Master's thesis

AQUATOX – ecological risk assessment model – A tool for impact assessment for waters

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ABSTRACT

Private companies are receiving increasingly larger numbers of assignments to evaluate ecological impacts on water bodies. Act on Environmental Impact Assessment Procedure (EIA) (468/1994) and the EU Water Framework Directive (WFD) add to the challenge of finding reliable tools for assessment work. There is a variety of different tools and models for evaluation to choose from on the market. Versatility in describing an entire water ecosystem, as well as the possibility to evaluate changes caused by various factors, can be seen as the strengths of the US Environmental Protection Agency (EPA) AQUATOX-ecological risk assessment model, which was tested in this work. Total phosphorus, total nitrogen and chlorophyll-a concentration in constant and dynamic conditions were simulated for Lake Pyhäjärvi in Säkylä municipality. The Nash-Sutcliff efficiency coefficient was negative in both conditions. The AQUATOX describes relatively well the magnitude of nutrient and chlorophyll-a concentration in constant conditions. In this sense, the model is useful for planning work. Temporal dynamics for simulated concentrations leaves room for improvement, and the calibration of the model is needed. A shortcoming of the AQUATOX is the lack of testing the model in boreal environments. In further studies, more focus should be given to the biological aspects of the model.

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TIIVISTELMÄ

Yritykset saavat yhä enemmän vesistövaikutusten arviointitoimeksiantoja. Laki ympäristövaikutusten arvioinnista (YVA) (468/1994) sekä EU:n vesipuitedirektiivi (VPD) asettavat haasteita löytää luotettavia arviointimenetelmiä. Markkinoilla on tarjolla lukuisia työkaluja ja malleja vesistövaikutusten arvioimiseksi. Koko ekosysteemiä kuvaavia malleja ei juuri ole, ja siksi tässä työssä haluttiin testata USA:n ympäristönsuojeluviraston (EPA) koko vesiekosysteemin kattavaa AQUATOX riskinarviomallia. Mallilla simuloitiin Säkylän Pyhäjärven kokonaisfosfori- ja – typpi-, sekä klorofylli-a -pitoisuutta dynaamisessa sekä vakiotilanteessa. Nash-Sutcliff- hyvyyskerroin oli negatiivinen sekä vakiotilanteen että dynaamisen tilanteen simuloinnissa. Simulointitulokset vastasivat vakiotilanteessa suuruusluokaltaan melko hyvin havaittuja pitoisuuksia, ja mallia voi siltä osin pitää käyttökelpoisena työkaluna. Ajallisen vaihtelun simulointia tulee parantaa mallin kalibroinnilla. Mallin puute on toistaiseksi sen testaamattomuus boreaalisen vyöhykkeen vesistöissä. Jatkossa tulee erityisesti kiinnittää huomiota malliin syötettäviin biologisiin tekijöihin ja niiden soveltuvuuteen pohjoisissa vesistöissä.

Contents

1. INTRODUCTION

Private companies are receiving increasingly larger numbers of assignments to evaluate different operations and their impacts on water bodies. Law of the Environment Impact Assessment (EIA) (468/1994) and Water Framework Directive (2000/60/EC) adds to the challenge for the work to protect our waters. Estimating impacts on water bodies with a certain degree of confidence, the operation appraiser requires suitable models and tools to resolve problems encountered. These models and tools should be fairly simple to use and reliable, as time consuming applications do not allow the use and control of complex models. Every model has its own characteristics such as model scope, user friendliness, methodology and availability. When choosing a model, it is necessary to consider which model is suitable for which purpose (Saloranta *et al.* 2004).

Aquatic models are useful for a number of reasons.They provide information on water bodies and can be used for making predictions, helping us to manage complex water systems. As quoted by Dahle (2003), models help to organize, synthesize and track information and scientific knowledge and hypothesis in a way that would not be possible otherwise possible. Several models have been developed to simulate physical, chemical, biological and geological processes. The pressure has been moved to private companies, as many tasks associated with impact assessments for waters have been removed from environmental centres, where some have concurrently operated as developers for models and tools. Currently in Finland, the development of aquatic models is primarily the responsibility of the Finnish Environment Institute.

The aim of this research project was to test in Lake Säkylän Pyhäjärvi the AQUATOX -ecological risk evaluation model developed by US Environmental Protection Agencies (EPA). The model is very interesting because of its versatile simulation possibilities and user friendly interface. There is not any published research about AQUATOX-simulations in Finland. The total phosphorus, total nitrogen and chlorophyll-a concentration were simulated in the lake during the period of 1992-2001 with two different methods, constant and dynamic condition.

In both methods, daily data for the lake water balance were included. In the constant condition, the input data used were derived from the observed averages during 1992 – 2001. Directed non point load and nutrient load from rivers remained constant throughout the entire simulation period. This represented a situation where no specific daily water quality measurements are available, which is often the case in water system simulations. In the dynamic condition, the input data was given as observed time series. The nutrient load data was entered from the rivers as a dynamic time series; however, the non point load was entered as a constant load, derived from the ten year observed average. Simulated concentrations of constant and dynamic conditions were compared to observed concentrations using Nash-Sutcliff efficiency coefficient. This was done in order to see the correspondence between the simulated and observed concentrations. According to the correspondence and used time for building up the Pyhäjärvi application, it was estimated how useful tool the model is for impact assessment of water bodies for private companies. The model calibration was not included in this study.

2. BACKGROUND

My study is a part of the TEKES (the Finnish Funding Agency for Technology and Innovation) funded Catch_Lake 1 and 2 scheme, in which a process-based lake modelling as well as a remote sensing and intensive measurements and related wireless information transmission technology is being developed.

The pilot area is significant in regards to the water supply and recreational use of the Säkylä Pyhäjärvi (154 km^2) catchment. Catch_Lake 2 is a continuation of the Catch_Lake 1 scheme that focuses on Pyhäjärvi research, where measuring technology is being developed and lake processes are being modelled using 3-D models. Involved in this scheme were SYKE (Finnish Environment Institute), Department of Radio Sciences of the Helsinki University of Technology, Pyhäjärvi-Institute, Environmental Centre of South-Western Finland, University of Turku Department of Biology, Reading University in England, EOMAP (Earth Observation and Mapping technologies) in Germany, NERI (National Environmental Research Institute) in Denmark, as well as the private companies South-West Finland Water and Environment Research Inc., Luode Consulting Inc., Numerola Inc., Fish and Water Reasearch Inc. and Pöyry Environment Oy (Lepistö *et al.* 2008). I completed my Master's Thesis as a part of my work in the project and during my employment at Ramboll Finland Oy.

At the end of 2007, the INCA-N (Whitehead *et al.* 1998) and SWAT (Neitsch *et al.* 2005) catchment models were applied to the Catch_Lake 1 and 2 schemes. At the beginning of 2008, the current and water quality model COHERENS (Luyten *et al.* 1999) was applied to the Catch_Lake 2 scheme. Testing of the AQUATOX, a model developed for fresh water and estuary simulation, was desired, concurrently with the scheme, due to its extremely versatile characteristics. The model has the potential to simulate an entire water ecosystem.

2.1. Phosphorus in the aquatic ecosystem

Eutrophication of fresh water can be controlled by reducing the input of nutrients, phosphorus (P) and nitrogen (N). Phosphorus is generally the most limiting factor for primary production in water bodies. Therefore most nutrient-control programs have focused on it (Kalff 2002).

Phosphorus enters water systems from the land and by direct atmospheric deposition on water surfaces (Kalff 2002). In fresh water phosphorus is found as dissolved phosphate phosphorus, dissolved organic phosphorus and particulate phosphorus. In addition, phosphorus is found from bottom sediment. Phosphorus can be bound to ions, for example iron and calcium. In neutral or slightly alkaline water phosphorus is found as calcium phosphate ($CaHPO_4$) in very alkaline water as sodium phosphate ($NaHPO_4$). In acidic water phosphorus is bound to iron (Särkkä 1996).

Only phytoplankton and macrophytes can utilize phosphate phosphorus. The growth of phytoplankton decreases phosphate phosphorus concentration in water at spring time. The amount of phosphate phosphorus in the water after winter time determines the productivity of phytoplankton in spring. Later in summer phytoplankton production depends on phosphorus which is excreted by animals and phosphorus which is released from decomposing phytoplankton. Most of the phosphorus bound to phytoplankton is releasing already in epilimnion and not reaching the hypolimnion at all (Särkkä 1996, Kalff 2002).

In aerobic conditions and the presence of iron phosphate phosphorus (PO_4) forms iron (III) phosphate ($FePO_4$) and is sedimenting as a solid to the bottom. If conditions turn to anaerobic and redox-potential decreases to +300 – 200 mV, ferric iron (Fe^{+++}) becomes reduced to ferrous iron (Fe^{++}) and phosphorus releases to the water in a soluble form. The release of elements from sediments to the overlying waters is known as internal loading (Särkkä 1996, Kalff 2002).

In Finnish lakes the average concentration of total phosphorus is 23 µg/l and that of phosphate phosphorus 4 µg/l (Särkkä 1996).

2.2. Nitrogen in the aquatic ecosystem

Nitrogen plays an important role in inland waters. Its supply has a great importance in determining the primary productivity of aquatic systems and microbial recycling of organic matter (Kalff 2002). Nitrogen can be a limiting factor in aquatic systems if the concentration of phosphorus or silicon is high because of erosion. The mean concentration of nitrate nitrogen in Finnish lakes at surface water is 92 µg/l, nitrite nitrogen 1 µg/l and ammonium nitrogen 24 1 µg/l (Särkkä 1996).

