($L_{dip}$≠0). Definitions of variables are provided in this section and also in Section 3.2.1. Definitions of input data that are needed to calculate these variables are given in Section 3.3 corresponding to original data (Section 3.3.1) and adapted data (Section 3.3.2)*

DIP flux (in kg $ha^{-1}$ $year^{-1}$) exported from land to rivers for both without ($RSdif_{ant,DIP}$, Ldip=0) and with ($RSdif_{ant,DIP}^{Ldip}$, Ldip≠0) is estimated by using the following formula (this is mathematically derived from eq.(26)):

$$RSdif_{ant,DIP,2000} = \frac{R_{2000} \cdot [DIP]_{2000}}{1000} \quad (39.a)$$

$$RSdif_{ant,DIP,2030} = \frac{R_{2030} \cdot [DIP]_{2030}}{1000} \quad (39.b)$$

$$RSdif_{ant,DIP,2050} = \frac{R_{2050} \cdot [DIP]_{2050}}{1000} \quad (39.c)$$

$RSdif_{ant,DIP,2000}$, $RSdif_{ant,DIP,2050}$ and $RSdif_{ant,DIP,2050}$ - are dynamic based DIP fluxes for 2000, 2030 and 2050 respectively, which are exported from the watershed (land) to the river (RS=river sources) and resulted from diffuse (dif) anthropogenic (ant) sources such as synthetic fertilizer and animal manure applications to the soil as well as DIP weathering over agricultural areas, (kg $ha^{-1}$ $year^{-1}$);
$[DIP]_{2000}$, $[DIP]_{2030}$ and $[DIP]_{2050}$ - are dynamic based averaged dissolved inorganic P concentration at watershed scale (g $m^{-3}$ or mg $L^{-1}$) calculated for 2000, 2030 and 2050 according to eq. (33.a), eq. (33.b) and eq. (33.c) respectively;
$R_{2000}$, $R_{2030}$ and $R_{2050}$ - is mean annual runoff from land to the river for 2000, 2030 and 2050 respectively, ($m^3$ $ha^{-1}$ $year^{-1}$);
1000 - is needed to convert units from g $ha^{-1}$ $year^{-1}$ to kg $ha^{-1}$ $year^{-1}$.

Dynamic based DIP flux exported from land to rivers as a function of river retention ($RSdif_{ant,DIP}^{Ldip}$, Ldip≠0) is derived on the basis of these formulas for 2000, for 2030 and 2050 using calculated values of $[DIP]^{Ldip}$ instead of [DIP] values (see Figure 16). $[DIP]^{Ldip}$ values are obtained from eq. (33), where $P_{ox,pool}^{Ldip}$ and $K_p^{Ldip}$ are used (see above).

– At the river mouth

DIP concentrations ($[DIP]_m$, $[DIP]_m^{Ldip}$) at the river mouth is derived from calculated DIP flux at the river mouth.

DIP fluxes for both without ($Yld_{DIP}$, $L_{dip}$=0) and with ($Yld_{DIP}^{Ldip}$, $L_{dip}$≠0) are calculated according to approach used in the Global *NEWS* model as the sum of DIP fluxes from different sources ($RSdif_{ant,DIP}$/$RSdif_{ant.DIP}^{Ldip}$+$RSdif_{ec,nat,DIP}$+$RSpnt_{DIP}$) multiplied by river-system export fraction ($FEriv_{DIP}$ or $FEriv_{DIP}^{Ldip}$ depending on whether river retention is excluded or included) (see Figure16). This is applied in eq. (30.a) for 2000, eq. (30.b) for 2030 and eq. (30.c) for 2050 (see above). Note that according to the dynamic approach $RSdif_{ant,DIP}$ and $RSdif_{ant,DIP}^{Ldip}$ is estimated by eq. (39) (see above). $RSdif_{ec.nat,DIP}$ and $RSpnt_{DIP}$ are estimated according to equations eq. (29) and eq. (5) respectively. $FEriv_{DIP}$ is directly can be taken from the model while $FEriv_{DIP}^{Ldip}$ can be estimated by using eq. (31).

DIP concentrations at the mouth for both without ($[DIP]_m$, $L_{dip}$=0) and with (($[DIP]_m^{Ldip}$, $L_{dip}$≠0) are estimated similarly to eq. (32) as:

$$[DIP]_{m,2000} = \frac{1000 \cdot Yld_{DIP,2000}}{Qact_{2000}} \quad (40.a)$$

$$[DIP]_{m,2030} = \frac{1000 \cdot Yld_{DIP,2030}}{Qact_{2030}} \quad (40.b)$$

$$[DIP]_{m,2050} = \frac{1000 \cdot Yld_{DIP,2050}}{Qact_{2050}} \quad (40.c)$$

$[DIP]_{m,2000}$, $[DIP]_{m,2030}$ and $[DIP]_{m,2050}$ - are averaged dissolved inorganic P concentration at the river mouth (g $m^{-3}$ or mg $L^{-1}$) calculated for 2000, 2030 and 2050 respectively;
$Yld_{DIP,2000}$, $Yld_{DIP,2030}$ and $Yld_{DIP,2050}$ - are DIP fluxes exported at the river mouth for 2000, 2030 and 2050 (expressed in kg $ha^{-1}$ $year^{-1}$) respectively. These fluxes are derived from eq. (30.a) for 2000, eq. (30.b) for 2030 and eq. (30.c) for 2050;

$Qact_{2000}$, $Qact_{2030}$ and $Qact_{2050}$ - are total river discharges (actual discharge) at the mouth after implementing irrigation and other water withdrawal systems for years 2000, 2030 and 2050 respectively (in $m^3$ $ha^{-1}$ $year^{-1}$). Its values for those years are directly available from the model (Section 3.3).
For $[DIP]_m^{Ldip}$ ($L_{dip}\neq0$), values of $Yld_{DIP}^{Ldip}$ are used instead of $Yld_{DIP}$.

The assumption that DIP fluxes at the mouth are not allowed to be changed by including river retention works here as well. However, manor changes in DIP export over time (from 2000 to 2050) are expected since dynamics involved in this case.

## 3.3 Required data to implement the dynamic approach

This section provides information regarding data required to implement P dynamics to the Global *NEWS* model. The section is divided into two parts. The first part presents information on original data, which is taken from the model and is used directly in calculations (Section 3.3.1). Second part gives information on data that have to be added and thus adapted to the model (Section 3.3.2).

### 3.3.1 Original data

The majority of input data that are needed for further calculations of variables such as P adsorption constant, DIP concentrations and DIP fluxes at both watershed scale and river mouth are derived from the Global *NEWS* model and thus called as original data. Table 12 and Table 13 provide information regarding input data required in order to estimate the P adsorption constant (Table 12), DIP concentrations and fluxes based on the steady state (Table 12) and dynamic approaches (Table 13). Their definitions are summarized in Table 14.

*Table 12*

*Input variables that are derived from the Global NEWS model and needed to estimate P adsorption constant ($K_P$), DIP concentrations and DIP fluxes at both watershed scale and river mouth (their abbreviations are given in Section 3.2.2) under the steady state approach. Plus (+) indicates where the input variable is used. Each DIP flux and/or concentration includes all input variables needed to its estimation. For instance, $RSdif_{ant,DIP}$ is used for [DIP], and input variables needed for $RSdif_{ant,DIP}$ are also included for [DIP].*

| Input variables | Year | KP | Calculated output variables under the steady sate approach | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Watershed scale | | | | River mouth | | | |
| | | | [DIP] | [DIP]Ldip | RSdifant, DIP | RSdifant, DIPLdip | [DIP]m | [DIP]mLdip | YldDIP* | YldDIPLdip* |
| DIPTant | 1970 | + | | | | | | | | |
| | 2000 | + | + | + | + | + | | | | |
| | 2030 | | + | + | + | + | | | | |
| | 2050 | | + | + | + | + | | | | |
| DIPTnat | 2000 | + | | + | | + | | | | |
| | 2030 | | | + | | + | | | | |
| | 2050 | | | + | | + | | | | |
| $FEws_{DIP}$ | 2000 | + | + | + | + | + | | | | |
| | 2030 | | + | + | + | + | | | | |
| | 2050 | | + | + | + | + | | | | |
| $FEws_{DOP}$ | 2000 | + | | | | | | | | |
| $WSdif_{fe,P}$ | 2000 | + | | | | | | | | |
| $WSdif_{me,P}$ | 2000 | + | | | | | | | | |
| $WSdif_{ex,P}$ | 2000 | + | | | | | | | | |
| R | 2000 | + | + | + | | | | | | |
| | 2030 | | + | + | | | | | | |
| | 2050 | | + | + | | | | | | |
| Qact | 2000 | | | | | | + | + | | |
| | 2030 | | | | | | + | + | | |
| | 2050 | | | | | | + | + | | |
| $Yld_{DIP}$* | 2000 | | | | | | + | + | + | + |
| | 2030 | | | | | | + | + | + | + |
| | 2050 | | | | | | + | + | + | + |
| $RSpnt_P$ | 2000 | + | | + | | + | | | | |
| | 2030 | | | + | | + | | | | |
| | 2050 | | | + | | + | | | | |
| $FEpnt_{DIP}$ | 2000 | + | | + | | + | | | | |
| | 2030 | | | + | | + | | | | |
| | 2050 | | | + | | + | | | | |

* *$Yld_{DIP}$ and $Yld_{DIP}^{Ldip}$ are referred as input variables because $Yld_{DIP}$ is directly taken from the Global NEWS model and $Yld_{DIP}^{Ldip}$ equals values of $Yld_{DIP}$ according to the made assumption (see Section 3.2.2).*

*Table 13*

*Input variables that are derived from the Global NEWS model and needed to estimate DIP concentrations and DIP fluxes at both watershed scale and river mouth (their abbreviations are given in Section 3.2.2) under the dynamic approach. Plus (+) indicates where the input variable is used. Each DIP flux and/or concentration includes all input variables needed to its estimation. For instance, $K_P$ is used for [DIP], and input variables needed for $K_P$ are also included for [DIP].*

| Input variables | Year | Calculated output variables under the dynamic approach | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Watershed scale | | | | River mouth | | | |
| | | [DIP] | $[DIP]^{Ldip}$ | $RSdif_{ant,DIP}$ | $RSdif_{ant,DIP}^{Ldip}$ | $[DIP]_m$ | $[DIP]_m^{Ldip}$ | $Yld_{DIP}$ | $Yld_{DIP}^{Ldip}$ |
| DIPTant | 1970 | + | + | + | + | + | + | + | + |
| | 2000 | + | + | + | + | + | + | + | + |
| | 2030 | + | + | + | + | + | + | + | + |
| | 2050 | + | + | + | + | + | + | + | + |
| DIPTnat | 2000 | | + | | + | + | + | + | + |
| | 2030 | | | | | + | + | + | + |
| | 2050 | | | | | + | + | + | + |
| $FEws_{DIP}$ | 2000 | + | + | + | + | + | + | + | + |
| | 2030 | | | | | + | + | + | + |
| | 2050 | | | | | + | + | + | + |
| $FEws_{DOP}$ | 2000 | + | + | + | + | + | + | + | + |
| $WSdif_{fe.P}$ | 2000 | + | + | + | + | + | + | + | + |
| $WSdif_{me.P}$ | 2000 | + | + | + | + | + | + | + | + |
| $WSdif_{ex.P}$ | 2000 | + | + | + | + | + | + | + | + |
| R | 2000 | + | + | + | + | + | + | + | + |
| | 2030 | | | + | + | + | + | + | + |
| | 2050 | | | + | + | + | + | + | + |
| Qact | 2000 | | | | | + | + | | |
| | 2030 | | | | | + | + | | |
| | 2050 | | | | | + | + | | |
| $FEriv_{DIP}$ | 2000 | | | | | + | + | + | + |
| | 2030 | | | | | + | + | + | + |
| | 2050 | | | | | + | + | + | + |
| $RSpnt_P$ | 2000 | | + | | + | + | + | + | + |
| | 2030 | | | | | + | + | + | + |
| | 2050 | | | | | + | + | + | + |
| $FEpnt_{DIP}$ | 2000 | | + | | + | + | + | + | + |
| | 2030 | | | | | + | + | + | + |
| | 2050 | | | | | + | + | + | + |

*Table 14*

*Definitions of input variables used to estimate P adsorption constant, DIP concentrations and DIP fluxes (Source: the Global NEWS model source code; Mayorga et al., 2010).*

| Input variables | Definitions of variables |
|---|---|
| DIPTant (= $P_{in}$-$P_{up}$) | Net total P diffuse inputs over agricultural areas, where fertilizer, manure and DIP weathering are considered |
| DIPTnat | Net total P diffuse inputs over natural areas, where only DIP weathering is considered |
| $FEws_{DIP}$ | Export fraction of P that is exported from watershed (land) to rivers as DIP |
| $FEws_{DOP}$ | Export fraction of P that is exported from watershed (land) to rivers as DOP |
| $WSdif_{fe.P}$ | TP inputs to the watershed (land) from synthetic fertilizer use in agriculture |
| $WSdif_{me.P}$ | TP inputs to the watershed (land) from animal manure use in agriculture |
| $WSdif_{ex.P}$ | TP export from the watershed (land) by crop harvesting and animal grazing |
| R | Mean annual basin runoff from land to streams (sometimes denoted as Rnat) |
| Qact | Total river discharge at the mouth after implementing irrigation and other water withdrawal systems |
| $Yld_{DIP}$ | DIP flux (yield) that exported at the river mouth |
| $FEriv_{DIP}$ | River-system export fraction of DIP that is exported at the mouth. This fraction includes DIP removal (DIP that is not exported at the mouth) in the river via water consumptive use and reservoir trapping. |
| $RSpnt_P$ | Emission of P to streams from point sources: human waste and detergents |
| $FEpnt_{DIP}$ | Export fraction of P from point sources that is exported to streams as DIP |

These variables are provided in excel documents of run 5 (available at http://marine.rutgers.edu/globalnews/mission.htm) (Table 15). There are two types of excel files, i.e. input excel files, which contain information about model inputs and output excel files, which have outputs of model calculations. Some variables have different names (abbreviations) in excel files of run 5 compared to names used in the paper of Mayorga et al., (2010). Therefore their abbreviations according to excel files are given in brackets in Table 15.

*Table 15*

*Source and units of input variables. Abbreviations of the variables provided in brackets correspond to abbreviations that are used in excel files of run 5 in the Global NEWS model*

| Input variables | Sources: The Global *NEWS* model, run5 | Given units according to the source | Units used in calculations |
|---|---|---|---|
| DIPTant(= $P_{in}$-$P_{up}$) | output excel file (as DIPTant) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| DIPTnat | output excel file (as DIPTnat) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| $FEws_{DIP}$ | output excel file (as DIPFEws) | fraction: 0-1 | fraction: 0-1 |
| $FEws_{DOP}$ | output excel file (as DOPFEws) | fraction: 0-1 | fraction: 0-1 |
| $WSdif_{fe.P}$ | input excel file (as $TP_{fe}$) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| $WSdif_{me.P}$ | input excel file (as $TP_{ma}$) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| $WSdif_{ex.P}$ | input excel file (as $TP_{ex}$) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| R | input excel file (as R) | mm $year^{-1}$ | $m^3$ $ha^{-1}$ $year^{-1}$ |
| Qact** | input excel file (as Qact) | $km^3$ $year^{-1}$ | $m^3$ $ha^{-1}$ $year^{-1}$ |
| $Yld_{DIP}$ | output excel file (as DIPyld) | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| $FEriv_{DIP}$ | output excel file (as DIPFEriv) | fraction: 0-1 | fraction: 0-1 |
| $RSpnt_P$ | input excel file (as TPsewhum, TPsewdet)* | kg $km^{-2}$ $year^{-1}$ | kg $ha^{-1}$ $year^{-1}$ |
| $FEpnt_{DIP}$ | output excel file (as DIPFEpnt) | fraction: 0-1 | fraction: 0-1 |

* *the Global NEWS model gives separately inputs for P exported from human waste (TPsewhum) and detergents (TPsewdet) in input excel files;*

** *values of Qact have to be converted into $m^3$ $ha^{-1}$ $year^{-1}$ by using basin area derived also from the Global NEWS model. This can be done by first converting values from $km^3$ $year^{-1}$ to $m^3$ $year^{-1}$ (multiply by $10^9$ since $1km^3=10^9m^3$). Then, values can be converted from $m^3$ $year^{-1}$ to $m^3$ $km^{-2}$ $year^{-1}$ (divide a value by basin area, which should be in $km^2$). Afterwards, values are converted from $m^3$ $km^{-2}$ $year^{-1}$ to $m^3$ ha $year^{-1}$ by dividing them by 100 ($1km^2=100ha$).*

In the excel files, inputs and outputs of model calculations are presented starting from scenario codes (g, a, t and o) following by year codes (7, 0, 3 and 5), where *c* means 'contemporary' depending on the year (1970 or 2000), *g*, *a*, *t* and *o* are global orchestration, adaptive mosaic, technogarden and order from strength scenarios of the MEA. Numbers such as 7, 0, 3 and 5 equal 1970, 2000, 2030 and 2050. Additionally Table 15 gives information on units used in the Global *NEWS* model for those variables and units used in equations to estimate adsorption constant, DIP concentrations and DIP fluxes. This information indicates variables, which units have to be converted before using them for further calculations.

### 3.3.2 Adapted data

Several input variables that are needed for calculations are not provided by the Global *NEWS* model. These are initial P concentration, P river retention ($L_{dip}$), bulk density (ρ), soil depth/thickness (T) and content of aluminium and iron oxides ($Al_{ox}+Fe_{ox}$) (see Table 16 and 17).

*Table 16*
*Input variables that are derived from different sources and needed to estimate P adsorption constant ($K_P$), DIP concentrations ([DIP] and $[DIP]^{Ldip}$) and DIP fluxes ($RSdif_{ant,DIP}$ and $RSdif_{ant,DIP}^{Ldip}$) under steady state (SS) and dynamic (D) conditions. Plus (+) indicates where the variable is used.*

| Input variables | Calculated output variables | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_P$ | [DIP] | | $[DIP]^{Ldip}$ | | $RSdif_{ant,DIP}$ | | $RSdif_{ant,DIP}^{Ldip}$ | |
| | | SS | D | SS | D | SS | D | SS | D |
| Initial P concentration | + | | + | | + | | + | | + |
| $L_{dip}$ | + | | | + | + | | | + | + |
| ρ | + | | + | | + | | + | | + |
| T | + | | + | | + | | + | | + |
| $Al_{ox}+Fe_{ox}$ | + | | + | | + | | + | | + |

*Table 17*
*Definitions of input variables that are derived from different sources and used to estimate P adsorption constant, DIP concentrations and DIP fluxes.*

| Input variables | Definitions of variables |
|---|---|
| Initial P oxalate content in 1900 | This is used in eq. (18) to calculate $P_{ox.1900}$ (see Figure 13, Section 3.2.1) |
| $L_{dip}$ | Fraction of DIP that is retained in the river system itself (e.g. DIP sedimentation). This abbreviation is used in the Global *NEWS* model |
| ρ | Bulk density |
| T | Soil thickness, referred to watershed depth at which P interacts with water draining to surface water |
| $Al_{ox}+Fe_{ox}$ | Content of aluminium and iron oxides in the soil |

Different sources were used to derive data for those variables. These sources are presented in Table 18. Additionally, there are also given units of those variables according to their sources and units that have to be used in equations.

For sensitivity analyses data for these variables are given in a range from minimum values to maximum values including also their averages (see Table 19). These three sets of values, minimum, average and maximum values. These are used in calculations. Initial concentration of oxalate P in 1900 ($P_{ox,1900}$) and maximum amount of readily available P in the soil ($P_{s,re,max}$) are calculated as a function of $Al_{ox}$+$Fe_{ox}$ content in the soil according to eq. (18) and eq. (15) (see also Section 3.2.1). They are also subjects for sensitivity analysis because of $Al_{ox}$+$Fe_{ox}$ content (Table 19).

*Table 18*

*Sources and units of input variables. Abbreviations of the variables provided according to their sources except for P river retention, which abbreviation is taken from the Global NEWS model.*

| Input variables | Sources | Given units according to the source | Units used in calculations |
|---|---|---|---|
| Initial P oxalate content in 1900 | Set at 0.02 times $Al_{ox}$+$Fe_{ox}$ (see Eq. 18) based on De Vries and Leeters (2001)[1] | mmol $kg^{-1}$ | g $kg^{-1}$ |
| $L_{dip}$ | Grizetti and Bouraoui (2006) | % | fraction |
| ρ | Batjes (1997) | kg $m^{-3}$ | kg $m^{-3}$ |
| T | Bouwman, pers. comm | m | m |
| $Al_{ox}$+$Fe_{ox}$ | Koopmans and van der Salm, 2010 | mmol $kg^{-1}$ | mmol $kg^{-1}$ |

[1] *This value is used in eq. (18) to estimate initial oxalate P concentration as a function of $Al_{ox}$+$Fe_{ox}$ content for the year 1900 ($P_{ox,1900}$) as shown in Table 19 (see also Section 3.2.1 and Figure 13 regarding its estimation).*

*Table 19*

*Values of input variables with a range from minimum to maximum, where average values are also considered. Units of variables are according to their sources (see Table 18).*

| Name and units of the variable | Values of variables | | |
|---|---|---|---|
| | Minimum | Average | Maximum |
| $L_{dip}$ | 10 | 25 | 50 |
| ρ | 1400 | 1500 | 1600 |
| T | 1 | 5 | 10 |
| $Al_{ox}$+$Fe_{ox}$ | 50 | 100 | 150 |
| $P_{ox.1900}$ (eq.18)* | 0.02·50 | 0.02·100 | 0.02·150 |
| $P_{s,re,max}$, (eq.15)** | 0.5/3·50 | 0.5/3·100 | 0.5/3·150 |

* *here $P_{ox,1900}$ is in mmol $kg^{-1}$ since content of $Al_{ox}$+$Fe_{ox}$ used in eq. (18) is in mmol $kg^{-1}$. Therefore, values of $P_{ox,1900}$ have to be converted to g $kg^{-1}$ before using in further calculations (see Section 3.2.1).*

** *$P_{s,re,max}$ is in mmol $kg^{-1}$ because content of $Al_{ox}$+$Fe_{ox}$ is also in mmol $kg^{-1}$. However, its values do not have to be converted into g $kg^{-1}$ because a conversion factor is already incorporated into further calculations (see Section 3.2.1).*

P river retention (indicated in this study as $L_{dip}$) was derived from a report by Grizetti and Bouraoui (2006). The report provides information on percentage of P retained in rivers that was estimated by a GREEN model for different river basins in Europe (see Section 2.1). Their calculations were based on net P inputs from diffuse and point sources. River retention is represented in their estimations as river reducing factor, which is affected by climate and physical characteristics of the basin (Grizetti and Bouraoui, 2006). They calculated that P river retention varies between 11% (for the Weser and Ems rivers) and 38% (for the Rhone River). P river retention for the Rhine, Elbe, Meuse and Seine rivers is between this range. Based on this information an assumption was made to use in this study 10% of P river retention as minimum value, 25% as average and 50% as maximum value. It has to be mentioned that these values are applied to all river basins in this study. Hence, some regional deviations between river basins are expected. For instance, there are significant differences among river basins regarding their capacity to retain P. In a paper of Chen et al. (2010) annual riverine TP retention in the ChangLe river (Chine) was reported to be in a range from 52.5% to 71.2%. They estimated TP retention on the basis of a mass-balance approach for the period of 2004-2006 (Chen et al., 2010). The other study (Schulz and Kohler, 2006) estimated P retention for the Spree river (Northern Germany) to be up to 20% of TP. However, here authors paid attention on TP retention only by macrophyts for the period of 1995-2002. Their estimations were also done on the basis of a mass-balance approach. Reinhardt et al., (2005) give overall retention efficiency about 23% of TP for wetlands (lakes are included). However, since the Global *NEWS* model does not include river retention for DIP, estimations by using these sets of values can be considered as a starting point.

The variation in the bulk density (ρ) is based on a global database described by Batjes (1997). The variation in soil thickness (T) is an assumption based on Bouwman (personal communication).

The soil content of Al- and Fe-oxides ($Al_{ox}$+$Fe_{ox}$) was derived from Koopmans and Van der Salm, (2010). They provided their content for various Dutch soils such as sand-non calcareous, sand calcareous, marine clay soils and organic sandy soils (Table 20).

*Table 20*

*The soil contents of Al- and Fe-oxides ($Al_{ox}$ and $Fe_{ox}$) in various Dutch soils on a molar basis, where n is number of samples (from Koopmans and van der Salm, 2010).*

| Soil type | Statistical parameters | $Al_{ox}$ (mmol $kg^{-1}$) | $Fe_{ox}$ (mmol $kg^{-1}$) |
|---|---|---|---|
| Sand-non calcareous | Minimum | 14.7 | 1.0 |
| (n=31) | Maximum | 115.4 | 85.4 |
| | Average | 52.5 | 23.0 |
| | Standard deviation | 27.6 | 17.2 |
| Sand- calcareous | Minimum | 2.5 | 9.7 |
| (n=5) | Maximum | 5.2 | 13.4 |
| | Average | 4.0 | 12.2 |
| | Standard deviation | 1.3 | 1.6 |
| Marine clay soils | Minimum | 14.9 | 77.4 |
| (n=5) | Maximum | 42.0 | 139.8 |
| | Average | 22.5 | 99.8 |
| | Standard deviation | 11.0 | 24.5 |
| Organic sandy soils | Minimum | 53.1 | 21.3 |
| (dalgronden; n=3) | Maximum | 78.6 | 29.9 |
| | Average | 64.4 | 26.1 |
| | Standard deviation | 13.0 | 4.4 |

Based on this information, an assumption was made to use Al- and Fe-oxides content in a range from 50 mmol $kg^{-1}$ as minimum values, 100 mmol $kg^{-1}$ as average values and 150 mmol $kg^{-1}$ as maximum value for all river basins in this study (see Table 19).

# 4 Model application/sensitivity analysis

This chapter presents results of applying dynamics for DIP in the Global *NEWS* model. First, results of the calculated P adsorption constants are discussed (Section 4.1). Next, sn analyses of DIP fluxes and concentrations, calculated on the basis of the steady state and dynamic approaches, is presented (Section 4.2).

## 4.1 P adsorption constant ($K_P$)

**Brief introduction**

In this study $K_P$ was estimated for 2000 based on the methodology presented in Section 3.2.1. Its estimation was performed for river basins of the world (1163 river basins) and also separately for river basins draining to coastal waters of each continent (see Chapter 1 regarding the study area and Table 21). For sensitivity analysis $K_P$ was estimated using minimum, average and maximum values for bulk density, soil thickness, initial P concentration and river retention (see Section 3.3.2, Table 19).

Some river basins have been excluded from the analysis. Table 21 gives information on the number of river basins and the percentage of their area that are taken into account in this study. River basins, whose $K_P$ values exceeded 99 $m^3$ $g^{-1}$ or equalled zero were excluded from the study, as such values are implausible. There are several reasons that can explain high or even infinite $K_P$ values calculated in this study. These situations can occur when river basins do not have agricultural areas, leading to zero inputs to land and calculated zero DIP export from land to rivers, implying a DIP concentration of zero and thus an infinitely high $K_P$ (see Section 3.2.1, Eq. 16). The DIP flux exported from soils to rivers can also be zero when the export fraction of DIP to rivers from land ($FEws_{DIP}$, see Section 3.2.1) is zero, implying that P is completely retained in the soil.

*Table 21*
*Number of river basins according to the study area and number of river basins (percentage (%) of their area) that is selected for an analysis the results of $K_P$ calculations and for further analyses of DIP fluxes and concentrations.*

| | Number of river basins according to the study area* | Selected number of river basins (% of their areas) |
|---|---|---|
| The world | 1163 | 506 (67%) |
| Africa | 176 | 116 (72%) |
| Australia | 75 | 34 (39%) |
| North America | 321 | 77 (57%) |
| South America | 115 | 73 (90%) |
| Europe | 137 | 73 (75%) |
| Oceania | 46 | 29 (65%) |
| North Asia | 134 | 15 (52%) |
| South Asia | 159 | 89 (59%) |

* *These are the basins, which number of grid cells is greater than 4 (see Section 1.2).*

Finally, the DIP flux can be very low when the runoff rate is very high (for instance around 2,31 $m^3$ $ha^{-1}$ $year^{-1}$ in Tamanrasett basin, African continent, drains to Atlantic Ocean), results in very low DIP concentrations (see Section 3.2.1, Eq 26), thus causing implausible $K_P$ values. Results of P adsorption constant are discussed below in terms of sensitivity analysis and a comparison of $K_P$ values of this study with literature values.

Results of P adsorption constant are discussed below in terms of sensitivity analysis and a comparison of $K_P$ values of this study with literature values.

**Sensitivity analysis**

Results indicate that $K_P$ values are sensitive to the addition of river retention to the model (Figure 17 and 18). $K_P$ values are considerably lower when river retention (Ldip≠0) is included compared to $K_P$ values when river retention is excluded (Ldip=0), being the case in the Global *NEWS* model. Since the DIP flux that is retained by river retention that was added to the watershed export, this increases the DIP concentration in watersheds export, thus lowering the estimated $K_P$ (see methodology in Section 3.2.1). Calculated average $K_P$ values for the watersheds of the world equal 14.52 $m^3$ $g^{-1}$ when river retention is neglected, 8.52 $m^3$ $g^{-1}$ when river retention is 10% (minimum value) and 2.95 $m^3$ $g^{-1}$ when river retention is 50% (maximum value) (Figure 17). The addition of river retention is also affected by the oxalate extractable P pool used to estimate $K_P$, but $K_P$ values do not change considerably by changing this P pool.

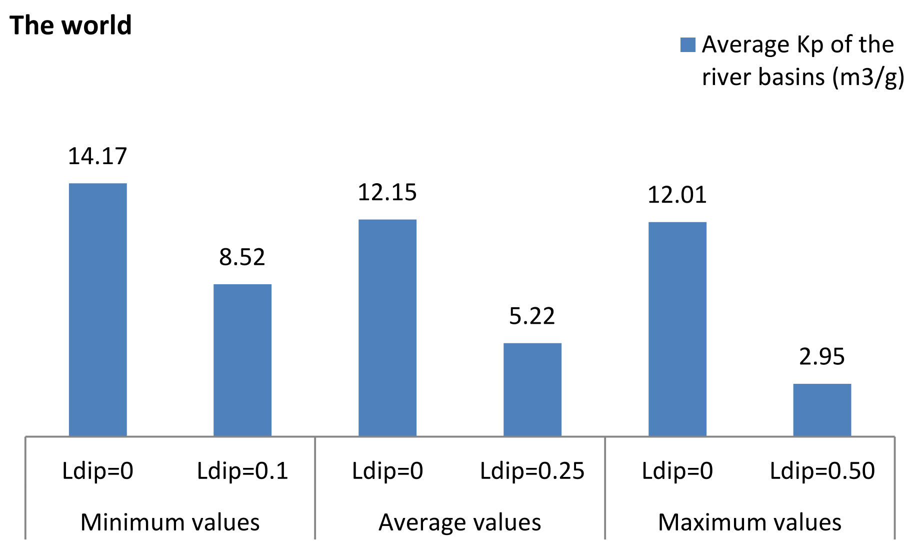



*Figure 17*

*Averaged values of $K_P$ (P adsorption constant) calculated for the world. Estimations of $K_P$ were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention indicated as Ldip. In all cases, the calculations were also made while neglecting river retention (Ldip=0).*

The impact of adding river retention on Kp varies among continents (Figure 18). Europe and North America react stronger to this addition than the other continents. For instance, average $K_P$ values calculated on the basis of minimum values (Ldip =0.1) decreased over 50% by adding river retention (from 9.01 $m^3$ $g^{-1}$ to 3.26 $m^3$ $g^{-1}$) in North America while in South America $K_P$ values decreased up to 25% (from 12.37 $m^3$ $g^{-1}$ to 8.97 $m^3$ $g^{-1}$). These variations among continents are due to different net P inputs and watershed characteristics (e.g. runoff).

Results also indicate that when Ldip is zero, there are no substantial differences in calculated $K_P$ values when using minimum, average and maximum values for bulk density, soil thickness and initial soil P concentration except for Europe (Figures 17 and 18). Table 19 presented in Section 3.3.2 gives minimum, average and maximum values for these variables. This indicates that $K_P$ is hardly sensitive to these variables. With respect to Europe, $K_P$ values are higher when they are calculated based on minimum values of those variables than based on their average and maximum values. This is specifically due to the difference in soil depth since the change in the P pool due to adsorption or desorption is faster within 1 m of soil (minimum value) compare to 5 m (average value) or 10 m (maximum value).