Nitrogen (N) is always present in aquatic systems. It is supplied to the system from drainage basins and atmosphere and it can be produced in situ through nitrogen fixation (Kalff 2002). Most of nitrogen exists in dissolved gas form. There are relatively small proportions of dissolved ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), urea ($CO(NH_2)_2$) and dissolved organic compounds. The most important form of dissolved nitrogen is nitrogen nitrate (Särkkä 1996). Nitrate and nitrite have to be reduced to ammonium before they can be assimilated in the cell, making ammonium the most energetically favorable nitrogen source for cell uptake. The proportion of nitrogen in its oxidized (nitrate) and reduced (ammonium) form differs between eutrophic and oligotrophic lakes. Ammonium occurs only in low amounts and shows little variation with water depth due to the presence of oxygen in oligotrophic lakes. In eutrophic lakes processes are more complicated owing to a high outflow of ammonium from sediment as s result of bacterial decomposition of organic material at low oxygen concentrations. The concentration of nitrate generally follows the oxygen curve (Brönmark & Hansson 1998).

Only a few species of aquatic micro-organisms have the ability to fix atmospheric nitrogen. They are photosynthetic bacteria, *Azotobacter,* several species of *Clostridium* and cyanobacteria, formerly called blue-green algae. Algal nitrogen fixation occurs in light since it requires energy in the form of ATP (adenosine triphosphate) which is derived from photosynthesis (Manahan 1994, Brönmark & Hansson 1998, Kalff 2002.

Nitrification, the transformation of ammonium to nitrate, is a common and extremely important process in water and in soil (Manahan 1994, Brönmark & Hansson 1998). Many bacteria and some fungi are involved in this process (Brönmark & Hansson 1998). In nature, nitrogen is absorbed by plants primarily as nitrate. Denitrification, the transformation of nitrate to molecular nitrogen (N_2), is the mechanism by which fixed nitrogen is returned to the atmosphere (Manahan 1994, Brönmark & Hansson 1998). Denitrifying bacteria gain energy by oxidizing organic carbon to carbon dioxide (CO_2) and carbonate (CO_3^{2-}) by using oxygen from nitrate. Bacteria use carbon to build up new biomass (Brönmark & Hansson 1998). Molecular nitrogen is lost to the atmosphere if not used in nitrogen fixation. The nitrification occurs in the presence of oxygen, whereas denitrification is an anaerobic process. These processes are performed by different types of bacteria (Brönmark & Hansson 1998).

3. MATERIAL AND METHODS

3.1. Description of the AQUATOX model

Environmental Protection Agency (EPA) has developed the AQUATOX -ecological risk assessment model, which simulates different variables, such as the impact of nutrients and organic chemicals on fish, invertebrates, and phytoplankton and macrophyte biomasses in an ecosystem (Park *et al.* 2008, Park & Clough 2008).

In 1972, the Clean Water Act, a keystone for surface water conservation, was passed in USA. The law calls for the development of new tools and approaches as well as associated appropriate technical guides and instructions for the advancement of ecosystem analysis of waterways. The AQUATOX is the latest model in the long development process that started in 1974 with the water ecosystem model "CLEAN". Richard Park, who developed the AQUATOX-model, was also involved in the development of this latest model. At the end of the 1970's, Richard Park, together with other researchers, developed the PEST-model, which has the additional possibility of simulating toxic agents (Park *et al.* 2008).

The model is suitable for simulating rivers, lakes, ponds, reservoirs and estuaries, where, in addition to other variables, also an option to determine the salt concentration of the water is included.

The AQUATOX describes the water ecosystem by simulating changes in concentration mg/l or g/m^3) for organisms, nutrients and chemicals, as well as sediments in units of water volume (= sediments in a unit volume of water) (Figure 1) (Park & Clough 2008).

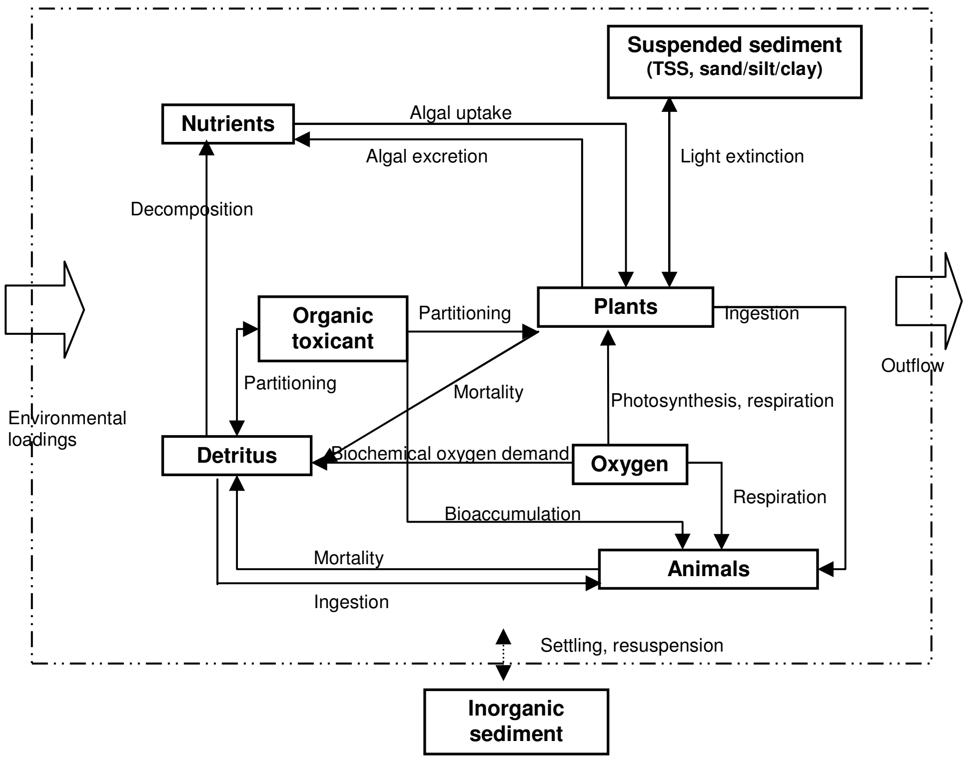

Figure 1. Flowchart of functions within the AQUATOX-model (Park & Clough 2008).

The AQUATOX, like any other ecosystem model, contains components that require data entry. These are the abiotic and biotic state variables. In the AQUATOX, the biotic state variables represent the trophic levels, nutrient intake groups, or species. The food web of the model is based on both detrital and algal-based trophic linkages (Figure 1). The variables which are used to run a simulation include temperature, light, and nutrient load, which determine the system behaviour. In the model, loads can be divided into atmospheric as well as into point and non-point loads. The load itself can be entered into the model as constant (always the same) or dynamic (continuously changing). The model can also be operated by setting the system to ignore loading, and the results can be compared to those achieved by running the program with loading values included.

The AQUATOX utilizes differential equations to represent changing values of state variables, normally with a reporting time step of one day. These equations require starting values or initial conditions to start the simulation. A simulation period can vary from few days to decades. Process equations contain another class of input variables: the parameters or coefficients that allow the user to specify key process characteristics. The AQUATOX is a mechanistic model with many parameters. Default values are available for parameters but the user should evaluate how applicable they are for studied site and edit the parameters if necessary. The system being modeled is characterized by site constants such as mean and maximum depths (Park *et al*. 2008, Park & Clough 2008). The principles of nitrogen and phosphorus cycle in the AQUATOX-model are described in Appendix 1.

The AQUATOX-model has been developed so that it offers the opportunity to obtain a very realistic picture of the water ecosystem with a relatively small amount of precise information on the subject and little need for calibrating the model. The required data to be entered are the external load data of the water body, characteristics of the target area, which include surface area, mean depth, maximum depth, evaporation and latitude, as well as the chemicals being simulated and their characteristics, and also, the biological characteristics of the simulated organisms.

The AQUATOX contains datasets on invertebrates, fish, phytoplankton and macrophytes. Species and species groups have been collected onto the databases along with a default value that includes data on the physiological and environmental requirements of the species, as well as the interactions within the species group.

The load information can be set using various load settings. These are point and non point loads, atmosphere load, as well as loading from upstream water bodies. The loading data can be entered as dynamic or constant data.

For simulation, data is required for on the site to be modelled (lake, river etc.), as well as on the time period, which can be days, weeks, months or decades. In order for the model to begin the simulation, initial values for carbon dioxide, soluble gases, as well as for ammonia, nitrate types and phosphate are required. Nutrients can also be entered as total nitrogen and total phosphorus. The model starts the calculations based on these initial values. The initial value for sediment detritus biomass is divided into labile, that is, easily degradable and assimilating detritus, and refractory detritus. The initial value for detritus within a water phase can be given as organic product, organic carbon, or as biological gas consumption. This value determines the nucleation as well as the non-decomposable portion.

AQUATOX is a box model, which represents average daily conditions for well-mixed aquatic systems. It can also be used to describe one dimensionally vertical change in the epilimnion and the hypolimnion in stratified conditions (Park & Clough 2008). This is obviously a limiting shortcoming in some lake applications as the model assumes immediate total mixing of entering loads and lake water.