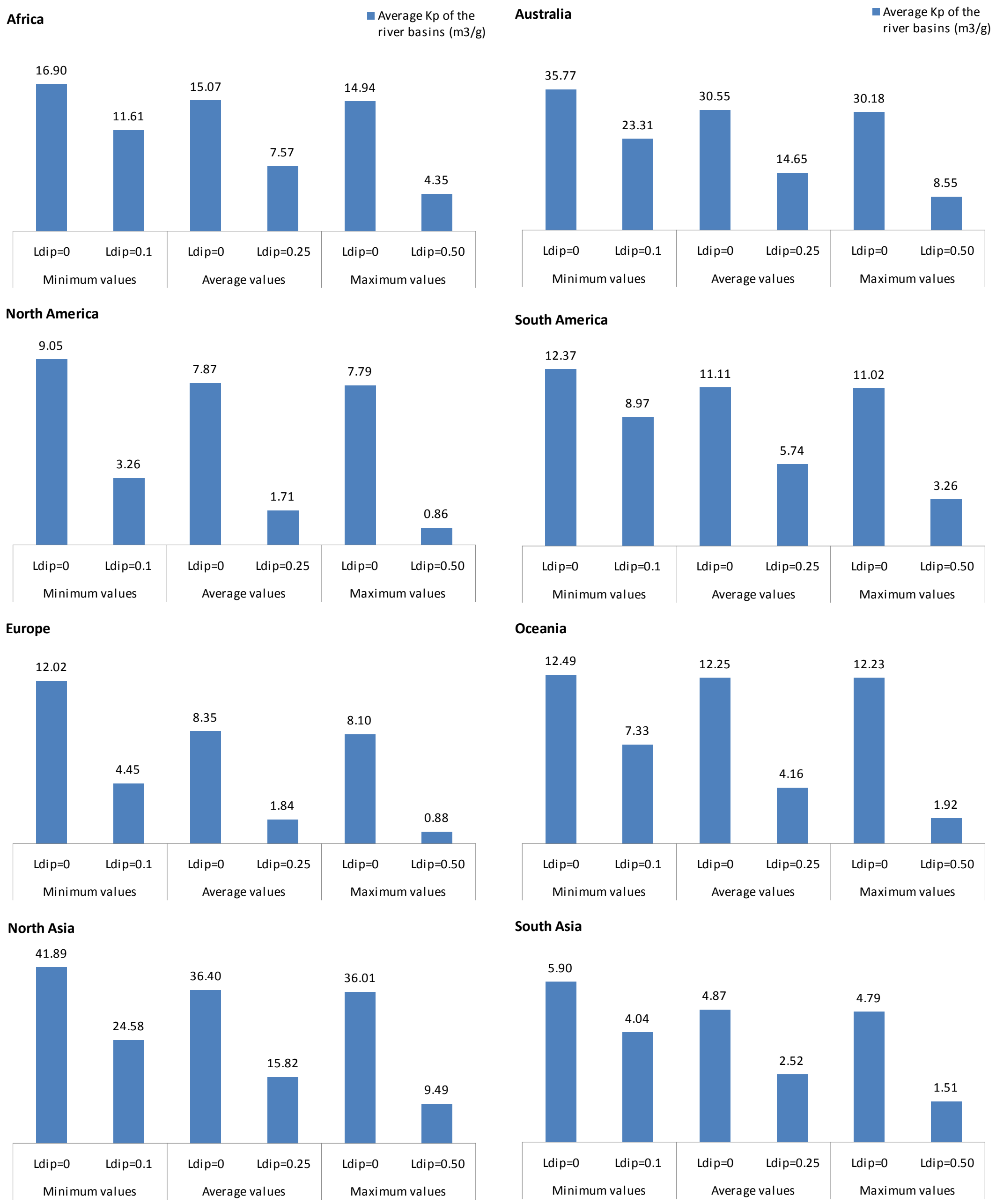



*Figure 18*

*Average values of $K_P$ (P adsorption constant) calculated for river basins of Africa, Australia, North and South America, Europe, Oceania, North and South Asia. Estimations of $K_P$ were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention indicated as Ldip. In all cases, the calculations were also made while neglecting river retention (Ldip=0).*

Concluding, the sensitivity analysis shows that $K_P$ is sensitive to the calculated DIP concentrations in watershed export but hardly to the other variables used in its estimation. However, it has to be noted that these DIP concentrations are derived from DIP fluxes that are exported from the watershed (land) to rivers and resulted only from diffuse anthropogenic sources such as animal manure, synthetic fertilizer use in agriculture as well as DIP weathering over agricultural areas. These fluxes are calculated according to the Global *NEWS* approach as a function of net P inputs (from those sources) to land and the export fraction, which considers DIP export from land to rivers. Hence, DIP fluxes depend on this fraction and their sources taken in estimations. The strong sensitivity of Kp values to DIP concentrations underlines the need for model validation on at least DIP fluxes and preferably DIP concentrations at watershed scale.

**Comparison with literature values**

$K_P$ values calculated in this study are compared to $K_P$ values taken from literature. A study of Koopmans and van der Salm (2010) provides an overview of $K_P$ calculated for Dutch soils on the basis of different methods namely average $K_P$ derived based on classical adsorption isotherms (Table 22), based on combined adsorption-desorption experiments (Table 23) and based on field data (Table 24). They give average $K_P$ values in L $mmol^{-1}$. These values are converted into $m^3$ $g^{-1}$ because this unit is used in this study.

*Table 22*

*Average in Langmuir adsorption constant ($K_P$) for various Dutch soils based on classical adsorption isotherms (from Koopmans and Van der Salm, 2010). In order to convert from L $mmol^{-1}$ to $m^3$ $g^{-1}$ $K_P$ values have to be divided by 31 (1 mol = 31 g P) considering that L $mmol^{-1}$ equals $m^3$ $mol^{-1}$.*

| Soil type | Average in $K_P$ | |
|---|---|---|
| | L $mmol^{-1}$ | $m^3$ $g^{-1}$ |
| Sand-non calcareous (n=31) | 15.6 | 0.50 |
| Sand- calcareous (n=5) | 10.7 | 0.35 |
| Marine clay soils (n=9) | 4.1 | 0.13 |
| Organic sandy soils (n=3) | 5.4 | 0.17 |

*Table 23*

*Average in Langmuir adsorption constant ($K_P$) for various Dutch soils based on desorption experiments of P loaded samples (from Koopmans and Van der Salm, 2010). In order to convert from L $mmol^{-1}$ to $m^3$ $g^{-1}$ $K_P$ values have to be divided by 31 (1 mol = 31 g P) considering that L $mmol^{-1}$ equals $m^3$ $mol^{-1}$.*

| Soil type | Average in $K_P$ | |
|---|---|---|
| | L $mmol^{-1}$ | $m^3$ $g^{-1}$ |
| Sand-non calcareous (n=13) | 10.3 | 0.33 |
| Clay -calcareous (n=5) | 10.8 | 0.35 |
| Peat soils (n=9) | 4.1 | 0.13 |

*Table 24*

*Average in Langmuir adsorption constant for various Dutch soils based on field data (from Koopmans and Van der Salm, 2010). In order to convert from L mmol[1] to $m^3$ $g^{-1}$ $K_P$ values have to be divided by 31 (1 mol = 31 g P) considering that L mmol[1] equals $m^3$ $mol^{-1}$.*

| Soil type | Average in $K_P$ | |
|---|---|---|
| | L $mmol^{-1}$ | $m^3$ $g^{-1}$ |
| Sand-non calcareous[1] | 273.8 | 7.64 |
| Sand-non calcareous[2] | 186.1 | 5.42 |
| Sand-calcareous | 18.7 | 0.60 |
| Clay -calcareous | 115.0 | 3.71 |
| Peat soils | 74.6 | 2.40 |

[1] *Dataset from Koopmans et al. (2006).*
[2] *Dataset from Chardon et al. (2007).*

Literature $K_P$ values according to the first two methods (Table 22 and 23) are comparable while $K_P$ values based on in-situ field data (Table 24) are significantly higher. Field data suggest $K_P$ values from 0.60 $m^3$ $g^{-1}$ to 7.64 $m^3$ $g^{-1}$ depending also on soil type. $K_P$ values based on classical adsorption isotherms and combined adsorption-desorption experiments lie between 0.13 $m^3$ $g^{-1}$ and 0.50 $m^3$ $g^{-1}$ depending on soil type.

The results of this study show that calculated average of $K_P$ values are much higher than adsorption isotherms and combined adsorption-desorption experiments and even higher than field data values, unless river retention is included (compare Table 25 with Table 22-24 , see also Figure 17 and 18). Average $K_P$ values are considerably higher when Ldip equals zero. For instance, average values of $K_P$ calculated for river basins in the world range from 14.71 $m^3$ $g^{-1}$ to 12.01 $m^3$ $g^{-1}$ (see Table 25 and Figure 17) while field values range from 7.64 $m^3$ $g^{-1}$ to 0.60 $m^3$ $g^{-1}$ (Table 23). Average $K_P$ values among continents are also high except for South Asia, where $K_P$ values can be compared to field data and North America, where $K_P$ values are close to field data. $K_P$ values with river retention can be comparable with literature field data but not for all continents (Table 25). Australia and North Asia are an exception here. They have average $K_P$ that are higher than the field data values. The other continents have relatively comparable values of $K_P$. In general, at the global scale (the world) average $K_P$ values are comparable with field data $K_P$ (Table 25).

*Table 25*

*Range in $K_P$ averages (expressed in $m^3$ $g^{-1}$) when using maximum and minimum values for the input variables used in this study (see Fig. 17 and 18 and Table 19 regarding input variables). Ldip indicates exclusion (Ldip=0) and inclusion (Ldip≠0) of river retention.*

| | Ldip=0 | Ldip≠0 |
|---|---|---|
| The world | 14.71 - 12.01 | 2.96 - 8.52 |
| Africa | 14.94 - 16.90 | 4.35 - 11.61 |
| Australia | 30.18 - 35.77 | 8.55 - 23.31 |
| North America | 7.79 - 9.05 | 0.86 - 3.26 |
| South America | 11.02 - 12.37 | 3.26 - 8.97 |
| Europe | 8.10 - 12.02 | 0.88 - 4.45 |
| Oceania | 12.23 - 12.49 | 1.92 - 7.33 |
| North Asia | 36.01 - 41.89 | 9.49 - 24.58 |
| South Asia | 4.79 - 5.90 | 1.51 - 4.04 |

The three main conclusions of the analysis are that:
(i) $K_P$ is sensitive to the calculated DIP concentrations in watershed export, while all other (soil) variables used in the calculations hardly affects the results;
(ii) inclusion of river retention gives calculated $K_P$ values that are close to the range of $K_P$ observed in the literature based on in-situ field data, suggesting the occurrence of significant river retention presently ignored in Global NEWS;
(iii) Kp values based on classical adsorption isotherms and combined adsorption-desorption experiments seem (far) too low in the field situation.

## 4.2 DIP concentrations and fluxes in 2000, 2030 and 2050

This Section is divided into three parts. The first part is associated with DIP partitioning over the various P forms and the various sources (Section 4.2.1). The second and third parts cover analyses of DIP concentrations and fluxes calculated according to the steady state (the Global *NEWS* approach) and dynamic approaches at the watershed scale (Section 4.2.2) and at the river mouth (Section 4.2.3) respectively.

### 4.2.1 DIP partitioning with DOP and PP and its major sources

**Brief introduction**
This section analyses (i) DIP partitioning over total P compared to the other P forms including DOP (dissolved inorganic P) and PP (particulate P), and (ii) the DIP sources and their trends from 2000 to 2050. This analysis is fully based on outputs derived from the Global *NEWS* model. There are no dynamic calculations involved.

The three sources of DIP export considered in the Global *NEWS* model are point sources, namely human waste and P-based detergents, anthropogenic diffuse sources including synthetic fertilizer, animal manure and including here also DIP weathering over agricultural areas and, a natural diffuse source due to DIP weathering over natural areas. Future trends in DIP sources are according to the GO (Global Orchestration) scenario of the MEA (Millennium Ecosystem Assessment) (see Chapter 2, Section 2.2, Alcamo et al., 2006).

An analysis of DIP, DOP and PP partitioning over total P is presented below on the basis of yields (kg $km^{-2}$ $year^{-1}$) that are exported at the mouth of rivers The analysis is limited to the year 2000. Next, DIP sources, their trends over the period of 2000-2050 are discussed. Attention is paid to both the global scale and continental scale (regional). Note that selected river basins were taken into consideration here. Their selection was done on the basis of calculated $K_P$ values (see Section 4.1 regarding exclusion of river basins).

**DIP partitioning**
Results indicate that P yields exported at the mouth of rivers are dominated by particulate forms rather than by dissolved inorganic P (DIP) and organic P (DOP) (Figure 19 and 20). Globally, DIP export includes only up to 20% out of total P (TP). This result is in line with Harrison et al., (2010) that also indicate that global riverine DIP export accounts for approximately 10% of TP only (1.5 Tg as DIP versus 20 Tg as TP). Slight differences in percentages of DIP between results of this study and Harrison et al., (2010) is most likely because in this analysis only 67% of the world area is taken into consideration (see Table 21). Seitzinger et al., (2010) also indicate that particulate P (PP) is the dominant P form in the river mouth at global scale. Only Europe differs considerably from the other continents, where on average 50% of TP is exported as DIP to its coastal zones. This is partly because the Europe has a higher connection to sewage systems than the other continents, and DIP is a main source in sewage (see below). Rivers in Oceania, African and Australia discharge the lowest amount of DIP (around 10% of TP) while the DIP flow in other continents is about 1/3 of TP. Regional differences in dominance of DIP export versus TP are shown in Figure 20.

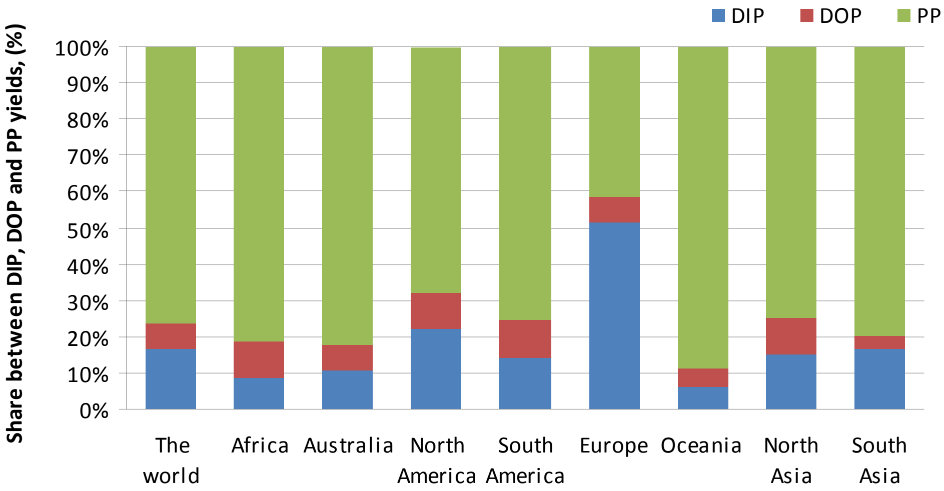



*Figure 19*

*Relative share between different forms of P yields (kg km² year¹) exported at the mouth of rivers draining to coastal waters of the world and continents for 2000. Different P forms are DIP (dissolved inorganic phosphorus), DOP (dissolved organic phosphorus) and PP (particulate phosphorus). Percentage is taken from the average yields of DIP, DOP and PP. The average yield for individual continent or the world was estimate as the sum of loads (kg year¹) of rivers draining into coastal waters of that continent divided by total area of those rivers. Sources: Mayorga et al., (2010); Seitzinger et al., (2010).*

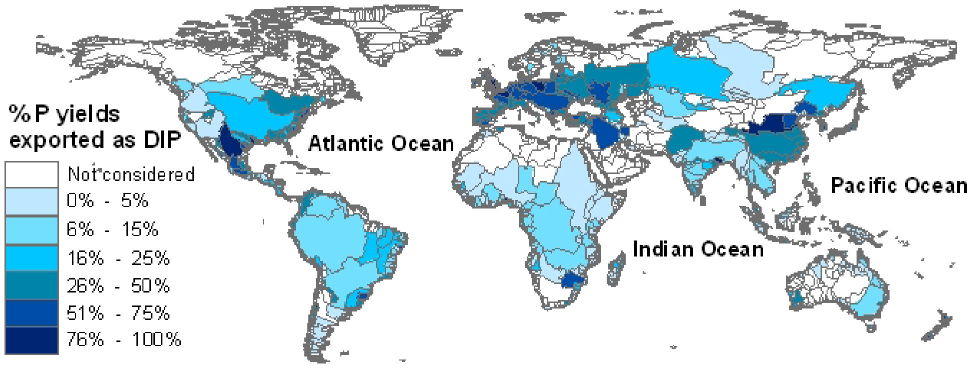



*Figure 20*

*Percentage of P yields (kg km² year¹) that are exported as DIP at the mouth of rivers for 2000. Percentage of DIP yield is estimated from the total P yield (DIP+DOP+PP) for each river basins for the year 2000. The Global NEWS outputs were taken for calculations. Delineation of river basins is taken from the Global NEWS model.*

### Major sources of DIP, their future trends

The Global *NEWS* model suggests that point sources are major exporters of DIP yields at the global scale in 2000 (Figure 21). This is in line with Seitzinger et al., (2010) whose analyses of global DIP export is also based on outputs of the Global *NEWS* model.

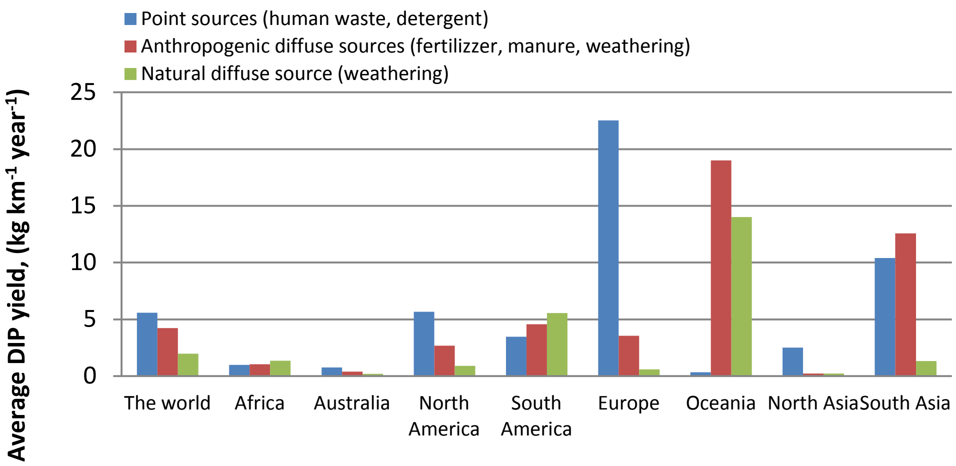



*Figure 21*
*Average DIP yields for 2000 exported at the mouth of rivers globally (the world) or to coastal waters of continents and resulted from point sources, anthropogenic diffuse and natural diffuse sources. The average yield for individual continent or the world was estimate as the sum of loads (kg year$^{-1}$) of rivers draining into coastal waters of that continent divided by total area of those rivers. The Global NEWS outputs were taken for calculations. Sources: Mayorga et al., (2010); Seitzinger et al., (2010).*

Results also show that there are differences in dominant DIP sources between continents for 2000 (Figure 21). Rivers draining into coastal zones of Europe, North America and North Asia receive DIP yields mainly from point sources (over 80% for Europe and North Asia, around 60% for North America). This can be due to urbanisation developments and connected population to sewage systems (Bouwman et al., 2009). The Global *NEWS* model estimates DIP flux from point sources on the basis of people connected to sewage and the percentage of nutrient removal via wastewater treatments (Mayorga et al., 2010). Thus the latter is also an important factor. Inversely, although South Asia is being considered populated zone in the world too (Bouwman et al., 2009), DIP fluxes at its coastal waters are dominated by anthropogenic diffuse sources, where agriculture is a key factor contributing above 2/4 of DIP yields. Oceania is another continent, where anthropogenic diffuse sources contribute significantly to DIP yields (up to 60%) at the mouth of rivers. The other continents such as Africa, Australia and South America receive DIP yields almost equally between the sources. These results indicate that sewage systems control DIP delivery to surface waters within urban areas while manure, fertilizer applications in agriculture and DIP weathering over rural areas control DIP delivery within agricultural areas. The relative contribution of DIP sources does not change dramatically from 2000 to 2030 and also from 2030 to 2050. The relative share between different DIP sources for the future years is presented in Annex 1 to this report.

Harrison et al. (2010) also made an analysis of DIP fluxes and their sources in the past and in the future based on the Global NEWS model too (see Figure 22). Results of this study slightly differ from their results. For instance, Oceania is dominated by non-anthropogenic P according to Harrison et al., (2010) (Figure 22) while results of this study show dominance by anthropogenic diffuse sources, which include DIP weathering over rural areas (Figure 21). This is because in this analysis only 65% of the continent area is taken into account, where agricultural activities might contribute significantly together with weathering of P contained substances in the soil. Another example is South Asia, where this study suggests dominance by anthropogenic diffuse source (Figure 21) while Harrison et al., (2010) suggest sewage point source (Figure 22). This can also be explained that only 59% of the area is considered in this analysis, where agriculture can be dominant source. (see also Section 4.1 regarding exclusion of river basins from the study).

Figure 21 also illustrates the magnitude of DIP yields for 2000. Europe, Oceania and South Asia contribute substantially to riverine DIP yields compared to the other continents. However, here DIP fluxes are given in yields (kg $km^{-2}$ $year^{-1}$) recommending magnitudes of pollution per square km among their areas rather than magnitudes of DIP contribution to coastal waters. Loads (kg $year^{-1}$) of DIP export might be an appropriate term in this case because it considers areas of river basins. According to Harrison et al. (2010), Asia continent is the largest exporter of DIP loads (around 38% among the other continents) than the others. This continent delivers around 0.7 Tg P per year to coastal waters while North America, South America, Europe and Africa contribute from 0.20 to 0.35 Tg P per year. Both Oceania and Austria deliver up to 0.12 Tg P $year^{-1}$ (Harrison et al., 2010). Thus, for instance, Oceania has high DIP yields but low DIP loads because the area of this continent is relatively small compare for instance to Asia area.

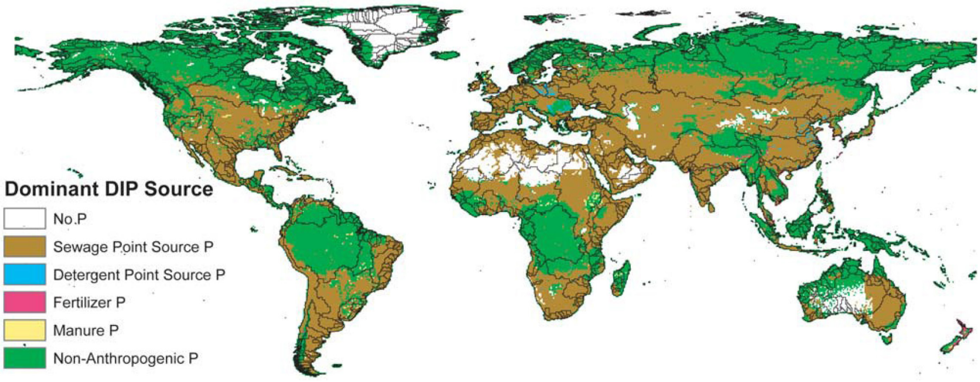



*Figure 22*
*NEWS-predicted dominant DIP sources at 0.5 by 0.5 degree cell. This map was provided by Harrison et al. (2010).*

Future trends in DIP sources vary also among continents (Figure 23). DIP yields resulted from anthropogenic diffuse sources (including DIP weathering over agricultural areas) are expected to increase over the period 2000 - 2050 (GO scenario) from almost all river basins except for Europe, Australia and several river basins in Africa. Significant increases by over 90% are found for a few river basins of South and North Asia, Africa, North and South America and Oceania. These increases can be associated with agricultural trends in the future.

Inversely, DIP yields at the mouth of rivers that were generated only from natural diffuse sources are calculated to decrease from 2000 to 2050 from all almost river basins except for North America and North Asia, where increases are up to 30%. These DIP fluxes are calculated on the basis of runoff in the model by using the export-coefficient approach (Mayorga et al., 2010). Therefore, changes in DIP fluxes from this source can be due to runoff changes in the future under the GO.

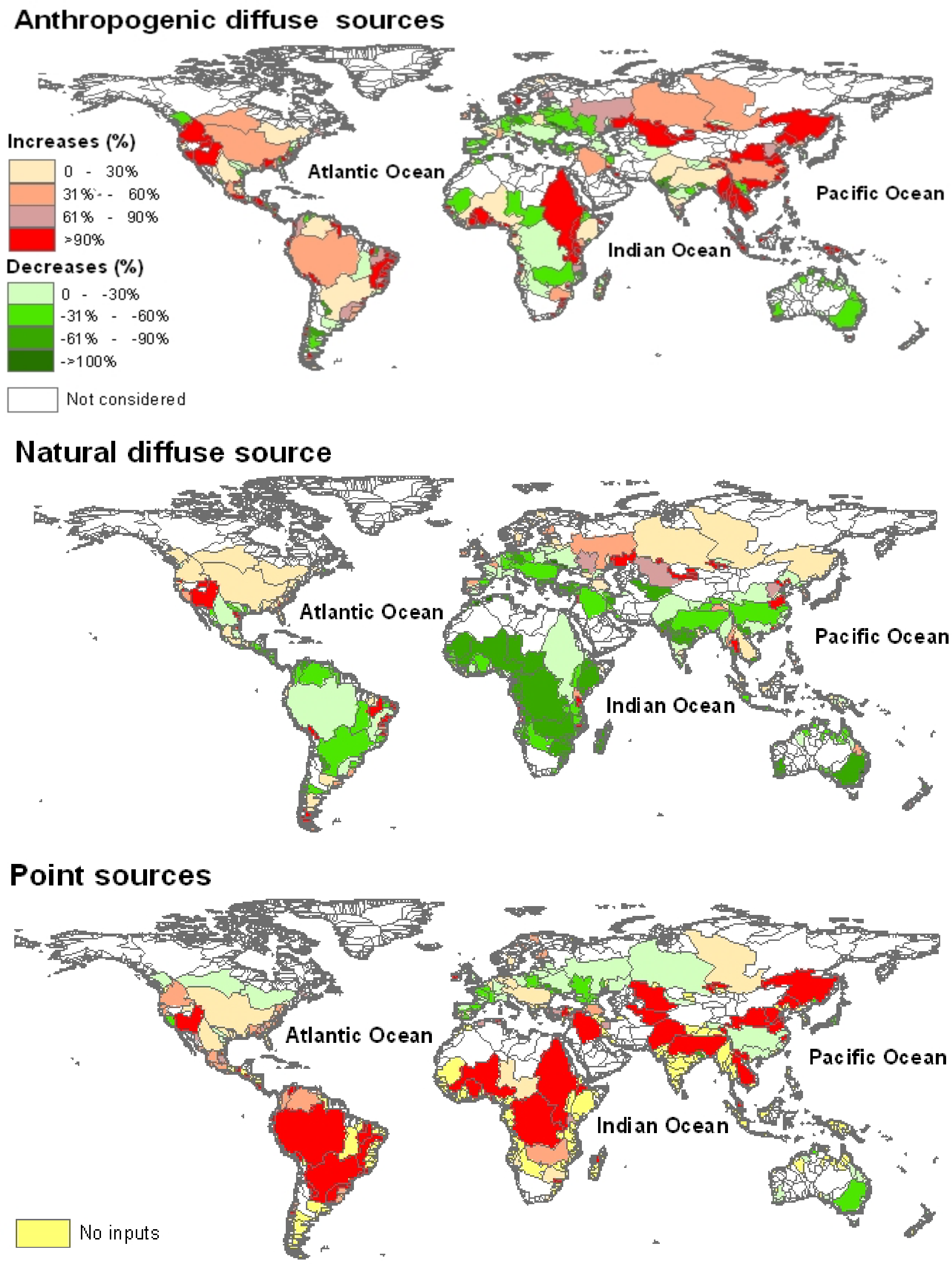



*Figure 23*

*Percentage changes (%) in riverine DIP yields (kg km$^{2}$ year$^{1}$) exported at the mouth of rivers from 2000 to 2050 (GO) and resulted from anthropogenic diffuse (fertilizer, manure and DIP weathering over agricultural areas), natural diffuse (DIP weathering over natural areas) and point sources (detergents and human waste). GO is a Global Orchestration scenario of Millennium Ecosystem Assessment scenarios. Sources: Mayorga et al., (2010), Seitzinger et al., (2010).*

Finally, DIP fluxes resulted from point sources are projected to increase in the future. Results indicate considerable increases in DIP yields in 2050 by over 90% compare to 2000 from river basins of Africa, South America and some basins of South Asia. This indicates urbanisation developments in the future. In addition, the GO scenario suggests economic developments including connection of people to sewage facilities with different degree of sewage treatments (see Section 2.2). Europe and several river basins of North Asia, Australia and North America are an exception in this case. There decreases are projected in DIP fluxes up to

30% and even larger in some individual rivers. This is associated with better sewage treatments in the future. Rivers of Oceania almost do not have inputs from point sources because majority of households are not connected to sewage systems (see also Figures 21 and 22). The same situation is found for a few river basins in Africa, South America and South Asia.

Seitzinger et al. (2010) and Bouwman et al. (2009) also did an analysis of nutrient export for the future including river export of DIP on the basis of the Global *NEWS* results. They found that river export DIP might increase from 2000 to 2030 under GO scenario in almost all continents except for Europe, where decreases are projected. These are in line with results of this study. According to Seitzinger et al., (2010) rivers draining to coastal waters of South Asia may deliver by 50% more DIP yields in 2030 than in 2000 under the GO while rivers draining to coastal waters of South America and Oceania might export around 17% and 15% more DIP in 2030 under GO than in 2000. These increases can be caused by agricultural activities (Seitzinger et al., 2010). Decreases in DIP from European rivers are assumed to be due to sewage treatment improvements in the future (Bouwman et al., 2009). More information about DIP export, sources and magnitudes can be found in scientific papers of Harrison et al. (2010), Seitzinger et al. (2010) and Bouwman et al. (2009).

To conclude this section, riverine P yields that exported as DIP accounts up to 20% globally and continentally too except for Europe, where DIP is dominated. Point sources are the largest contributors of DIP export by rivers at the global scale. There are differences in source contribution among continents, where point sources are versus anthropogenic diffuse sources. In the future, under the GO DIP yields generated from point and anthropogenic sources are projected to increase with different degree in majority of river basins except for European basins. Inversely, DIP fluxes generated from natural diffuse sources are expected to decrease from almost all studied river basins except for a few basins of North America and North Asia. Future trends in agricultural managements and in developments of sewage facilities determine trends in DIP export within agricultural and urban areas respectively.

### 4.2.2 DIP concentrations and fluxes at the watershed scale

**Brief introduction**
In this study DIP export at the watershed scale is defined via DIP concentrations (denoted as [DIP]) and DIP fluxes (or yields, denoted as $RSdif_{ant,DIP}$), which are resulted from anthropogenic diffuse sources (animal manure and synthetic fertilizer including here also DIP weathering over agricultural areas) and exported from the watershed (land) to surface waters. Their estimations were done according to methodology illustrated in Section 3.2.2 on the basis of the steady state (the Global *NEWS* approach) and dynamic approaches. Summarized information regarding the steady state and dynamic calculations is given in Figure 15 and Figure 16 respectively. Input data that are needed for the calculations are presented in Section 3.3. Estimations of dynamic DIP were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip). The latter is included in estimations of steady state DIP export. In all cases, the calculations were also made while neglecting river retention (Ldip=0). DIP concentrations and fluxes were estimated for 2000, 2030 and 2050. For future years an analysis is based on the GO scenario of MEA (see Chapter 2, Section 2.2). An analysis of DIP concentrations and fluxes are done in mg $L^{-1}$ and kg $ha^{-1}$ $year^{-1}$ respectively. Their results are discussed on the global scale based on calculated averages of DIP concentrations and fluxes of river basins. Regional scale (continental) is also considered. River basins used here are the basins, which have been selected according to the calculated $K_P$ values (Section 4.1).

**Analyses of the results**
For the current situation (2000), results show that there are no substantial differences between the dynamic and steady state approaches regarding DIP concentrations and yields on the global (Figures 24A and B) and regional scales (Figures 25 and 26). This can be caused by that 2000 was assumed to be a reference year in dynamic estimations (Chapter 3, regarding methodology).

Results demonstrate that DIP concentrations and yields are sensitive to inclusion of river retention for both approaches (Figures 24A and B, Figures 25 and 26). Generally, DIP concentrations and yields are going up with including fractions of river retention from 0 to 0.50, where 50% of river retention (0.50) suggests the highest increases compare to the other fractions (Figures 24-26). These increases can be associated with extra amount of DIP that was added to the watershed (land) as a results of river retention. Nevertheless, a response to this addition is similar between the approaches for only 2000 because of the reference year. Globally, for instance, DIP concentrations (on average) estimated to increase by up to one-fold under 10% of river retention, around two-fold under 25% river retention and over six-fold under 50% of river retention for both approaches for 2000 (Figure 24A). Regionally, for instance, steady state DIP concentrations of river basins in 2000 equal to dynamic DIP concentrations of those river basins under fractions of river retention 0, 0.10, 0.25 and 0.50 (Figure 25 and Figure 26 regarding the steady state and dynamic approaches respectively). Furthermore, there are no differences in dynamic DIP concentrations in the river basins between minimum, average and maximum values of input variables used in the dynamic approach for the year 2000 (Figure 26). This indicates that different values of these input variables namely bulk density, soil depth, content of aluminium and iron oxides in the soil have similar impact on DIP export for 2000. This also means that DIP export is not sensitive to different values of those variables for the background year (2000).

Inversely, for future years (2030 and 2050), there are found differences in dynamic DIP export between three sets of used input values neglecting river retention (Ldip=0). Minimum values suggest higher DIP concentrations and yields in 2030 and 2050 compare to 2000 than the others (Figure 24). This might be explained by the fact that these sets of input variables include 1 m of soil thickness suggesting higher efficiency of DIP leaching over time from the soil to surface waters compare to 5 m (average) and 10 m (maximum) values. In addition to this variable, content of aluminium and iron oxides ($Al_{ox}$+$Fe_{ox}$) in the soil might contribute also to this situation. With increasing their content in the soil, DIP availability is decreasing in soil solution due to their ability to bind P. Bulk density, which is the other variable used for the sensitivity purpose, does not have large variations between its minimum (1400, kg $m^{-3}$), average (1500, kg $m^{-3}$) and maximum (1600, kg $m^{-3}$) values. Therefore, this variable hardly contributes to changes in DIP export regarding this case.

There are different responses in DIP export to inclusion of fractions of river retention between both approaches in the future (Figures 24-26). The steady state DIP export is estimated to increase in the coming decades with increasing fractions of Ldip compare to 2000. Dynamic based DIP export is also estimated to increase but slowly compare to the steady state approach (Figures 24-26). It can be caused by that this approach does not suggest large changes in DIP export over future years (see below about future trends).