The calibration of the model is carried out like for other models, that is, by comparing observed values with values simulated by the model. The aim is to achieve as accurate a correspondence as possible by changing only a few parameters. The models use several parameters that have been given initial values. Many of these parameters are fairly universal, however editing is possible in the models.

No material has been published on the functionality of the model in Finnish waters. The model has been successfully applied e.g. in creeks in USA (Rashleigh 2003, Rashleigh *et al.* 2009), in rivers in Asia (Bingli *et al.* 2008), and in reservoirs and in rivers in Europe (Morkoc *et al.* 2008, Sourisseau *et al.* 2008). The model has the advantage of it being applicable with a relatively small amount of initial data. The user interface of the model is very user-friendly, and importing material from e.g. Microsoft Excel is easy.

The AQUATOX-program is free and can be downloaded from the Environmental Protection Agency (EPA) homepage http://www.epa.gov/waterscience/models/aquatox/, where also the manuals for the model are available.

3.2. AQUATOX-application for Lake Pyhäjärvi

3.2.1. Study area

The subject area of my study is Lake Pyhäjärvi (Figure 2), located in the municipalities of Säkylä, Eura and Yläne. Since 1980, the major concerns regarding the state of the lake have been eutrophication and an increase in the occurrence of blue-green algae bloom (Malve *et al.* 1994). Studies on Lake Pyhäjärvi date back quite a while, and the hydrology and water chemistry of the lake have been monitored since 1960's, up until today. Intensive research on nutrients and plankton communities began in 1980 (Malve *et al.* 1994).

Lake Pyhäjärvi is mesotrophic and shallow. The mean depth of the lake is 5.4 m, with the maximum depth of 25 m. The area of the lake, at average water level, is 154 km^2. The lake is undivided and open. The water volume in Lake Pyhäjärvi is 840 million m^3 (Malve *et al.* 1994). The theoretical retention time of the water is 3-5 years (Malve *et al.* 1994, Malve 2007).

Compared with the area of the lake, the catchment area of Lake Pyhäjärvi is relatively small, only 615 km^2. The rivers Pyhäjoki and Yläneenjoki are the major rivers discharging into Lake Pyhäjärvi, along with the Eurajoki flowing out of it. The catchment areas of the Pyhäjoki and the Yläneenjoki together cover 68 % of the entire catchment area of the lake (Malve *et al.* 1994).

In Pyhäjärvi, heavy internal loading occurs, releasing nutrients from the bottom sediments into the water. This is affected, among other factors, by the acidity of the water layer near the bottom, the resuspension caused by waves and currents, as well as the activities of the benthos and the fish (Malve *et al.* 1994, Huttula 1994). Also large spatial heterogeneity exists in the lake which has been confirmed by new remote sensing and spatial in situ-measurements (Lepistö *et al.* 2008).

In my study, I used observation material derived from the sampling station 93va93 (Hertta-database), which is the deepest point at Lake Pyhäjärvi.

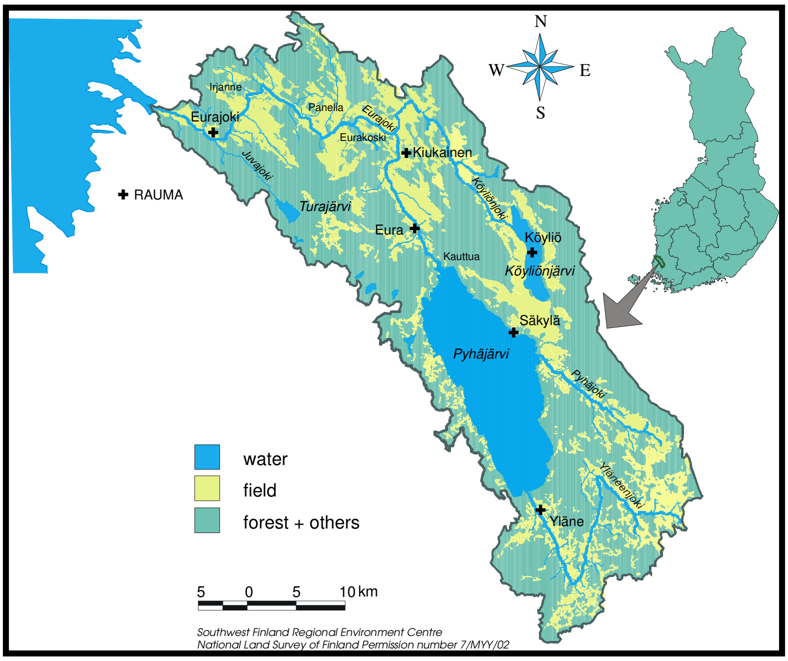

Figure 2. The catchment area of the Lake Pyhäjärvi (Lepistö *et al.* 2008).

3.2.2. Input data and initial values for state and driving variables

The input data and initial data for certain parameters are needed for the simulation run. They have been divided into 19 steps, during which the help “Wizard” of the program directs the user. The data can be entered as constant values or as dynamic time series. Among these 19 steps, there are sections in which the initial values of key variables are entered, for the model to begin the simulation. In the following, I go through all these steps, as well as the initial values and input data for both the constant and dynamic conditions in Pyhäjärvi. The leaching of oxygen has been turned off in both simulations. Rests of the hundreds of the parameters of the model which are included automatically into the simulations are using default values of the model (AQUATOX Release 3 beta). Also the time consumed for building up the application, was estimated.

Step 1: Simulation type

I used simulation type “Lake” for both constant and dynamic conditions.

Step 2: Simulation time period

In the application for the constant and dynamic conditions in Pyhäjärvi, the simulated time-period is 1.1.1992-31.12.2001. I chose the beginning of 1992 as the starting point, because during that year, Pyhäjärvi was extensively studied (Malve *et al.* 1994). I used the data collected in these studies to enter the input values for the model, and also, to gain understanding on the Pyhäjärvi water ecosystem on a more general level. As the simulation time-period, I chose 10 years, as the retention time is approximately 3-5 years (Malve 2007, Malve *et al.* 1994). By a 10 year simulation I made sure that the effect of the initial values was eliminated.

Step 3: Nutrients

I entered initial concentrations for total nitrogen (0.4 mg/l) (Hertta-database), total phosphorus 0.015 mg/l (Hertta-database), carbon dioxide 0.77 mg/l (Dr. Richard Park, EPA, personal communication) and oxygen 6 mg/l (Hertta-database). Ammonium as nitrogen was turned off for both constant and dynamic conditions, because it hardy exists in Lake Pyhäjärvi. A carbon dioxide concentration was used as a default value for the state of equilibrium, in order not to limit the growth of algae (Dr. Richard Park, EPA, personal communication). I took the initial concentration values for nutrients and oxygen from the SYKE's Hertta-database, and they are averages of the first observations in March in the 93va93 of the entire water phase from years 1992-2001. Previous observations for the winter season were not available. The values were the same for both the constant and dynamic simulations.

Step 4. Detritus in sediment bed

Detritus refers to inorganic material, decomposers, bacteria and fungi. In this step, detritus is divided into two categories, and initial values are entered for these:

- Labile detritus (g/m^2, dry)
- Refractory detritus (g/m^2, dry)

As no specific information was available, I determined the amount of detritus in the sediment as zero in both the constant and dynamic simulations.

Step 4. Detritus in water column

I used initial concentration of 0.5 mg/l, which is an estimate of the dry concentration of organic material in Pyhäjärvi. The estimate is based on a 3.5 mg/l concentration of solid matter in Pyhäjärvi, which is an average of the entire water phase during 1992-2001. The solid matter consists of at least two fractions, organic and mineral (Malve *et al.* 1994). The information was gathered from the Hertta-database. In addition to this, I estimated the distribution of detritus in the water column into particulate detritus (20 %) and refractory detritus (50 %) according to the developer of the model (Dr. Richard Park, EPA, personal communication). I used the same values for both the constant and dynamic conditions.

Step 5. Phytoplankton

I chose the species/groups of species shown in the window from the plankton database of the program with their initial values for biomasses, which were based on samples taken in Pyhäjärvi during 1992-2001 (Ventelä *et al.* 2007). I calculated an average for each year and a ten-year average from these, which I used as the initial concentration for the simulation. The concentrations are presented in mg/l in fresh concentration, and to convert these into mg/l dry concentration required by the model, I multiplied the concentration by 0.45 (Reynolds 2006). Converted initial value for diatoms was 0.34 mg/l dry, greens 0.035 mg/l dry, bluegreens 0.198 mg/l dry, dinoflagellate 0.03 mg/l dry and cryptomonad 0.05 mg/l dry. I simulated initial values with spin-up command. AQUATOX saves the end results as initial conditions. This is useful procedure because initial conditions are often unknown. Then the whole simulation will be run without spin-up to get final results. If there is a need to change some value, the simulation needs to run again with spin-up command and then without it. Spin-up is only saving biotic initial conditions. The concentration data used for both the constant and dynamic conditions were the same.

Step 6. Invertebrates

Invertebrate species and initial values for biomasses used in the simulation were estimates based on reference simulations in American lakes, included in the AQUATOX-program (AQUATOX Release 3 beta). I used 0.36 g/m^2 dry for *Chironomid*, 0.2 mg/m^2 dry for *Oligochaete*, 0.007 g/m^2 dry for *Daphnia*, 0.000008 g/m^2 dry for *Cladoceran*, 0.02 $\mu g/m^2$ dry for *Keratella* and 0.4$\mu g/m^2$ dry for the group called predatory Zooplankton. I used the same values for both the constant and dynamic conditions.

Step 7. Fish

Fish species and their initial values for biomasses chosen for the simulation were estimates based on the reference simulations in American lakes included in the AQUATOX-program (AQUATOX Release 3 beta). In simulation I used fish species which are taken from the AQUATOX database. The data abut fish is based on American fish species. I entered initial values for yellow perch 0.0002 mg/l dry, smelt 1.18 mg/l dry, trout 0.0008 mg/l dry, whitefish adult 0.45 mg/l dry, northern pike 0.002 mg/l dry and vendace (< 1 year old) 2.6 x 10 (-18) mg/l dry. I used the same values for both the constant and dynamic conditions.

Step 8. Site characteristics

Site length or reach refers to the distance a wave can travel unhindered and without breaking. In the model, it defines the mixing depth in layered systems and equals the mean depth of the lake. I entered 10 km value for defining the reach. It is based on calibration made using the model, in order to match the simulated mixing depth with the real mean depth of 5.4 m (Malve *et al.* 1994). I used 154 million m^2 for the surface area and the maximum depth of the lake 25 m (Malve *et al.* 1994). The mean evaporation in the simulation I marked as zero, due to the fact that the model assumes the rate of evaporation being constant during the entire simulation period, also during winter, when the lake has an ice cover. I included evaporation in the water volume calculations for the lake (See Step 9). Lake Pyhäjärvi is located on the latitude of 61 ° N. Site characteristic data for both the constant and dynamic conditions were the same.

Step 9. Water volume data

I used an option where water volume is constant in the lake. In this application I used a daily time series of net inflow into the lake, derived from the Watershed Simulation and Forecasting System (WSFS) (Vehviläinen 1994) by the Finnish Environment Institute, in which the input from rivers, the catchment area and rain are included, as well as the loss of water by evaporation. The outflow was not determined, in order to keep the water volume constant. The data for water volume were the same for both the constant and dynamic conditions. I entered 813 million m^3 as an initial value for the water volume. I acquired the initial value for the water volume by multiplying the mean depth by the area of the water body. The water volume data for both constant and dynamic conditions were the same.

Step 10. Water temperature

As the initial value for water temperature I used 1.2 °C, which is an average for temperatures measured from one meter depth in March during 1992-2001 (Hertta-database). For constant conditions, I used a mean temperature of 12 °C for the epilimnion, which is an average of epilimnion temperatures measured in 1992-2001, and a range of 18 °C, which is the mean range between the minimum and maximum temperatures in 1992-2001 (Hertta-database). Corresponding temperatures used for the hypolimnion were 7 °C and 8 °C. The temperatures for the hypolimnion were not based on actual observations in Pyhäjärvi, as those would have been very close to the temperatures of the epilimnion, resulting no stratification in the simulation. In order to include stratification, lower values for the hypolimnion temperatures had to be given. For dynamic conditions, I picked daily values for epilimnion temperature at a measuring depth of 1 m, and for the hypolimnion, at a measuring depth of 20 m (Hertta-database). The view gives the option to determine whether stratification of the lake is included in the simulation or not. I chose the option "Yes".

Step 11. Wind data

In the Pyhäjärvi application, I used a constant value of 3 m/s, which is the average of wind speed values in summer 1992 (Malve *et al.* 1994). I used same speed for both the constant and dynamic conditions. Daily values for ten year simulation period were not available in the Finnish Environment Institute databases.

Step 12. Light data

To simulate the constant conditions, I used an average together with a range, where the calculations are adapted for the latitude initially given for the subject area. The average value I entered was 217 Ly/day and the range 400 Ly/day. Finnish Meteorological Institute measures total radiation and gives the yearly total radiation of 217 Ly/day for Jokioinen observation station, the nearest one to Pyhäjärvi, this being an average during 1971-2000. For the dynamic conditions, I used monthly averages measured in Jokioinen in 1971-2000 (Ilmatieteen laitos). Finnish Meteorological Institute gives total radiation values in units of MJ/m^2. Daily values were not available in the Finnish Environment Institute databases.

Step 13. pH of water

To describe the constant conditions in the Pyhäjärvi application, I used the value of 7.2, which is an average of pH-values measured in Pyhäjärvi during 1992-2001 (Hertta-database). To describe the dynamic conditions, I used a daily time series of 10 years (Hertta-database).

Step 14. Inorganic Solids

I did not include inorganic solids in my simulations.

Step 15. Chemicals

I did not include organic chemicals in my simulations.

Step 16. Inflow loading data

I ignored the ammonium nitrogen and ammonia concentration. To describe the constant conditions, I used the value of 1.7 mg/l (Hertta-database) for the concentration of total nitrogen and total phosphorus 0.085 mg/l (Hertta-database) load from the rivers, which are the averages of total nitrogen and total phosphorus concentrations in the Pyhäjoki and the Yläneenjoki during 1992-2001.

To describe the dynamic conditions, I derived the daily concentrations of total nitrogen and phosphorus in the Pyhäjoki and the Yläneenjoki during 1992-2001 from the Hertta-database. In order to determine the total phosphorus loading (mg) (Appendix 2) and total nitrogen loading (mg) (Appendix 2) from each river separately, I multiplied the concentration measured in the river (mg/l) by the total daily discharge of the river (l). I added the load data for both rivers and divided the result by the combined water volume of the rivers. This gives a concentration value describing the concentration coming from the rivers required for the model called flow-weighted concentration. For carbon dioxide concentration, I used 0.77 mg/l as the constant value, as recommended by the developer of the model (Dr. Richard Park, EPA, personal communication) and for soluble oxygen, a constant value of 11 mg/l, which is an average of oxygen concentrations in the Pyhäjoki and the Yläneenjoki during 1992-2001. As the constant value for dissolved and insoluble detritus, I used estimation 10 mg/l in dry concentration, which is 50 % smaller than the average of solid material from the rivers during 1992-2001 according to the Hertta-database.

I used the seed value 0.0005 mg/l dry (Park *et al.* 2004) for all organisms chosen for the simulation (see steps 5, 6 and 7). If the information of the concentrations of organisms is not available, the manual recommends using this value. I used this value in both constant and dynamic conditions.

Step 17. Direct precipitation loading

In the simulations, I concentrated on the loading from the rivers and from non point loading, which is why I omitted precipitation loading from the calculations. In 1980-1991, the portion of precipitation loading of the total loading in Pyhäjärvi was 28 % regarding nitrogen, and 21 % regarding phosphorus (Malve *et al.* 1994).

Step 18. Point source loading

In my simulations, I ignored point source loading, as no such sources exist on the shores of Pyhäjärvi.

Step 19. Nonpoint source loading

I ignored the loads of ammonium nitrogen, ammonia, and soluble oxygen. I used as a constant value for total phosphorus load of 1600 g/d and total nitrogen load of 140 kg/d (Salmela *et al.* 1997, Kirkkala & Ventelä 2009) for both the constant and dynamic simulations. The loads are monthly averages from 1992-2000. As a constant value for the dissolved and insoluble detritus load, I used the 1992 solid material load from the catchment area, 3013 kg/d (Malve *et al.* 1994), assuming that 75 % of it, 2262 kg/d, consists of organic material, which is the value I used for the simulations.

3.2.3 Model verification

Model verification is used to test the correspondence between concentrations simulated by the model and the actual concentrations observed. Verification can be used to evaluate how well the model is suited for simulating the desired subject and how reliable results can be achieved (Kettunen 1986). The numerical verification method used in this study was the Nash-Sutcliff efficiency coefficient R^2 (Nash & Sutcliffe 1970). Nash-Sutcliff efficiency coefficient is much used in hydrological and catchment scale models as a criterion of fitness of simulated and observed values (Metsäranta 2003, Moriasi *et al.* 2007). In addition to this, an important and primary method for evaluating the efficiency of the model is visual estimation, although it lacks scientific validity. It is used to provide an opinion whether using the model is viable.

The Nash-Sutcliff efficiency coefficient is defined as follows:

X_{obs} = observed value at certain time

X_{sim} = simulated value at certain time

$\overline{X}_{obs}$ = mean value of observed values

Nash–Sutcliffe efficiencies can range from $-\infty$ to 1. An efficiency of 1 ($R^2 = 1$) corresponds to a perfect match of simulated data to the observed data. An efficiency of 0 ($R^2 = 0$) indicates that the model predictions are as accurate as the mean of the observed data. If an efficiency is less than zero ($R^2 < 0$) it occurs when the observed mean is a better predictor than the model or, in other words, when the residual variance (described by the nominator in the expression above), is larger than the data variance (described by the denominator).

The observed concentrations of total nitrogen and –phosphorus in the epilimnion and the hypolimnion used in verification were chosen by two methods. The concentration observations for the epilimnion were derived at the depth of 1 m, and for the hypolimnion, at 20 m (Hertta-database). In addition to this, I used a method of depth-weighted averages, in which concentrations observed in the epilimnion were proportioned to the volume of the epilimnion, as well as for the hypolimnion correspondingly (Hertta-database). I used the efficiency coefficient to compare the differences between constant and dynamic condition simulations. I also used it to evaluate how well the simulated concentrations correspond to observed concentrations.