For the future (2030 and 2050), results indicate that DIP export differs significantly between the steady state and dynamic approaches. The dynamic approach suggests lower DIP concentrations and yields in the future. Globally, for 2050, without considering river retention (Ldip=0), dynamic DIP concentration on basis of minimum values of input variables accounts around ¾ of steady state DIP and 2/4 of the steady state DIP on the basis of average and maximum values (Figure 24A). Including river retention, dynamic DIP concentrations are also about ¾ (minimum value, Ldip=0.10) and 2/4 of stead state values in 2050 (Ldip=0.25 and Ldip=0.50) (Figure 24A). Global DIP yields follow this pattern. This is also implied on the regional scale (Figures 25 and 26). For instance for the year 2050 when Ldip equals zero, majority of river basins of Africa are expected to have steady sate DIP concentrations between 0.006 and 0.055 mg per L. Dynamic approach shows lower DIP concentrations under minimum, average and maximum values of input variables. These are in a range of 0.006 and 0.010 mg per L (Figures 25 and 26 regarding the steady state and dynamic approaches respectively). In addition to this, there are differences in DIP concentrations among river basins. One example is river basins of South Asia continent, which are expected to have larger DIP concentrations under both approaches compared to the other continents. It has to be noted that DIP concentrations were estimated considering runoff. Thus, future trends in runoff could affect future trends in DIP concentrations. The differences between the approaches are associated with that the dynamic approach takes into account time dimension in P adsorption-desorption processes in the soil leading to relatively lower rate of DIP release from the soil to surface waters while the steady state approach does not account this.

Regarding future trends in DIP export, changes in dynamic DIP export over the period of 2000-2050 is lower than in the steady state appraoch (Figures 24 and 27). At the global scale when Ldip is zero DIP concentration is increased by about 80% from 2000 to 2050 according to the steady state while by about 60%, 10% and 3% according to the dynamic approach on the basis of minimum, average and maximum values of input variables respectively (Figure 24A). Under river retention of 10% (minimum value), steady state DIP concentrations show increase over this period by above 100% whilst dynamic DIP concentrations show increase by about 50%.

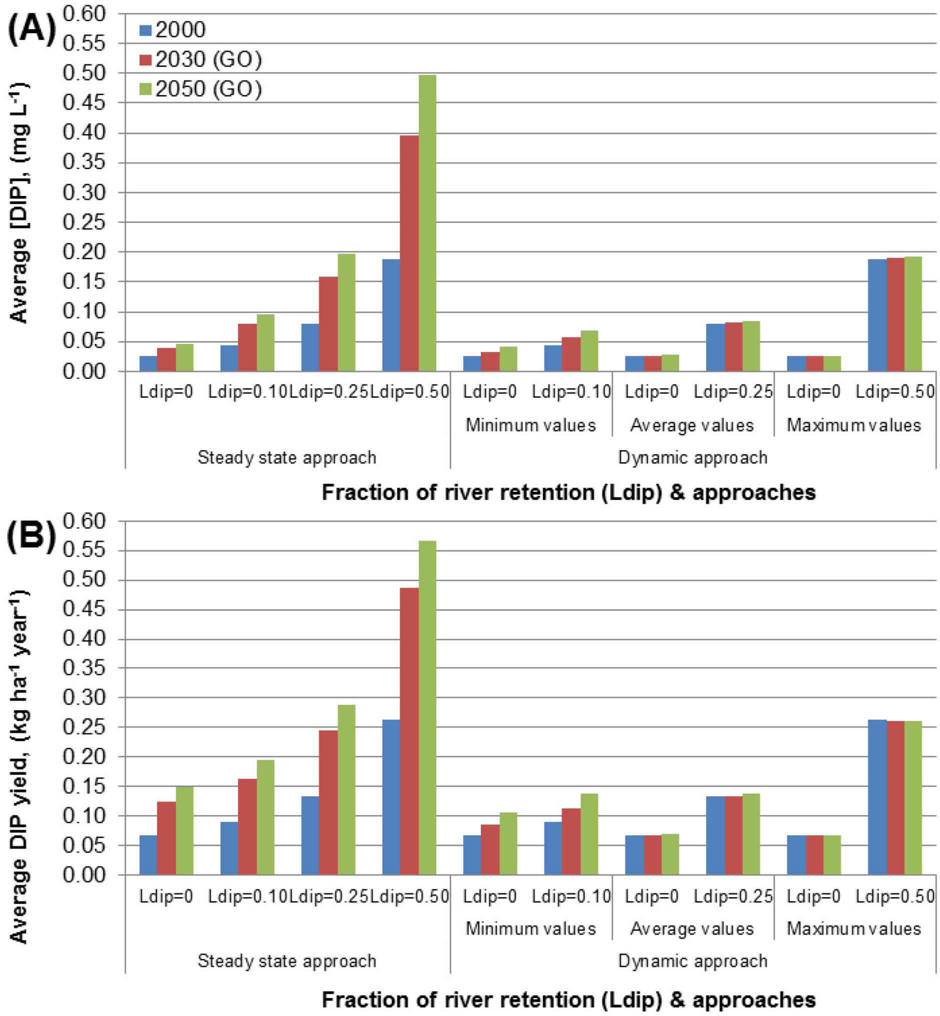



*Figure 24*

*Average DIP concentrations ([DIP], mg $L^{-1}$) (A) and fluxes (kg $ha^{-1}$ $year^{-1}$) (B) of studied river basins of the world at the watershed scale calculated on the basis of the steady state and dynamic approaches. The average of DIP fluxes for river basins of the world was estimate as the sum of loads (kg $year^{-1}$) of those rivers divided by total area of the rivers. The Global NEWS inputs and outputs were used in calculations of both approaches. In addition, estimations of dynamic DIP concentrations and fluxes were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip with the fractions of 0.10, 0.25 and 0.50) (Table 18 and 19). River retention was included in estimations of steady state DIP concentrations and fluxes. In all cases, the calculations were also made neglecting river retention (Ldip=0). The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment.*

When river retention is 25% (average value) and 50% (maximum value), dynamic DIP concentrations are hardly changed over this period while steady sate values show changes by above 100% compare to 2000. This concerns global DIP yields too (Figure 24B). Regionally, changes in dynamic DIP concentrations for river basins are also higher according to the steady state approach than according to the dynamic approach (Figure 27).

**Steady state approach**

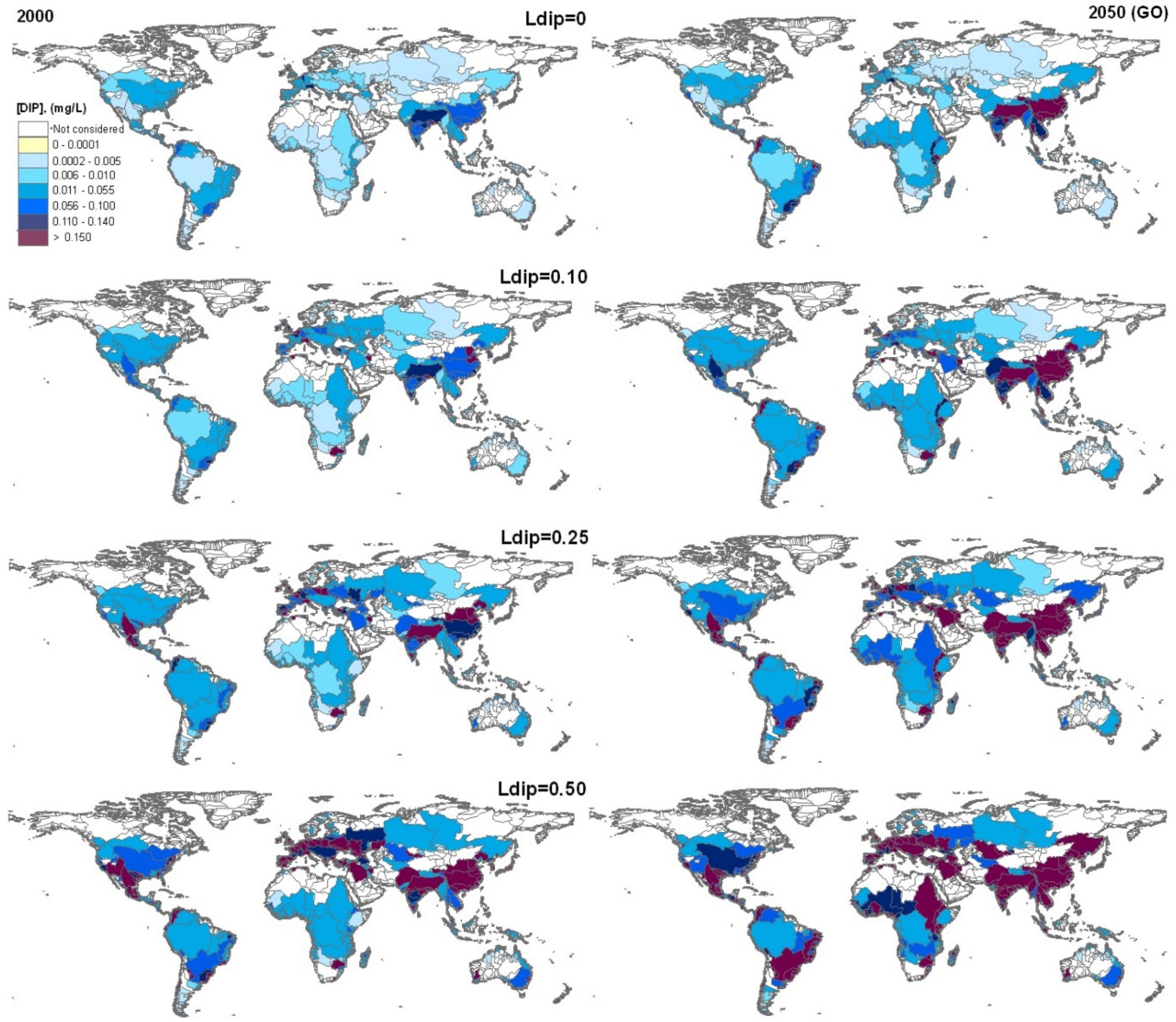
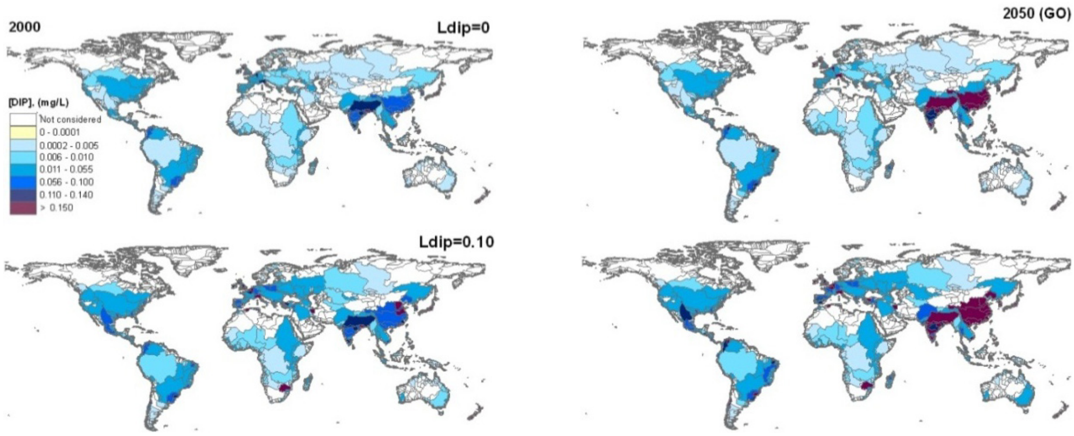



***Figure 25***

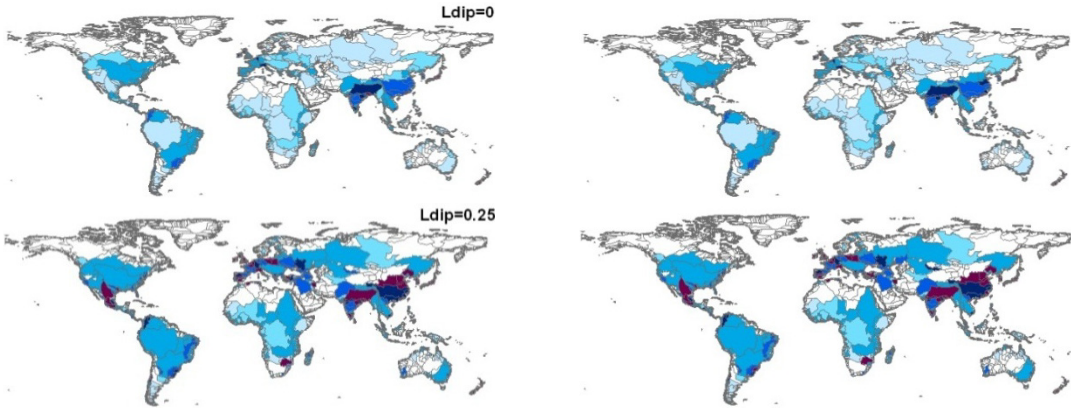
*DIP concentrations ([DIP], mg/L) for the river basins at the watershed scale according to the steady state approach in 2000 (left column) and 2050 (right column) when fraction of river retention is not considered (Ldip=0) and when river retention is considered with different its fractions including 0.10, 0.25 and 0.50. Their estimations were performed accoring to methodology presented in Chapter 3. The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment. Deliniations of river basins are from the Global NEWS model.*

## Dynamic approach

On the basis of minimum values of input variables




On the basis of average values of input variables




On the basis of maximum values of input variables

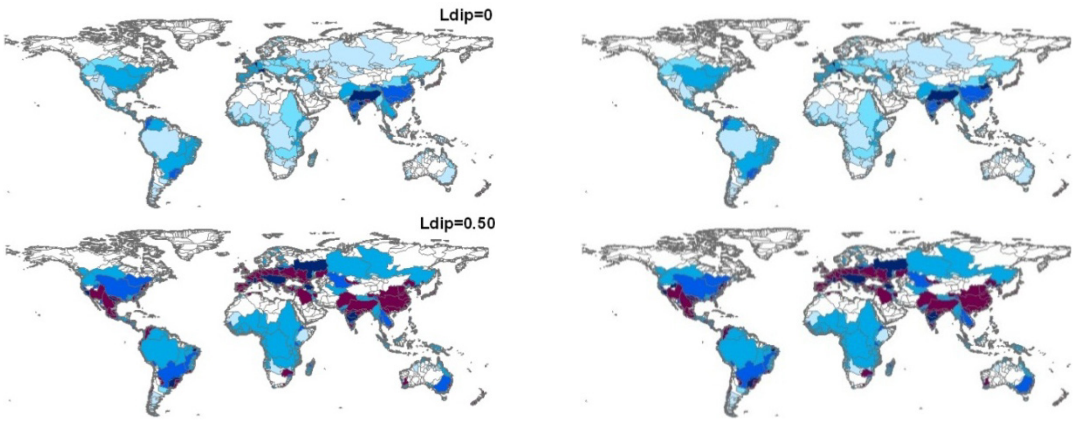
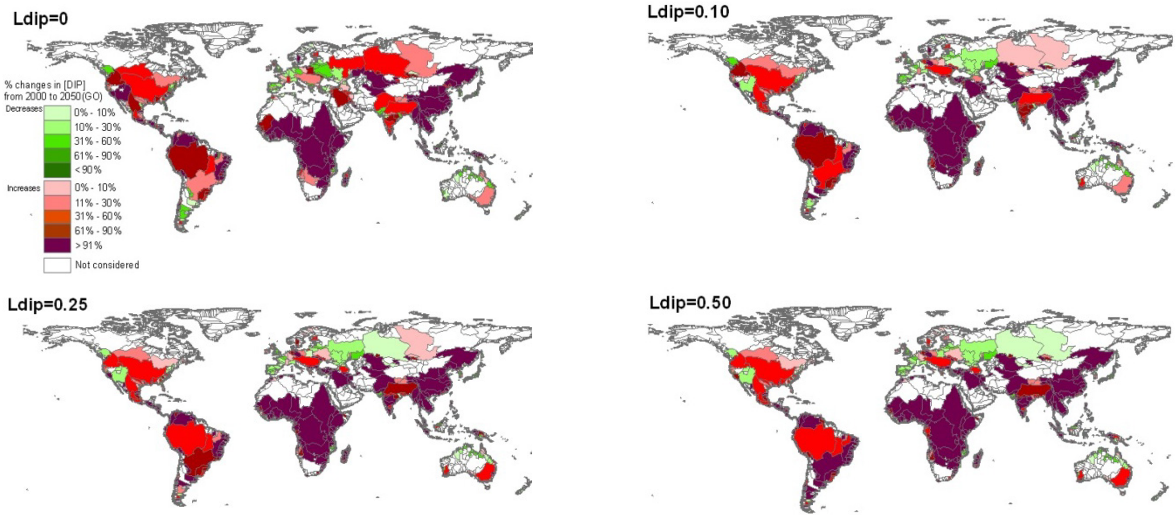



***Figure 26***

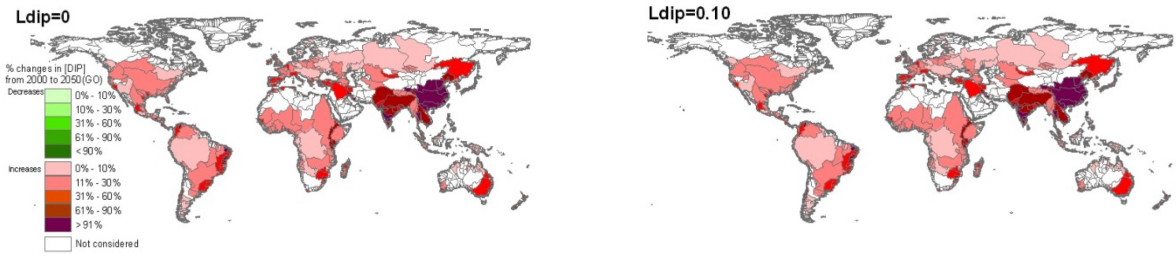
*DIP concentrations ([DIP], mg/L) for the river basins at the watershed scale according to the dynamic approach in 2000 (left column) and 2050 (right column). Their estimations were performed accoring to methodology presented in Chapter 3. Estimations were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip with the fractions of 0.10, 0.25 and 0.50) (Table 18 and 19). In all cases, the calculations were also made neglecting river retention (Ldip=0). Deliniations of river basins are from the Global NEWS model .*

**Steady state approach**

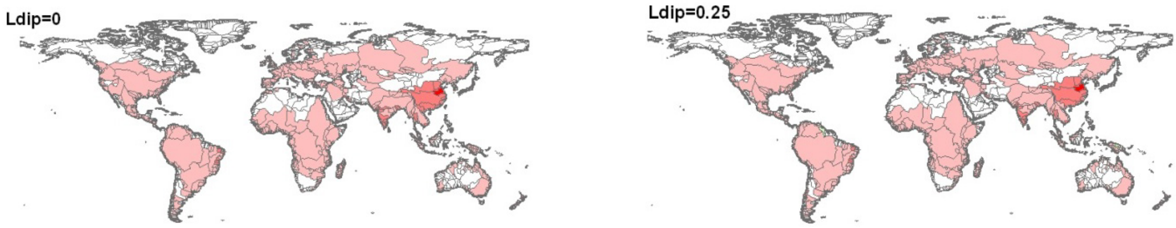



**Dynamic approach**

*On the basis of minimum values of input variables*




*On the basis of average values of input variables*




*On the basis of maximum values of input variables*

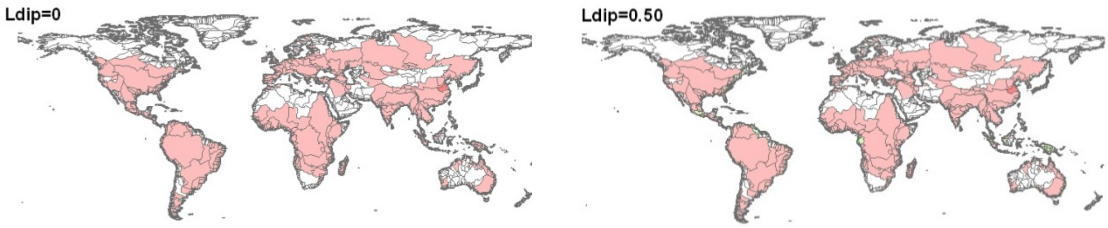



*Figure 27*

*Percentage changes in DIP concentrations ([DIP], mg/L) from 2000 to 2050 (GO) for the river basins at the watershed scale according to the steady state and dynamic approaches. Estimations of [DIP] were performed accoring to methodology presented in Chapter 3. The Global NEWS inputs and outputs were used in calculations of both approaches. In addition, estimations of dynamic DIP concentrations were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip with the fractions of 0.10, 0.25 and 0.50) (Table 18 and 19). River retention was included in estimations of steady state DIP concentrations. In all cases, the calculations were also made neglecting river retention (Ldip=0). The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment. Deliniations of river basins are from the Global NEWS model*

Additionally, percentage changes in its concentrations are relatively higher under minimum values rather than under average and maximum ones (Figure 27). River basins draining into coastal waters of South Asia might have dynamic based DIP concentrations by 60% - 90% higher in 2050 compare to 2000 under minimum values while only up to 10% under average and maximum values. One of reasons related to these differences can be linked to used soil thicknesses in a range from 1 m to 10 m of the soil (see above and also Table 19 regarding its values). According to the steady sate approach DIP concentrations in several river basins might be reduced over this period. This concerns mostly European river basins and several basins of North Asia only under Ldip of 0.25 and 0.50 (see Figure 27 regarding steady state approach). This can be because of future managements connected to nutrient inputs via agriculture practices applied in the GO scenario. Regarding the dynamic approach, even though there are applied the same future managements of nutrient inputs (because the same scenario is used in both approaches with the same inputs), increases in DIP export might be expected in those river basins (Figure 27 regarding the dynamic approach). This may be due to response mechanisms involved within watersheds, where DIP is releasing continuously over time from soils to surface rivers. This could have negative implications for future agricultural managements suggesting difficulties to reduce DIP in surface waters. However, on the other hand, this also shows one of positive aspects of the dynamic approach versus the steady state approach, where these mechanisms can be taken into account in future decision-making.

To conclude this section, the dynamic approach has large impact on DIP export at the watershed scale especially over future years suggesting lower DIP concentrations and yields as well as their increases in the future compared to the steady state approach. Since 2000 was taken as a reference year, there are no differences in DIP concentrations and yields between both approaches for the current situation. An inclusion of river retention has affected DIP concentrations and yields in a way of increasing them. Besides, it is crucial to consider river retention because $K_P$ values, which are the basis in the dynamic approach, are more rational than without river retention (see Section 4.1). And, thus this is also associated with more reliable results for dynamic DIP concentrations and yields. To this end, differences in dynamic DIP concentrations and yields between three sets of applied input variables (minimum, average and maximum) are found, where minimum their values show higher changes in DIP export in the future than the others.

### 4.2.3 DIP concentrations and fluxes at the river basin scale

**Brief introduction**

DIP export at the river basin scale is defined via DIP concentrations (denoted as $[DIP]_m$, mg $L^{-1}$, where m indicates a mouth of the river) and fluxes (denoted as $Yld_{DIP}$, kg $ha^{-1}$ $year^{-}1$, where Yld indicates yields of DIP export) exported at the river mouth. They are generated from different anthropogenic diffuse (synthetic fertilizer and animal manure including here also DIP weathering over agricultural areas) and point (human waste and detergent effluents) and, natural diffuse (DIP weathering over natural areas) sources (see also Chapter 2, Section 2.2).

In this study these concentrations and fluxes are discussed on the basis of the steady state (the Global *NEWS* approach) and dynamic approaches. Estimations of DIP concentrations and fluxes were done based on methodology presented in Chapter 3. Here an assumption regarding inclusion of river retention plays an important role. According to the assumption DIP export is affected by including river retention only at the watershed scale while DIP fluxes at the river mouth stay without changes.

An analysis of DIP export is performed for 2000, 2030 (GO) and 2050 (GO) (see Chapter 2 and 3). DIP export is discussed on the global scale on the basis of calculated averages in DIP concentrations and fluxes of the studied river basins. Regional scale is also under consideration.

**Analyses of the results**

For the current situation (2000), results show that DIP concentrations and yields are similar between the steady state and dynamic approaches (Figures 28 A and B). This is caused by that 2000 was assumed is the reference year in dynamic calculations (see Chapter 3 regarding methodology).

For future years, 2030 and 2050, minor differences in DIP export are found between the steady state and dynamic approaches (Figures 28 and 29). Generally, dynamic based DIP export is relatively lower compare to steady state export. One example is majority of river basins in South America. There steady sate DIP concentrations are estimated to increase from 2000 to 2050 whilst dynamic based concentrations are estimated to decrease over that period (Figure 29). Differences between both approaches also depend on whether river retention is considered (different fractions) or neglected (Ldip=0) and also depend on which set of input values (minimum, average and maximum) was used in dynamic estimations.

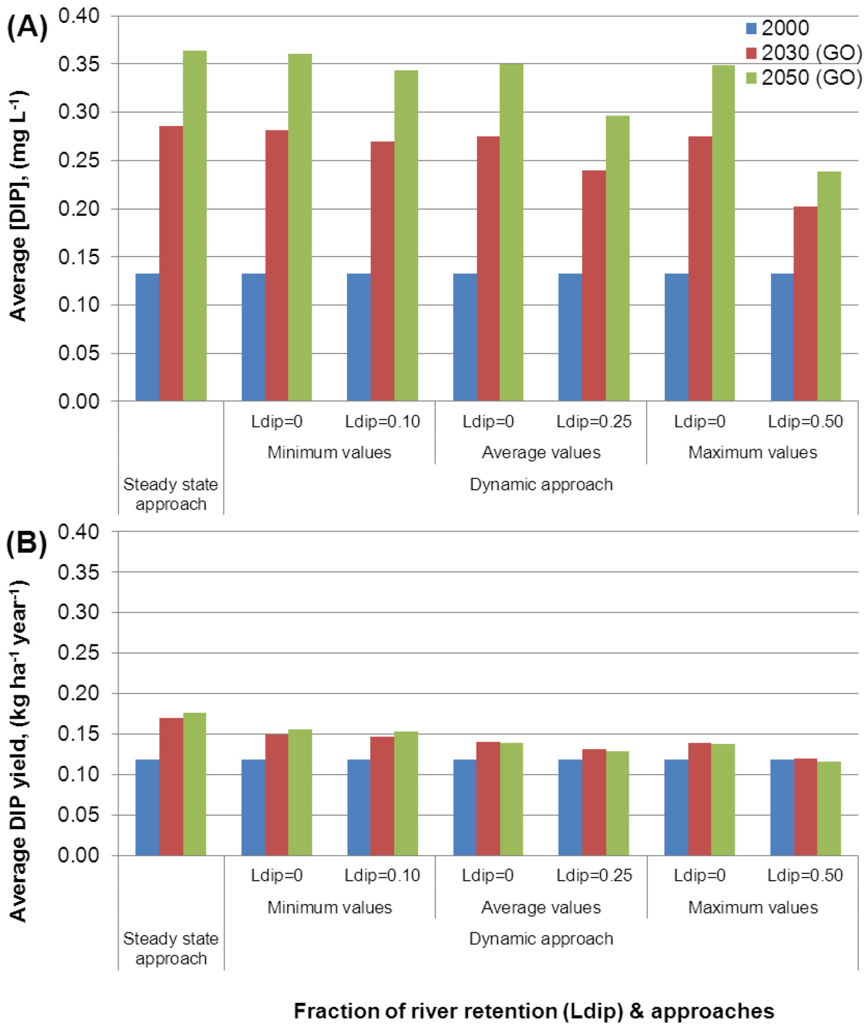
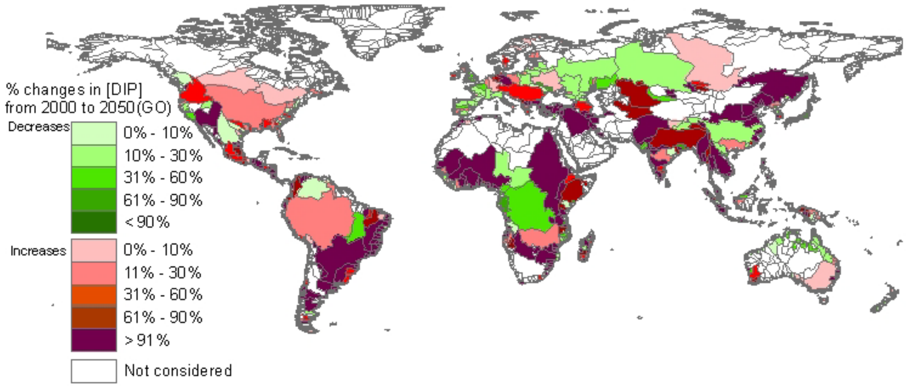



*Figure 28*

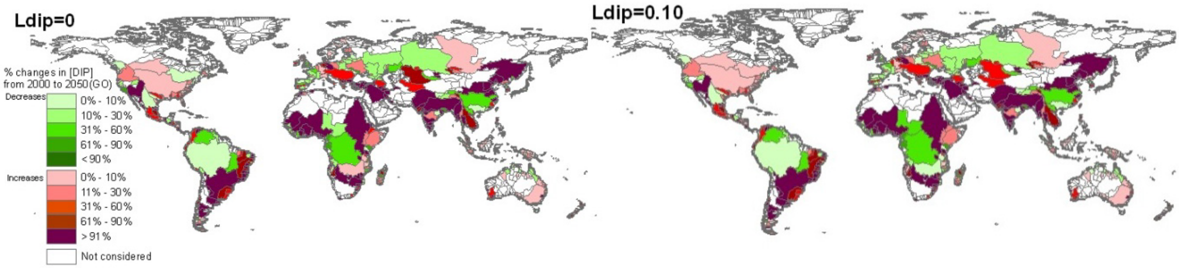
*Average DIP concentrations ([DIP], mg $L^{-1}$) (A) and fluxes (kg $ha^{-1}$ $year^{-1}$) (B) of studied river basins of the world, exported at the river mouth on the basis of the steady state and dynamic approaches. The average of DIP fluxes for river basins of the world was estimate as the sum of loads (kg $year^{-1}$) of those rivers divided by total area of the rivers. The Global NEWS inputs and outputs were used in calculations of both approaches. In addition, estimations of dynamic DIP concentrations and fluxes were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip with the fractions of 0.10, 0.25 and 0.50) (Table 18 and 19). In all cases, the calculations were also made neglecting river retention (Ldip=0). The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment .*

**Steady state approach**

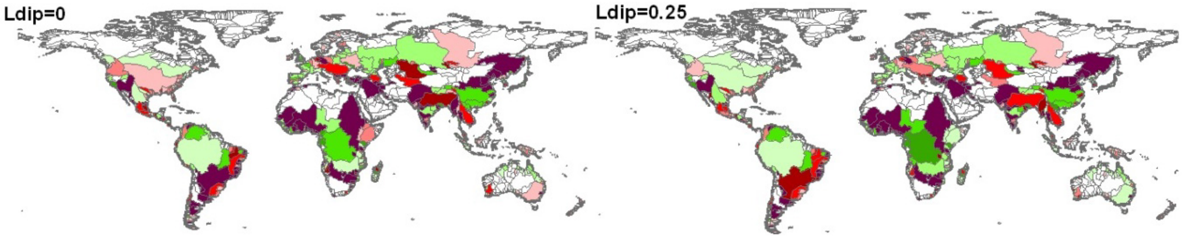



**Dynamic approach**

*On the basis of minimum values of input variables*




*On the basis of average values of input variables*




*On the basis of maximum values of input variables*

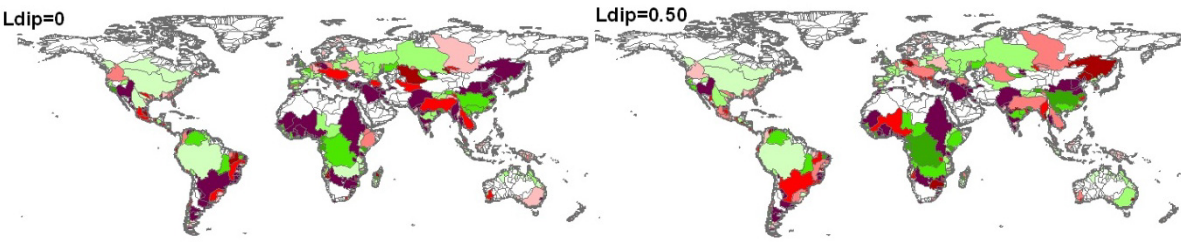



*Figure 29*

*Percentage changes in DIP concentrations ([DIP], mg/L) from 2000 to 2050 (GO) for the river basins at the river mouth according to the steady state and dynamic approaches. Estimations of [DIP] were performed accoring to methodology presented in Chapter 3. The Global NEWS inputs and outputs were used in calculations of both approaches. In addition, estimations of dynamic DIP concentrations were based on minimum, average and maximum values of bulk density, soil thickness and initial soil P concentration and river retention (Ldip with the fractions of 0.10, 0.25 and 0.50) (Table 18 and 19). In all cases, the calculations were also made neglecting river retention (Ldip=0). The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment. Deliniations of river basins are from the Global NEWS model.*

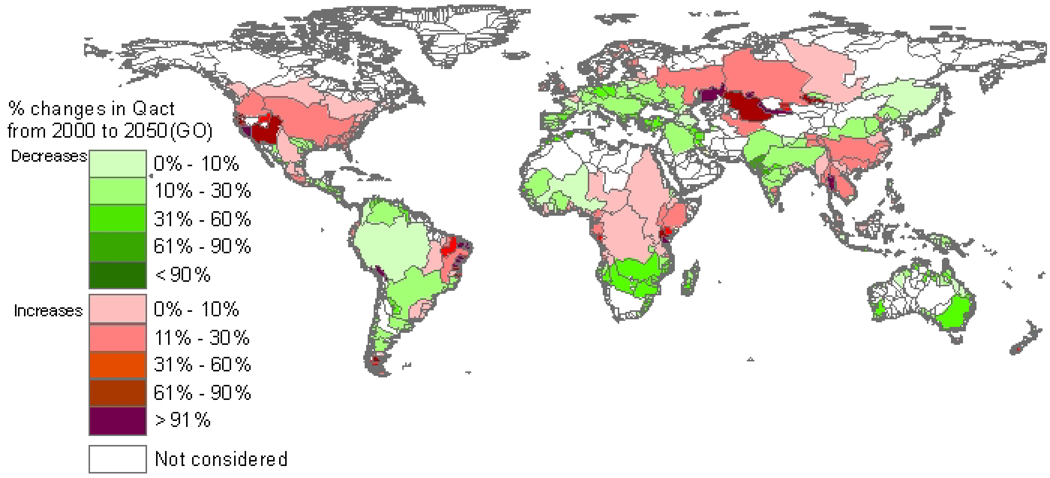



*Figure 30*

*Percentage changes in actual water dichanges (Qact, in $m^3$ $km^{-2}$ $year^{1}$) from 2000 to 2050. The GO is the Global Orchestration scenario of the Millennium Ecosystem Assessment. Outputs of the Global NEWS model were taken and converted from $km^3$ $year^{1}$ to $m^3$ $km^{-2}$ $year^{1}$. This was done by first converting values from $km^3$ $year^{1}$ to $m^3$ $year^{1}$ (multiply by $10^9$ since $1km^3=10^9m^3$). Then, values can be converted from $m^3$ $year^{1}$ to $m^3$ $km^{-2}$ $year^{1}$ (divide a value by basin area, which should be in $km^2$) (see Chapter 3). Deliniations of river basins are from the Global NEWS model*

Steady state DIP concentrations and yields are not affected by including river retention because of the assumption mentioned above (see also Chapter 3). Inversely, dynamic based DIP export has been slightly affected even under that assumption. This can be explained by the fact that time dimension is included in P processes within watersheds (Figure 28). Therefore, Figure 28 and 29 illustrate river retention (Ldip) only for the dynamic approach.