4. RESULTS

4.1. Constant condition simulation of nutrients and chlorophyll-a

The Nash-Sutcliff efficiency coefficient for total phosphorus concentrations in constant condition is less than zero. The simulated concentrations corresponded only slightly better to observations in the epilimnion at the depth of 1 m (Figure 3) than to depth-weighted mean concentrations (Figure 4). Simulated concentrations of total phosphorus in the hypolimnion corresponded better to concentration observations in the depth of 20 m (Figure 5) than to depth-weighted mean concentrations (Figure 6). Simulated concentrations in the epilimnion did not coincide well in time with the observed concentrations. In the hypolimnion, the situation was opposite (Figure 5 and 6). Observed peak concentrations correspond to simulated peak concentrations very well according time.

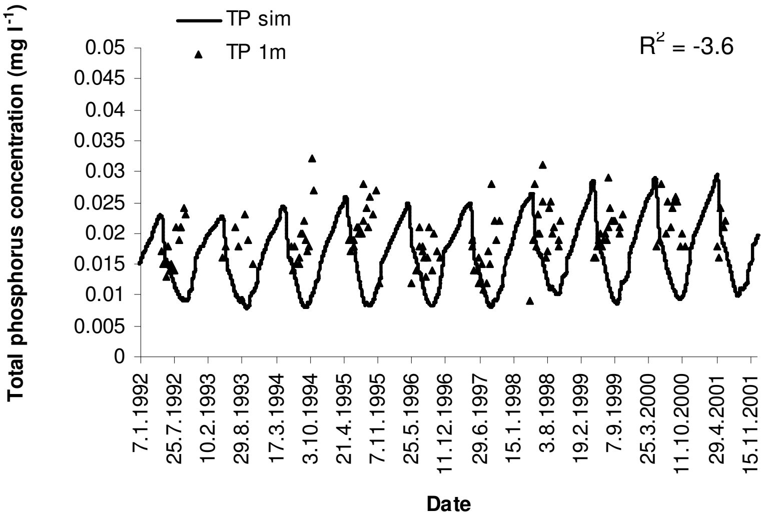

Figure 3. Simulated and observed (depth of 1 m) total phosphorus concentrations at epilimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

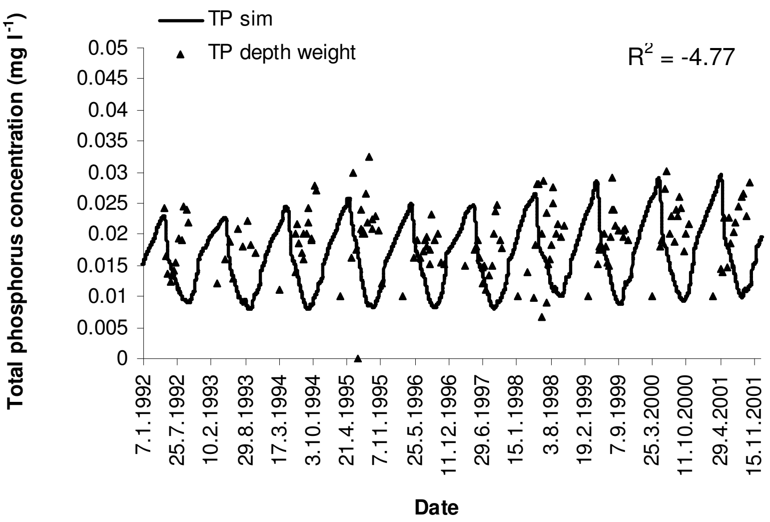

Figure 4. Simulated and observed (depth weighted) total phosphorus concentrations at epilimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

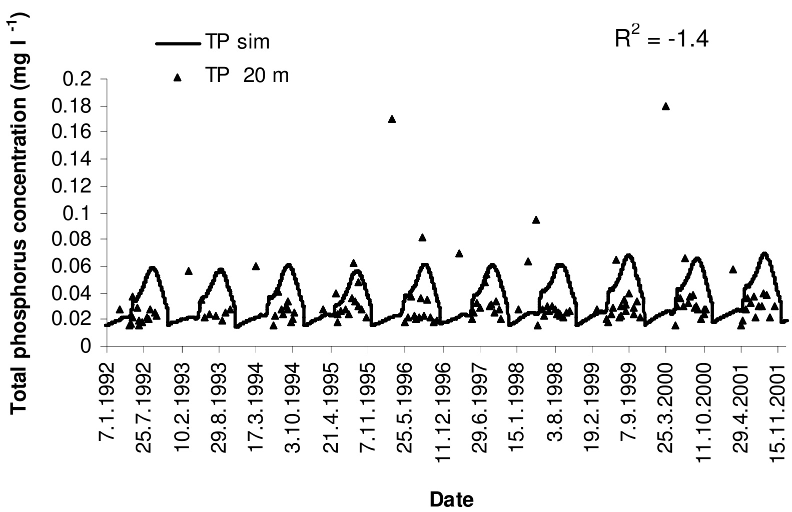

Figure 5. Simulated and observed (depth of 20 m) total phosphorus concentrations at hypolimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

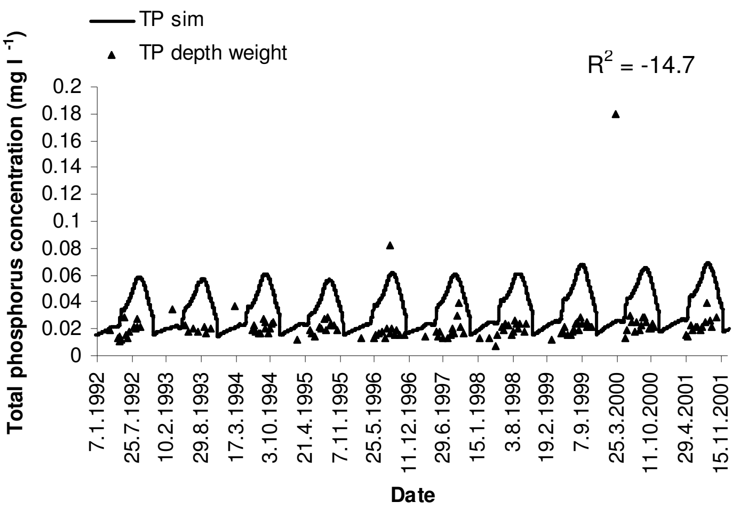

Figure 6. Simulated and observed (depth weighted) total phosphorus concentrations at hypolimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

Simulated concentrations of total nitrogen in the epilimnion corresponded slightly worse to concentrations observed at 1 m depth (Figure 7) than to depth-weighted mean concentrations (Figure 8). In the hypolimnion, the situation was opposite. Simulated concentrations of total nitrogen corresponded better to the observed concentrations at 20 m (Figure 9) than to depth-weighted mean concentrations (Figure 10). Correspondence was pretty good according to R^2 which was 0.7.

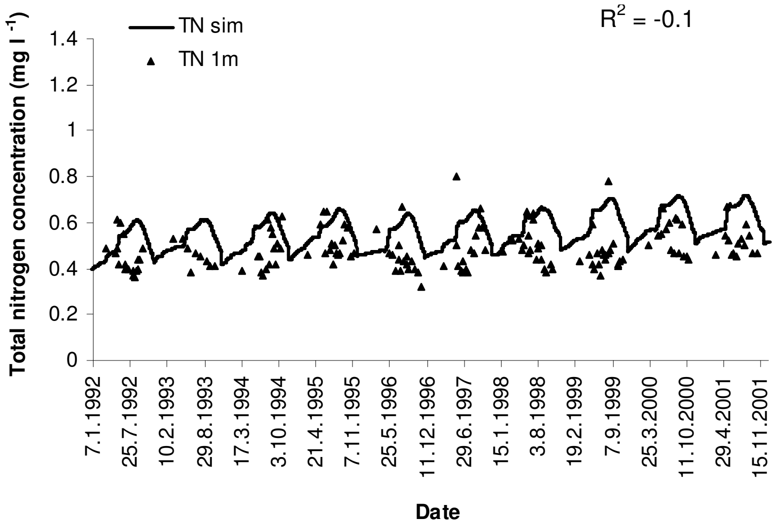

Figure 7. Simulated and observed (depth of 1 m) total nitrogen concentrations at epilimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

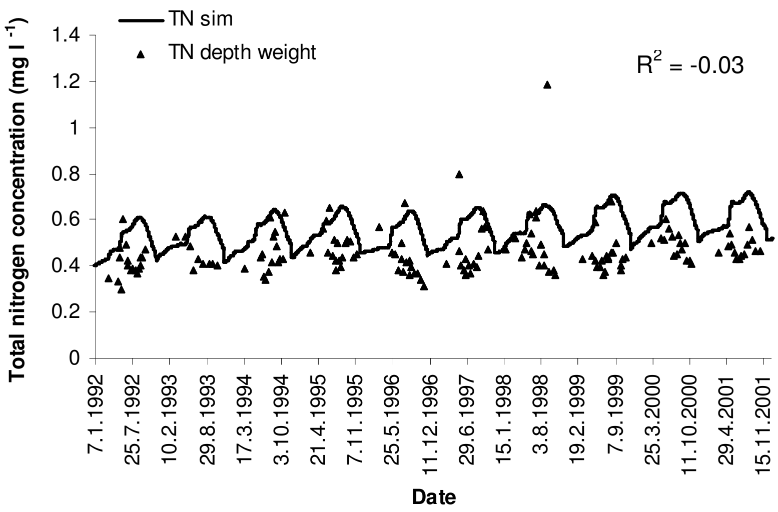

Figure 8. Simulated and observed (depth weighted) total nitrogen concentrations at epilimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