Result show that dynamic DIP export at the mouth is relatively sensitive to the inclusion of river retention but less sensitive to different values of input variables (minimum, average and maximum their values). Regarding global DIP concentrations, there are no significant changes between three sets of input variables when river retention is excluded (Ldip=0) (Fig. 28A). However, with including river retention in addition to those variables, slight differences in global DIP concentrations between these three sets of variables can be found (Figure 28A). Results indicate that there are small reductions in global DIP concentrations (Figure 28A) and fluxes (Figure 28B) with including fractions of river retention, where 0.50 suggests relatively higher their decreases than the other fractions over time. This is because with increasing fraction of river retention P pool at the watershed is increasing too (see previous section) leading to less response to changes in P inputs under the GO scenario over time. This follows less DIP export from land to surface waters and thus less DIP export at the mouth. For instance in 2050, on the basis of minimum values of input variables, global DIP concentration was estimated to be around 0.36 mg per L without river retention (Ldip=0) and around 0.34 mg per L with river retention of 10% (Ldip=0.10). Global DIP concentrations on the basis of maximum values are 0.35 mg per L without river retention (Ldip=0) and reduced up to 0.23 mg per L with including river retention of 50% (Ldip=0.50). Global DIP fluxes (Fig. 28B) show similar pattern to DIP concentrations.

Regionally, there are no significant differences in future trends of dynamic DIP concentrations between three sets of values (Figure 29). Nevertheless, some variations are found among river basins. For instance, on the basis of minimum values, DIP concentrations in majority of river basins draining into coastal waters of North America increased over the period 2000-2050 for both without (Ldip=0) and with (Ldip=0.10) river retention while decreased on the basis of average and maximum values. Furthermore, some differences are also found among river basins between DIP without river retention and with river retention (Figure 29). River basins of North America are one example considering average values of input variables (Figure 29). Here, several basins may receive higher DIP concentrations (some of them up to 10%, others even higher) in 2050 compared to 2000 when Ldip is zero while Ldip is 0.25 DIP concentrations can be reduced in the future up to 10%. Taking as an example maximum values of input variables, around half of river basins in Australia might bring DIP concentrations to its coastal waters by 10% more when Ldip is zero while up to 30% less when Ldip is 0.50 in 2050 relative to 2000. These slight differences in DIP export between three sets of variables can be caused by their different values. For the other river basins, whose future trends in DIP concentrations almost do not changes between these three sets of values. In this case, 50 years (from 2000 to 2050) might be not enough to see large changes in DIP export between 2000 and 2050, since DIP is releasing from the soil slowly over time, but continuously according to the dynamic approach.

Future changes (percentages) in DIP concentrations among river basins and also between both dynamic and steady state approaches can also be partly explained by future changes in dominant sources of DIP export among river basins. When anthropogenic diffuse sources are dominant, small differences between both approaches can be noticed. This is because dynamics applied only for DIP resulted from these sources. For instance, these sources are important exporters of DIP yields to river basins in Oceania continent (see Section 4.2.1, Figure 21). In the future, DIP yields are expected to increase from this source (Figure 23). In this case difference in DIP export between two approaches is visible, where the dynamic one suggests lower increases (up to 10%) while the steady state higher (several basins even higher than 90%) increase from 2000 to 2050. River basins of South Asia also receive majority of DIP yields from anthropogenic diffuse sources (Figure 21). For a few river basins dynamic approach recommends lower increases in DIP concentrations over the period of 2000-2050 compared to the steady state approach (Figure 29). Inversely, North American river basins receive over half of DIP yields from point sources rather than from anthropogenic diffuse sources (Figure 21). Despite of this, the inclusion of DIP dynamics influenced its export at the mouth depending whether river retention is included or excluded and which set of input variables was considered (Figure 29). This could be explained that dominance of point sources can be reduced in the future because of better sewage treatments (no strong increases for the future, maximum up to 30% depending on river basins) while anthropogenic diffuse sources might become to contribute more DIP than in the past (stronger increases compare to point sources) (see Figure 23). Difference in changes of DIP concentrations over that period between both approaches is also considerable for river basins of South America (Figure 29). This might also be linked to future trends in DIP sources in the future. Here, natural diffuse source is dominant contributors of DIP yields at the river mouth (Figure 21). However, future trends show that contribution of this source is projected to decrease while anthropogenic diffuse and point sources increase (Figure 23).

Results show that there are difference in future trends between DIP concentrations and yields under both steady state and dynamic approaches (see Figures 28 A and B). For instance, steady state global DIP concentration is projected to increase by over 1.5 times in 2050 compared to 2000 while average DIP yield is expected to increase only about 30% (Figure 28). In general, global DIP yields show less increases for the future or even descreases (that depends on whether river retention is excluded or included) compared to DIP concentrations (Figures. 28 A and B). Regionally (among river basins), differences in future trends between DIP concentrations and yields are anticipated too. Actual water discharge (Qact) might partly contribute to this situation via dilution or vice versa effects. This is because this factor was used in estimations (see Chapter 3, Figures 15 and 16 regarding equations). Therefore, future trends in Qact may also influence future trends in DIP concentrationsFuture trends in actual water discharge are illustated in Figure 30.

The main conclusions of this analysis are that:
- Overall, the impact of a dynamic approach is limited due to large contribution of point sources.
- The impact of dynamic approach depends on several factors.
- Regionally, there are differences between a dynamic and steady state approaches.

# 5 Discussion, conclusion and recommendation

## 5.1 Discussion

Inclusion of P (phosphorus) dynamics in modelling of its export at a river basin scale is crucial because of considering P export over time rather than at static conditions. In order to get insight into existing P models, their review was performed. These are models that quantify P export at regional and global scale. Scarcity of data was a main reason to limit this review to twenty seven models. Many models at a river basin scale are based on a steady sate approach because of mostly data availability. The *NEWS* (Nutrient Export from WaterShed) model is a representative in this case. Therefore, this study was focused to develop a dynamic approach that can be applied to the Global *NEWS* model regarding P export at the river basin scale. Assessment of P export based on both dynamic and steady state approaches, was another objective of this study. Additionally, the study aimed to assess the impact of included river retention on DIP export presently neglected in the Global *NEWS* model.

The Global *NEWS* model considers static conditions for riverine nutrient export (nitrogen, phosphorus, carbon and dissolved silica). The model estimates P export from watersheds (land) to surface waters and along the river system to coastal waters. Regarding P, estimations are done for dissolved inorganic (DIP) and organic (DOP) phosphorus as well as particulate phosphorus (PP). Many studies have been used the model to address environmental problems related to nutrient export at the river basin scale. Majority of these studies was focused on a global scale. Some of them are riverine export of dissolved forms of nutrients (Harrison et al., 2010; Harrison et al., 2005), particulate forms of N, P and C (Beusen et at., 2005) and dissolved silica (Beusen et al., 2009). A few studies used the model to analyze nutrient export for specific regions. These are nutrient export by the Changjiang river basin (Yan et al., 2010), nutrient export to coastal waters of the North Sea by the Seine River and the Scheldt River (Thien et al., 2010), riverine export of nutrients by rivers to coastal waters of South America (Van der Struijk and Kroeze, 2010) and Africa (Yasin et al., 2010). The Global *NEWS* model was validated on the global scale. For instance, model performance for DIP export in term of the coefficient of determination ($R^2$) is 0.51 (Mayorga et al., 2010). Nevertheless, since the basis for modelling is static conditions, nutrient export might be either over or/and underestimated.

Since the Global *NEWS* model is the basis in this study, the study area covers river basins of the world. The model estimates nutrient export for over six thousands river basins. In this study, over one thousands river basins were decided to be in use, which areas cover more than four grid cells of 0.5 by 0.5 degree. This is because the model performs better for large rivers. Later, this number of river basins was limited to over five hundreds. The other basins were excluded due to absence of agricultural areas, very low runoff and/or very low P inputs to land. These aspects affected implementation of a dynamic approach to the model.

Several limitations were made in this study with respect to implementing P dynamics to the model. P dynamics was limited to DIP export at the watershed scale (within land). This is because DIP is considered as the most bio-reactive form that interacts with the soil P pool than the other P forms (Harrison et al., 2010; Busman et al., 2002; Scheffer, 2004). Furthermore, PP export is estimated differently from dissolved P forms in the Global *NEWS* model. Dissolved P forms are estimated on the basis of a mass-balance approach while particulate P is estimated on the basis of a regression analysis and relationship with TSS (total suspended solid) (Mayorga et al., 2010). This makes it difficult to apply P dynamics to the model.

DIP dynamics within the river system was not into consideration in this study. This can be motivated by lack of time and knowledge in this aspect.

Application of P dynamics was also limited to DIP sources at the watershed scale. In this study DIP that is generated from diffuse anthropogenic sources were considered. These are the sources that the Global *NEWS* model distinguishes including animal manure and synthetic fertilizer. Weathering of P contained materials over agricultural areas from additional diffuse source and was also considered in P dynamics. Point sources of DIP were not considered because these are directly discharged to surface waters and thus no connection to the watershed (land). However, in reality households that are not connected to sewage systems can contribute significantly to P export via land to rivers, for instance in developing countries. Natural sources of DIP export were not incorporated in dynamics too.

DIP export was considered via concentrations and fluxes, which were estimated according to the steady state and dynamic approaches.

In this study, some steady state calculations were done outside of the model followed by the Global *NEWS* approach (Mayorga et al., 2010). These concerns mainly DIP fluxes and concentrations at the watershed scale. Some equations that were used in this study to estimate DIP export were not according to equations presented in a paper of Mayorga et al., (2010). This is about DIP yields resulted from diffuse anthropogenic sources. In this study, fertilizer, manure and DIP weathering over agricultural areas were combined into one term as anthropogenic diffuse sources. In the paper of Mayorga et al., (2010) DIP weathering over agricultural areas is separated from the others because of different formulas that are used to estimate DIP export from them (Mayorga et al., 2010). The model directly provides net P inputs from anthropogenic diffuse sources (already corrected for P export/uptake) over agricultural areas, where all these three sources are included. In order to estimate DIP that is coming to surface waters from the watershed (land), net P inputs have to be multiplied by an export fraction according to the model approach (the Global *NEWS* source code). This fraction is responsible for DIP export from land to surface waters. Since these net P inputs are available and the fraction is also taken from the model, DIP export at the watershed scale was derived (see Chapter 3).

Dynamic calculations were done outside of the Global *NEWS* model. In the dynamic approach equilibrium between irreversible (not active) and reversible (active) P pools was assumed for DIP concentrations at the watershed scale according to the Langmuir equation (Van der Zee, 1988; Schoumans, 1995; Schoumans and Groenendijk, 2000). In reality, perhaps, this equilibrium can be disturbed by human activities. For instance, intensive synthetic fertilizer and animal manure applications to soils may affect this buffer system in the soil. Therefore, more detailed models usually apply partly equilibrium and partly not equilibrium in their dynamic approaches.

Dynamic calculations are simplified in this study. The fraction of soil P accumulation within the watershed is kept constant for future years (2030 and 2050) based on the year 2000. In real situation this fraction changes over time with changes in P pools. However, because of data scarcity this simplification was made. P accumulation over time was calculated from 1900 to 2050 based on four time-steps including 1900-1970, 1970-2000, 2000-2030 and 2030-2050. The accumulation in the period 1900-1970 was estimated based on an assumption that the P surplus ($P_{in}$-$P_{up}$) increases linearly from 0 in 1900 to the Global *NEWS* value in 1970. It was also assumed that P surplus in 1900 was zero (the amount of P input equals P outputs). Linear extrapolation was assumed for other periods too from the known values in 1970, 2000, 2030 and 2050.

In the dynamic approach, P adsorption constant ($K_P$) is a key factor that is responsible for P adsorption/ desorption process between solid and solution phases in the soil. This parameter can be measured. Methodologically, the parameter is a function of soil properties (for instance, pH, content of aluminium and iron oxides, bulk density). In this study, $K_P$ is a function of basin characteristics (watershed DIP concentrations, river retention, net P inputs and the fraction of P accumulation) and soil properties (bulk density, content of aluminium and iron oxides, soil thickness) estimated for the year 2000. Basin characteristics were taken from the model and these are specific for each river basin. Input data for the other variables including bulk density, content of aluminium and iron oxides, soil thickness and river retention were derived from different sources. Furthermore, these are variables that are generic for all river basins. Therefore, they were assumed to be a subject for sensitivity analysis.

An assumption was made that an inclusion of river retention affects only DIP export at the watershed scale. There is a reason behind of this assumption. According to the model estimations, DIP concentrations at the watershed scale are considerably low that leads to very high or even infinite values of $K_P$. Due to this reason, the study area was narrowed down from over one thousand river basins (around 90% of the world area) to over five hundreds (around 70% of the world area). Therefore, in order to improve this situation, watershed DIP concentrations were increased by the addition of extra DIP resulted from river retention. This substantially improved estimations of $K_P$. Plausibility of $K_P$ was tested in this study. The calculated P adsorption constants are comparable with literature data when river retention is included in its estimations. This might also improve Global *NEWS* underestimations of DIP export at the watershed scale from anthropogenic diffuse sources. This is a strong indication that river retention is an important aspect that has to be included to the Global *NEWS* model.

In this study, a dynamic model was not validated. This is because time limitation to collect data for this purpose. Nevertheless, results show that according to the dynamic model watershed systems do not react directly to P inputs while they do react according to the steady state approach. This seems realistic since P is accumulating over time within the watershed leading to time dependent P release from the soil to surface waters and thus less response in P export to P inputs. This is an advantage of this dynamic model versus steady state model. This dynamic approach is rather simple making it easy to apply to the model.

## 5.2 Conclusion

Phosphorus (P) plays an essential role in the environment by controlling primary productivity. This also depends on P forms, where dissolved inorganic P (DIP) is most bio-reactive among the other forms and, hence, contributes significantly to changes in the environment. However, globally it accounts small portion around 10%-20% of total P. Over the past several decades P export has been influenced by anthropogenic activities, where agriculture contributes mostly to P export at the watershed scale (land) whilst point sources to P export at the river basin scale.

Quantification of P export is an important task in order to be able to control its export, to prevent water pollution and also to cope with already existing environmental problems related to its export (for instance, eutrophication). Models have been vastly used for this purpose especially where data are scarce. This usually concerns P export at large scale such as watershed, national, river basin scales and others. In this study twenty seven models were reviewed by using literature information. Almost all of them (twenty six) are focused on P export estimated for an individual unit on a regional scale namely soil/field scale (less than 1/3 of models), P in water bodies (over 1/3 of models) and watershed/river basin scale (2/4 of models). Around 2/3 of these models include P dynamics in their estimations. This is a good indication of dynamic importance. That is also because P has ability to build up (to be accumulated) over time in the soil that affects directly its transport to surface waters. Besides, this process depends on net P inputs to land (human influence), soil properties and relation between solid phase and soil solution phase. This relation is controlled by P adsorption constant ($K_P$), which is also a key factor in P dynamics. Ignorance of P dynamics in models might either under- or overestimate P export that may have negative implications for future nutrient managements. Inclusion of P dynamics is a weak point especially in global models. The Global *NEWS* (Nutrient Export from WaterShed) model is one well-known example that estimates nutrient export (including P) on the basis of static conditions. This model quantifies nutrient export at a river basin scale.

Therefore, objectives of this study were to develop a dynamic approach, which can be applied to the Global *NEWS* model and to assess the impact of the dynamic approach on P export at the river basin scale. The model does not consider P retention by the river itself only P retention in the river system via water consumptive use and by reservoirs. Thus, the study was also aimed to assess the impact of included river retention in the Global *NEWS* model.