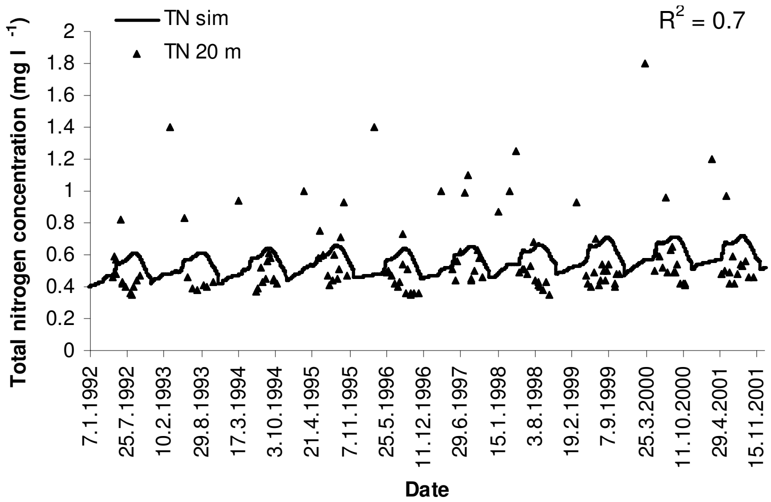

Figure 9. Simulated and observed (depth of 20 m) total nitrogen concentrations at hypolimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

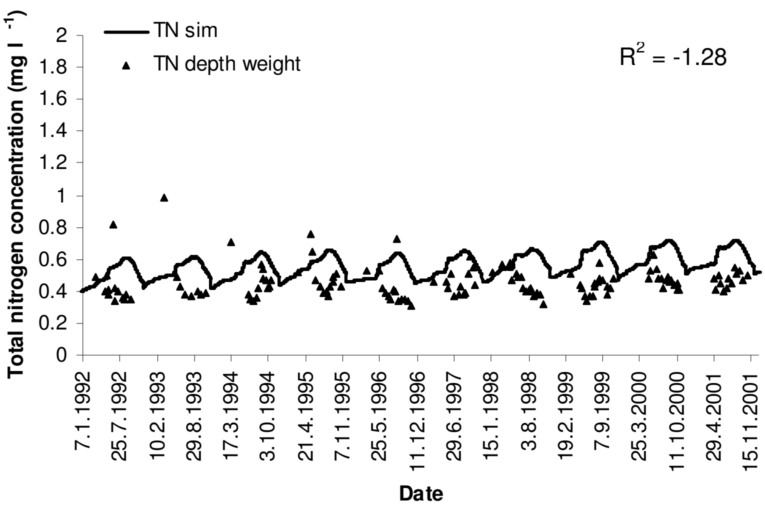

Figure 10. Simulated and observed (depth weighted) total nitrogen concentrations at hypolimnion in constant conditions and Nash-Sutcliffe efficiency coefficient.

In constant conditions, simulated concentrations of chlorophyll-a did not correspond very well to observed concentrations according to efficiency coefficient (R^2 = - 0.95). Simulated concentration peaks however appeared 1 to 4 months earlier than the observed concentrations, depending on the year. According to the simulation, the highest concentrations occurred yearly at the end of May (Figure 11).

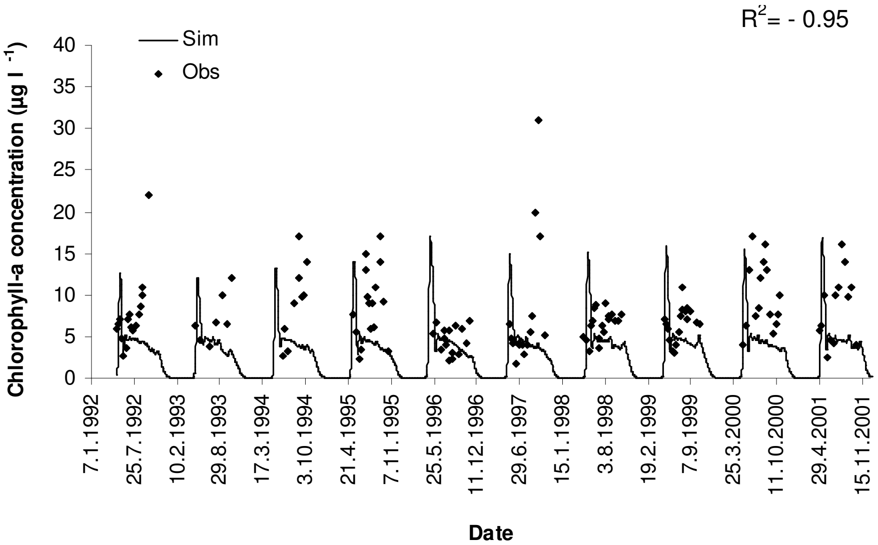

Figure 11. Simulated and observed chlorophyll-a concentration in a constant condition.

4.2. Dynamic condition simulation of nutrients and chlorophyll-a

The efficiency coefficient for total phosphorus shows that in the epilimnion, simulated concentrations corresponded better to observations at 1 m depth (Figure 12) than to depth-weighted averages (Figure 13). In the hypolimnion, the situation is similar; simulated concentrations corresponded to observed concentrations at 20 m depth (Figure

14) better than to depth-weighted averages (Figure 15). Simulated concentration peaks grew almost to double compared with observed concentrations in both the epilimnion and the hypolimnion. This is expressed by the large negative R^2-figures. Simulated concentrations did not follow the observed temporal dynamic of concentrations in either water layer very well.

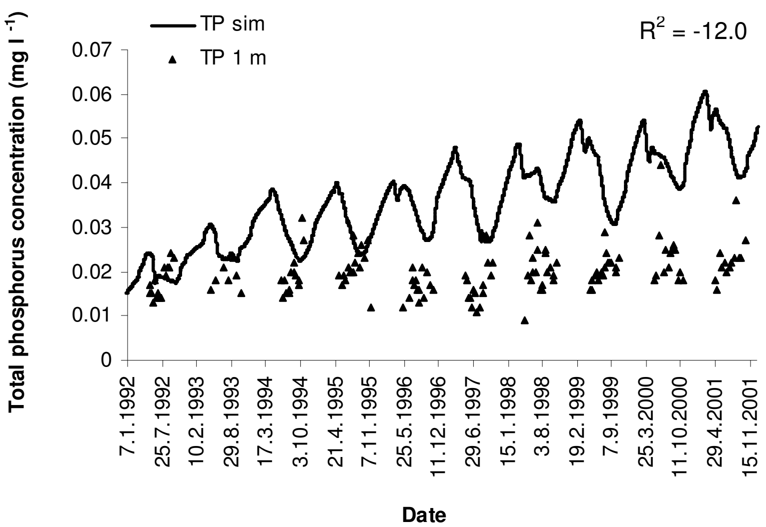

Figure 12. Simulated and observed (depth of 1 m) total phosphorus concentrations at epilimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

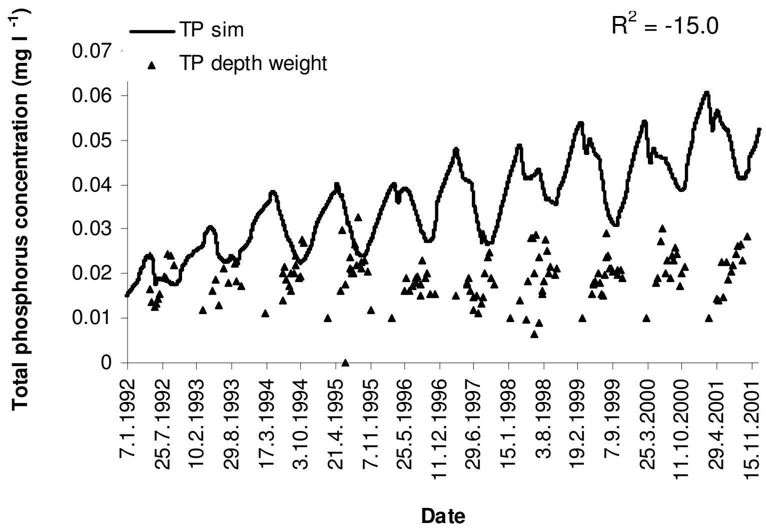

Figure 13. Simulated and observed (depth weighted) total phosphorus concentrations at epilimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

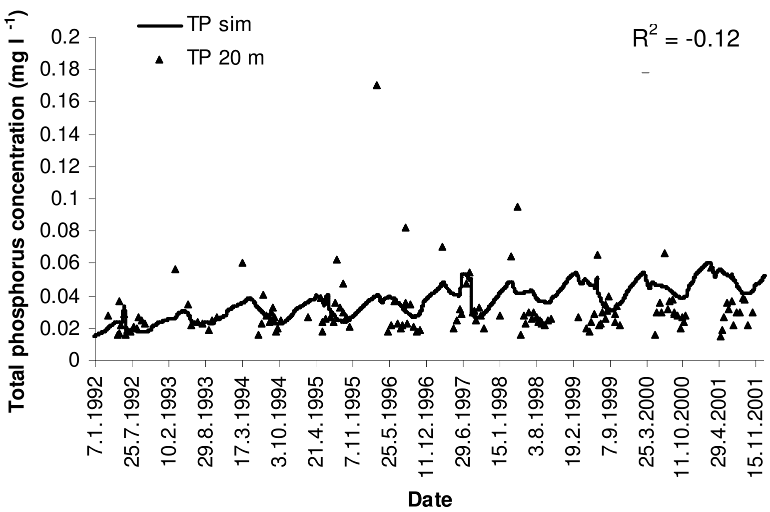

Figure 14. Simulated and observed (depth of 20 m) total phosphorus concentrations at hypolimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

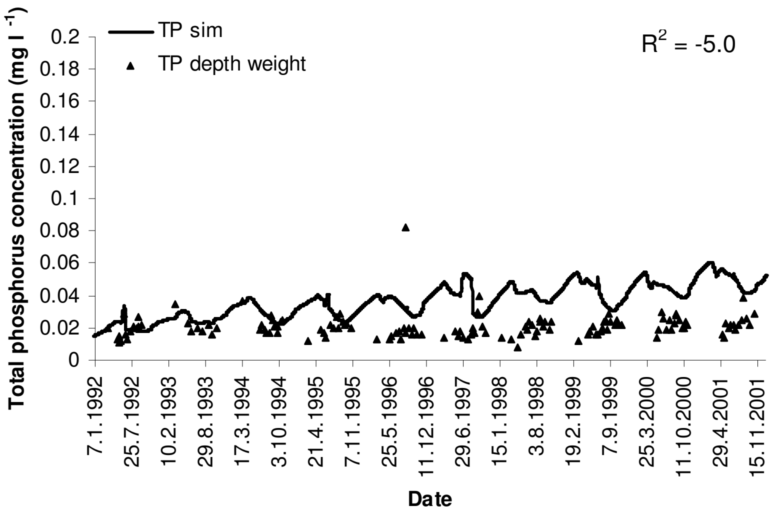

Figure 15. Simulated and observed (depth weighted) total phosphorus concentrations at hypolimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

Simulated concentration of total nitrogen in the epilimnion, according to the efficiency coefficient, corresponded better to depth-weighted mean concentrations (Figure 17) than to observed concentrations at the depth of 1 m (Figure 16). In the hypolimnion the situation was opposite. Simulated concentrations corresponded better to concentrations observed at 20 m (Figure 18) than to depth-weighted mean concentrations (Figure 19). At the end of the 10-year period, simulated concentrations of total nitrogen grew almost double compared with observed concentrations in both the epilimnion and the hypolimnion. The simulated concentrations corresponded however relatively well with annual temporal dynamics of observed concentrations.

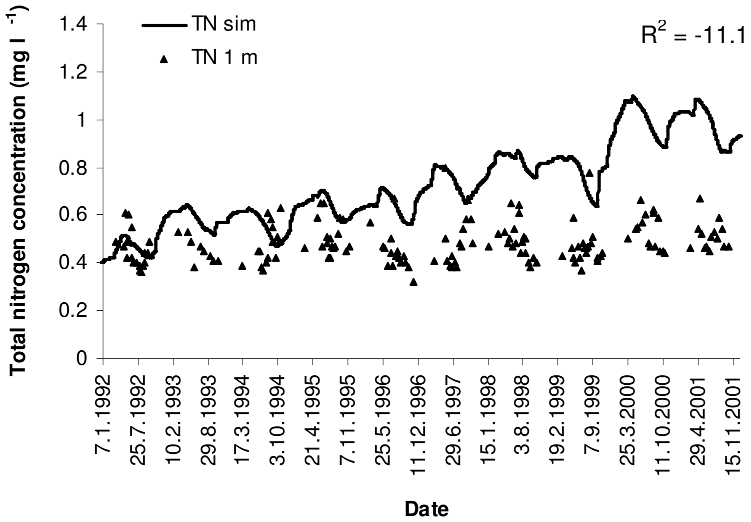

Figure 16. Simulated and observed (depth of 1 m) total nitrogen concentrations at epilimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

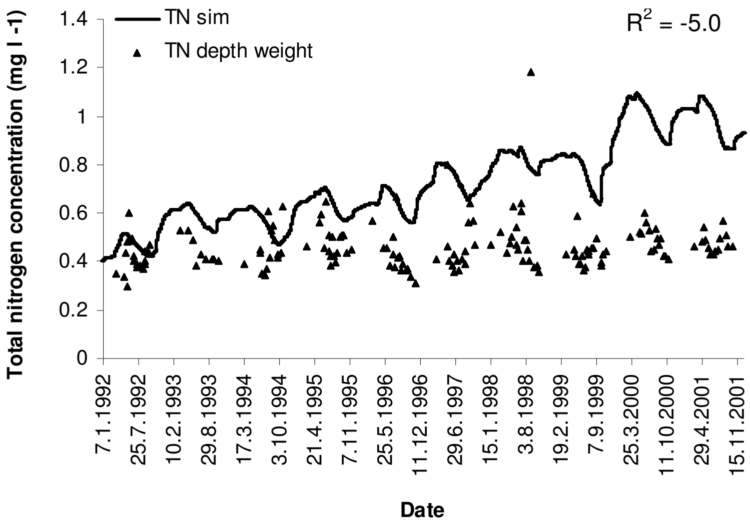

Figure 17. Simulated and observed (depth weighted) total nitrogen concentrations at epilimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

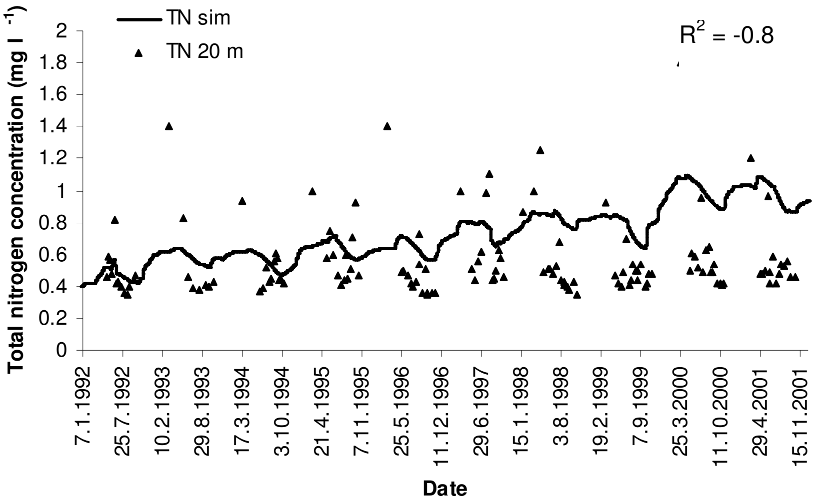

Figure 18. Simulated and observed (depth of 20 m) total nitrogen concentrations at hypolimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

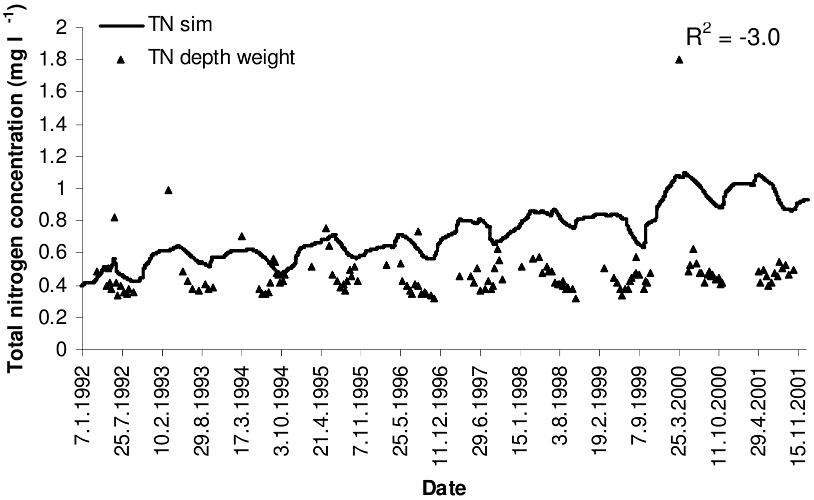

Figure 19. Simulated and observed (depth weighted) total nitrogen concentrations at hypolimnion in dynamic conditions and Nash-Sutcliffe efficiency coefficient.

According to the efficiency coefficient in dynamic conditions, the simulated and observed concentrations of chlorophyll-a corresponded poorly to each other. The magnitude of the simulated concentrations equaled with that of the observed concentrations in 1992-1995, but after that, simulated concentration peaks grew very high, 2-3 times the observed concentrations. Simulated conditions in 1996 – 2001 produced two concentration peaks. First was at the end of March and the second at the end of June and the beginning of July, the latter of which corresponded to observed concentration peaks in time (Figure 20).