The study area included river basins of the world with their areas covering more than 4 grid cells by 0.5x0.5 degree. These are 1163 river basins taken from the Global *NEWS* model. However, at later stage of the study the study area was narrowed down to 506 river basins due to methodological aspect namely calculated P adsorption constant ($K_P$). P dynamics was developed only to DIP export at the watershed scale resulted from anthropogenic diffuse sources including synthetic fertilizer and animal manure. DIP weathering over agricultural areas was included too for this purpose. In order to identify the impact of the dynamic approach on DIP export analyses were performed for DIP export at the watershed as well as at the river basin (DIP exported at river mouth) scales according to both steady state and dynamic approaches. In this study DIP export was defined via DIP concentrations and fluxes (or yields).

Methodology to estimate DIP export according to the steady state approach was derived from the Global *NEWS* model, where a paper of Mayorga et al., (2010) is the basis. Calculations of DIP fluxes at the watershed scale were done outside of the model since it was not directly available from the model. Calculations of DIP fluxes at the mouth of rivers were taken directly from the model except for those fluxes, where river retention is included. An inclusion of river retention was followed by the assumption that river retention influences only DIP fluxes at the watershed scale while at the mouth of rivers these fluxes stay without any changes. DIP concentrations were estimated on the basis of DIP fluxes taking into account runoff at the watershed scale and actual water discharge at the river basin scale. Almost all Input data needed for this purpose were derived from the model except for river retention.

Methodology to estimate DIP export according to the dynamic approach concerns only its export at the watershed scale, where first DIP concentrations were calculated and afterwards, DIP fluxes were derived. In this study a dynamic model for DIP export is based on soil properties including bulk density and content of aluminium and iron oxides as well as on oxalate extractable P pool, where P accumulation over time was taken into account, maximum amount of P that is readily available in the soil and P adsorption constant ($K_P$). There are several assumptions made in order to simplify a dynamic model. Equilibrium was assumed for watershed DIP concentrations with the reversible soil P pool (active), according to the Langmuir equation. Accumulation of P in the soil was calculated for the period of 1900-2050, where the P surplus was assumed to be zero in 1900. Linear extrapolation was assumed regarding P accumulation over this period on the basis of only four known values for 1970, 2000, 2030 and 2050, derived from the Global *NEWS* model. The fraction of P accumulation was estimated only for 2000 and kept constant for future years. In this study $K_P$ was estimated for the year 2000 as a function of basin characteristics and soil properties. The inclusion of river retention was done according to the assumption mentioned above. Input data needed for dynamic calculations were derived from the Global *NEWS* model for each river basin except for bulk density, soil thickness, content of aluminium and iron oxides and fractions of river retention. These input variables were taken from literature including their minimum, average and maximum values. These variables are not specific for each river basin and thus they are a subject for a sensitivity analysis. Calculated values of $K_P$ are found to be more reliable when river retention is included because its values are comparable with field data from literature. $K_P$ is sensitive to DIP concentrations used in its estimations.

Inclusion of P dynamics has large impact on DIP export at the watershed scale. The dynamic approach suggests lower DIP concentrations and yields as well as their increases from 2000 to 2050 compared to the steady state approach. Globally, for 2050 (GO scenario), dynamic DIP concentrations estimated based on minimum values of input variables are 3/4 of steady state DIP concentrations. According to maximum values of input variables dynamic DIP concentrations are 2/4 of steady state DIP values. Regarding future trends, DIP concentrations over the period of 2000-2050 under the GO scenario are expected to increase significantly by about 80% according to the steady state approach. The dynamic approach suggests lower increases that are about 60%, 10% and 3% based on minimum, average and maximum values of input variables respectively neglecting here river retention. Differences between both approaches can be explained by that the dynamic approach accounts time dimension in P adsorption-desorption processes in the soil leading to time dependent DIP release from the soil to surface waters. Additionally minor sensitivity of the dynamic approach to used different values of input variables was found. Under maximum values, DIP concentrations show hardly changes from 2000 to 2050 compared, for instance, to minimum values. This demonstrates that within 10 m of the soil (maximum value) considering 150 mmol per kg of aluminium and iron oxides (maximum value, they have strong ability to bind P) in the soil the efficiency of DIP export is less than within 1 m of the soil with 50 mmol per kg of aluminium and iron oxides (minimum values). Average values of these inputs show similar patter to maximum values. Sensitivity to bulk density might not be visible in this study since its used minimum, average and maximum values are almost similar.

Watershed DIP export is significantly sensitive to the inclusion of river retention according to both steady state and dynamic approaches. With increasing fractions of river retention from 0 to 0.50, DIP concentrations and yields were estimated to increase in 2000. For future years, 2030 and 2050, there are higher increases according to the steady state approach and lower increases according to the dynamic approach. By including 10% of river retention, steady state DIP concentrations in 2030 and 2050 might increase by over 100% while dynamic concentrations might increase by about 50% for future years on a global scale. By adding 50% of river retention, increases in watershed DIP concentrations for 2030 and 2050 are about ten0 times and six times higher compared to 0% of river retention according to the steady state and dynamic approaches respectively on the global scale. Increases in watershed DIP export can be caused by extra amount of DIP flux that was added to estimations, which was resulted from its river retention within the watershed.

The dynamic approach has limited impact on DIP export at the river basin scale compared to DIP export at the watershed scale. This is because P dynamics were included only to watershed scale and only for DIP export from anthropogenic diffuse sources. Nevertheless, minor differences between steady state DIP export and dynamic DIP export were found. Generally, changes in DIP concentrations and yields at the river mouth in the future are less according to the dynamic approach than according to the steady state approach. This also depends on whether river retention is included or excluded and depends on which set of input values (minimum, average and maximum) was used in dynamic estimations. These differences are especially visible for individual river basins of the world. One example is majority of river basins in South America, where according to the dynamic approach decreases in DIP concentrations over the period of 2000-2050 might be instead of increases that are according to the steady state approach.

Future change in DIP concentrations at the mouth of rivers among river basins and also between both dynamic and steady state approaches can be associated with future changes in DIP dominant sources among those river basins. Difference between both approach can be visible for river basins, where anthropogenic diffuse sources are dominant and will stay dominant in the future too. For instance, river basins of Oceania and South Asia receive majority of DIP yields at their mouth from these sources and will receive in the future as well. The dynamic approach shows lower increases in DIP concentrations than the steady state approach. DIP yields in river basins of North America are delivered at their mouth mainly from point source. However, in the future the relative contribution of diffuse anthropogenic sources might increase while point sources decrease due to better sewage treatments. Nevertheless, the dominance of point sources of DIP exported at the river mouth limits the impact of included P dynamics at the watershed scale.

DIP export at the river basin is not sensitive to the inclusion of river retention because of the assumption mentioned above. Despite of this assumption, dynamic DIP export was slightly influenced. For instance in 2050, on the basis of minimum values of input variables, global DIP concentration was estimated to be around 0.36 mg per L without river retention (Ldip=0) and around 0.34 mg per L with river retention of 10% (Ldip=0.10). Global DIP concentrations on the basis of maximum values are 0.35 mg per L without river retention (Ldip=0) and reduced up to 0.23 mg per L with including river retention of 50% (Ldip=0.50). This is opposite to its effect at the watershed scale, where DIP export was increased. This is because with increasing the fraction of river retention P pool at the watershed is increasing too via watershed DIP concentrations, where increases are higher under the steady state approach and lower under the dynamic approach. Consequently, $K_P$ is decreasing that affects the efficiency of DIP adsorption/desorption process between solid phase and soil solution within the watershed. This influences DIP availability in soil solution and thus DIP leaching from this solution to surface waters. Considering these conditions, there is lower response of the watershed system to changes in P inputs under the GO scenarios over time. This follows less DIP export from land to surface waters and thus less DIP exported at the river mouth.

Annual runoff and actual water discharge were used in estimations either DIP concentrations and DIP fluxes. Thereofore, their changes over time may affect also DIP export over time via, for instance, dilution effect.

Summarizing, the inclusion of dynamics for DIP export in the Global *NEWS* model is valuable. Dynamic DIP export is lower than steady state at both watershed and river basin scales. Furthermore, the impact of the dynamic approach is high at the watershed scale and limited at the river basin scale because of large contribution of point sources. The inclusion of river retention to both approaches is crucial too. It improves calculations of P adsorption constant in the dynamic approach, which can then be compared with literature data. The dynamic approach that has been applied in this study is rather simple. This enhances its change for future applications. However, still there are some rooms for improvements in the future.

## 5.3 Recommendation

Since this is the first attempt to include P dynamics in the Global *NEWS* model, there are many improvements that can be done for future elaboration of this study.

The dynamic approach is simplified because of time and data availability. Initial P concentration for 1900 used in the estimation of P accumulation over the period of 1900-2050 should be reconsidered in the future. P accumulation over period of this period should be done for each year. The fraction of P accumulation should not be kept constant and thus it has to be estimated for each year too. Input data for bulk density, content of aluminium and iron oxides and soil types are better to be adjusted for each river basin. This will improve calculations of $K_P$, dynamic based DIP concentrations and fluxes. Consequently, data collection is strongly required in order to be able to implement dynamic approach in the Global *NEWS* model.

Calculations of DIP export according to both approaches were performed outside of the Global *NEWS* model. Hence, in the future it might be reasonable to include these into the model progamme (written in python).

The Global *NEWS* model does not take into account P sources namely atmospheric P deposition and P inputs to land from households, which are not connected to sewage facilities. Therefore, inclusion of these sources to the model might improve situation with very low DIP concentrations at the watershed scale.

More research is needed to get insight into P river retention, for instance, via P accumulation in the sediment of the river, P retention by microphyts in the river etc. Afterwards, it will be possible to select appropriate fractions of river retention for each river basin. To this end, it is recommended to validate a developed dynamic model.

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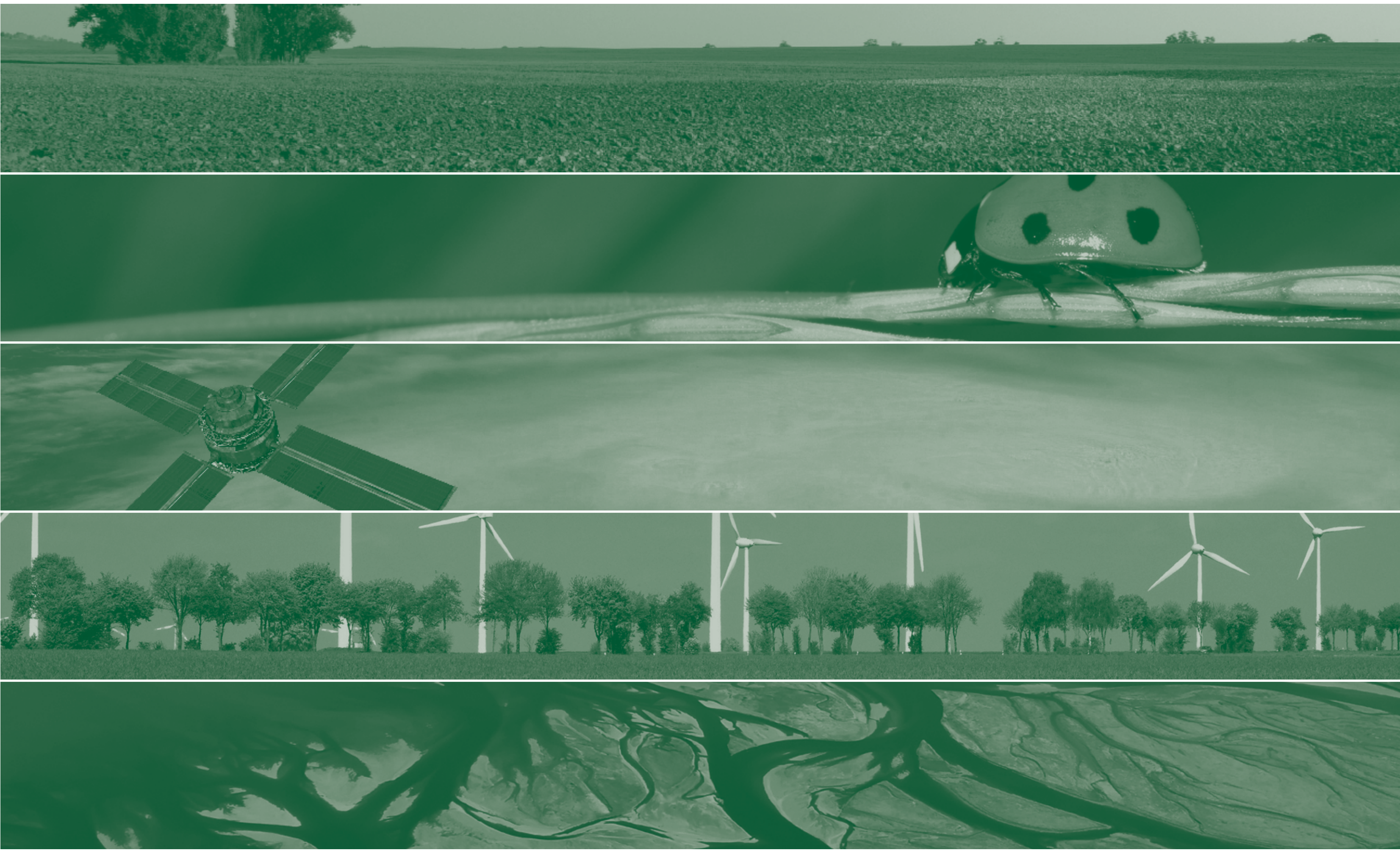
# Annex

*Table 1*
*Relative share between different sources of DIP yields (averages) for 2030 according to the GO (Global Orchestration) scenario of Millennium Ecosystem Assessment expressed in percentage (%) and average yields. The average yield for individual continent or the world was estimate as the sum of loads (kg year$^{-1}$) of rivers draining into coastal waters of that continent divided by total area of those rivers. The Global NEWS outputs were taken for calculations.*

| Percentage (%) | Point sources (human waste, detergent) | Anthropogenic diffuse sources (fertilizer, manure, weathering) | Natural diffuse source (weathering) | Total Yields |
|---|---|---|---|---|
| The world | 51% | 40% | 9% | 100% |
| Africa | 57% | 33% | 10% | 100% |
| Australia | 51% | 39% | 10% | 100% |
| North America | 62% | 31% | 7% | 100% |
| South America | 38% | 37% | 25% | 100% |
| Europe | 83% | 15% | 2% | 100% |
| Oceania | 11% | 67% | 23% | 100% |
| North Asia | 80% | 15% | 5% | 100% |
| South Asia | 47% | 50% | 3% | 100% |
| Average yields | | | | |
| The world | 8.66 | 6.77 | 1.60 | 17.03 |
| Africa | 2.69 | 1.56 | 0.49 | 4.74 |
| Australia | 0.68 | 0.51 | 0.13 | 1.32 |
| North America | 7.73 | 3.94 | 0.84 | 12.51 |
| South America | 7.31 | 7.27 | 4.87 | 19.45 |
| Europe | 20.51 | 3.74 | 0.56 | 24.81 |
| Oceania | 6.75 | 41.52 | 14.08 | 62.35 |
| North Asia | 3.55 | 0.66 | 0.21 | 4.42 |
| South Asia | 19.51 | 20.58 | 1.19 | 41.28 |

*Table 2*
*Relative share between different sources of DIP yields (averages) for 2050 according to the GO (Global Orchestration) scenario of Millennium Ecosystem Assessment expressed in percentage (%) and average yields. The average yield for individual continent or the world was estimate as the sum of loads (kg year[1]) of rivers draining into coastal waters of that continent divided by total area of those rivers. The Global NEWS outputs were taken for calculations.*

| Percentage (%) | Point sources (human waste, detergent) | Anthropogenic diffuse sources (fertilizer, manure, weathering) | Natural diffuse source (weathering) | Total Yields |
|---|---|---|---|---|
| The world | 51% | 41% | 9% | 100% |
| Africa | 56% | 37% | 8% | 100% |
| Australia | 53% | 38% | 9% | 100% |
| North America | 59% | 34% | 7% | 100% |
| South America | 37% | 40% | 23% | 100% |
| Europe | 82% | 16% | 3% | 100% |
| Oceania | 15% | 68% | 17% | 100% |
| North Asia | 80% | 16% | 5% | 100% |
| South Asia | 49% | 48% | 3% | 100% |
| Average yields | | | | |
| The world | 8.92 | 7.18 | 1.51 | 17.62 |
| Africa | 3.32 | 2.18 | 0.45 | 5.95 |
| Australia | 0.61 | 0.43 | 0.10 | 1.13 |
| North America | 7.80 | 4.48 | 0.86 | 13.14 |
| South America | 7.11 | 7.68 | 4.48 | 19.27 |
| Europe | 18.18 | 3.52 | 0.56 | 22.26 |
| Oceania | 12.29 | 56.99 | 14.05 | 83.33 |
| North Asia | 4.24 | 0.83 | 0.24 | 5.31 |
| South Asia | 20.50 | 20.13 | 1.15 | 41.78 |



Alterra is part of the international expertise organisation Wageningen UR (University & Research centre). Our mission is 'To explore the potential of nature to improve the quality of life'. Within Wageningen UR, nine research institutes – both specialised and applied – have joined forces with Wageningen University and Van Hall Larenstein University of Applied Sciences to help answer the most important questions in the domain of healthy food and living environment. With approximately 40 locations (in the Netherlands, Brazil and China), 6,500 members of staff and 10,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the exact sciences and the technological and social disciplines are at the heart of the Wageningen Approach.

Alterra is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

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