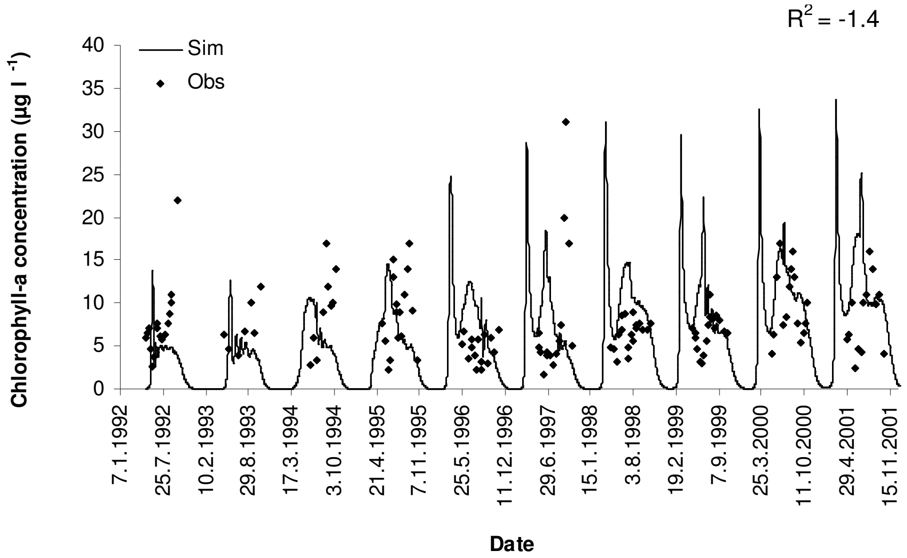

Figure 20. Simulated and observed chlorophyll-a concentration in a dynamic condition.

5. DISCUSSION

5.1. AQUATOX-simulations

The Nash-Sutcliffe efficiency coefficient was negative in both constant and dynamic conditions for total phosphorus and total nitrogen. The efficiency coefficient was 0.9 in constant condition for chlorophyll-a, but negative in dynamic condition. According to efficiency coefficient the simulation of constant conditions corresponded slightly better observed concentrations than simulation of dynamic conditions. In the simulation of the dynamic conditions, concentrations of total phosphorus and –nitrogen grow cumulatively almost to double during the 10 year analysis period. This cannot be attributed to resuspension caused by wind, as the model does not assume it taking place in lakes with a mean depth of more than 1 m. Also remineralization must be excluded, as parameters directing it were the same also in constant conditions, where no similar growth of concentrations could be seen. In the simulations, the hypolimnion remains oxic therefore this neither can cause the release of nutrients from the sediment into the water phase. In reality, the 93va93, according to water samples taken in March in 1992-2001, is anoxic (Hertta-database). The reason may lie in concentration peaks occasionally occurring in phosphorus and nitrogen loads (Appendix 2), which may cause an increase in lake water concentrations. Generally, simulated concentrations of total phosphorus in both the constant and dynamic conditions were altogether higher than observed concentrations. Annual fishing removes approximately a quarter of total phosphorus from Pyhäjärvi (Sarvala & Jumppanen 1988, Ekholm 1998, Sarvala *et al.* 2000), which may partly explain the high simulated total phosphorus concentration in the water phase near the bottom. In this study, loading from atmosphere was ignored. The role of atmosphere loading is relatively large in the Pyhäjärvi case, for nitrogen, about 30 %, and for phosphorus, about 20 % of total loading (Malve *et al.* 1994). In constant conditions, the simulated concentration of total nitrogen in the hypolimnion corresponds better to observed concentrations than that of total phosphorus. This can also be due to the fact that by fishing (an operation ignored in the AQUATOX), only a few percents of the nitrogen loading entering Pyhäjärvi is removed, while for phosphorus, this amount is significantly larger (Sarvala & Jumppanen 1988).

Simulated nutrient concentrations in the epilimnion and the hypolimnion corresponded better to observed values at 1 m and 20 m than to depth-weighted averages. Reasons for this might be in the sampling accuracy of observed samples and also the large spatial heterogeneity (Lepistö *et al.* 2008) of the lake. The time lag in the observed concentrations compared to simulations might have been caused by slow nutrient transport from the main river mouths to the observation site where as in the model the incoming waters and nutrients are immediately mixed in the whole lake. Observation site 93va93 as a subject area does not represent the whole lake, which is otherwise rather shallow. In reality, the stratification of the lake also varies greatly. Water mixing can occur several times during the open water season, which can be seen in water quality results derived from the Hertta-database. The heavy internal loading and resuspension in the lake, together with the previously mentioned factors, make Pyhäjärvi a very dynamic lake and a challenging subject for simulation.

Examining chlorophyll-a with efficiency coefficient, the simulated and observed concentrations are slightly better in the simulation of the constant conditions than in the dynamic conditions. I assume that the reason for poor correspondence especially in dynamic condition is that nutrient load from rivers is changing every day. AQUATOX assumes that nutrients are immediately mixing in the water and respond can be seen in chlorophyll- a concentrations. For example during 1996 – 2001, the dynamic condition simulation produced two clear concentration peaks, the later of which matched well with observed chlorophyll-a concentrations. The first simulated concentration peak may have been caused by an increase in the amount of phytoplankton such as the diatom, which typically occurs in the spring and benefits from the nutrient load peaks. The initial values I entered for the phytoplankton may also have been too rough generalizations to describe the initial concentration. In the AQUATOX-model, phytoplankton is one of the key factors in simulating nutrient concentrations. Simulating phytoplankton has indeed proved to be a most challenging task (Bilaletdin *et al.* 1993).

In reality, nutrient particles bound to particles in Pyhäjärvi, are sinking to the bottom of the lake and are easily resuspended several times before final sedimentation (Huttula 1994). The lake withholds more than 80 % of the external loading. According to the mass-balance calculations, external loading regulates the mean annual nutrient concentration in Pyhäjärvi only partially. Annual variation in nutrient concentrations correlates only lightly with external loading. Pyhäjärvi can be regarded as a lake with heavy internal loading, with the assumption that biological factors such as fish, algae and zooplankton affect the annual nutrient variation (Ekholm *et al.* 1997).

In my work in Ramboll Ltd, I applied the AQUATOX to Kollaja of the Iijoki River (Anon. 2009), simulating concentrations of total nitrogen and –phosphorus. After calibration, the nutrient concentrations corresponded very well to observed concentrations. In the application, I ignored phytoplankton, fish, macrophytes and invertebrate. According to my experience, simulated concentrations fitted better to observed concentrations in River Iijoki than in Lake Pyhäjärvi. The one main reason might be that I did not calibrate the Pyhäjärvi application at all but for Kollaja I did with the fraction of phosphate loading that is available versus that which is tied up in minerals. In France it was simulated biomass dynamics of various biological compartments with AQUATOX (Soursisseau *et al.* 2008). Calibrated model was able to adequately describe the dynamics. Phytoplankton and nutrients were simulated in the Omerli reservoir in Turkey (Morkoc *et al.* 2008). Blue greens biomasses corresponded quite well to seasonal changes and simulation was successful in reconstructing ammonia. In North Carolina Contentnea Creek was simulated to determine the response of fish to moderate levels of physical and chemical habitat alterations (Rashleigh 2003). Conclusion about simulation was that AQUATOX utility should be determined further in other study areas and ecoregions. Most important reason for successful simulations seems to be the model calibration.

5.2. Conclusion

There is a variety of different tools and models to help evaluating environmental impacts in water bodies available. In order to serve the user reliably, the tools must be tested in the environment they will be used in. Versatility in describing an entire water ecosystem, as well as the possibility to evaluate changes caused by various factors, can be seen as the strengths of the AQUATOX-model presented in this work.

Based on the results simulated for Pyhäjärvi, the AQUATOX describes relatively well the magnitude of nutrients and chlorophyll-a concentration in constant conditions even the Nash-Sutcliffe efficiency coefficient was mostly negative. Temporal dynamics leaves room for improvement because simulated temporal dynamics does not match with observed one.

More thorough consideration of biological factors in AQUATOX-simulations would be important in future studies. Especially in Pyhäjärvi simulation phosphorus removed by fishing and also the role of atmospheric loading should be included in the study. Besides these the daily load from non point source should be entered into the model. The accuracy of sampling of the observed samples must be taken into account, when evaluating the results of the simulation. Spatial heterogeneity of the Pyhäjärvi should be noted when interpreting the results. It might be useful to use observed concentrations of other site of Lake Pyhäjärvi beside 93va93 concentrations. The calibration of the model should be carried out. For future modeling work for Lake Pyhäjärvi, 3D-models are recommended. Lake heterogeneity is so high that such box-model like AQUATOX can not well enough interpret changes in water phase.

According to this study, AQUATOX is recommending to use in impact assessment work to have rough estimations of the magnitude of nutrient concentrations. In the model the lake system is quite complex like in reality and parameters are many. This tool is challenging for beginner. The model user needs to have good understanding of functions of water ecosystem. The building up the Pyhäjärvi application together with the familiarization of the model took approximately 3 - 4 months. It should be noted that the model has not been tested widely enough in Finnish water bodies or validated with independent material.

ACKNOWLEDGEMENTS

I have reached this far with the help and comments by numerous people. I wouldn’t mind continuing the journey, but this is a good place to end this stage. Special and biggest thanks belong to my instructor Timo Huttula, who endowed me with the AQUATOX-model, which to start with appeared to me as a Rubik’s Cube entirely mixed, but in which the pieces slowly started to find their place. I guess Alice did indeed visit Wonderland. A big thank you belongs also to the developer of the model, Richard Park, who helped me understand the “psyche” of the model, and also to the EPA, for enabling Park’s assistance with the model. I would also like to extend my sincere thanks to Ramboll Finland Ltd for making this all possible, and also to my other instructor, Veli-Matti Hilla, who was willing to adopt a Thesis-writing student fumbling with a Rubik's Cube. Several people in the Finnish Environment Institute helped me along. A warm thank for help! And then Heikki, Lauri and Vilja. This would never have been possible to start with without your unselfish support. Thank you.

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APPENDIX 1.

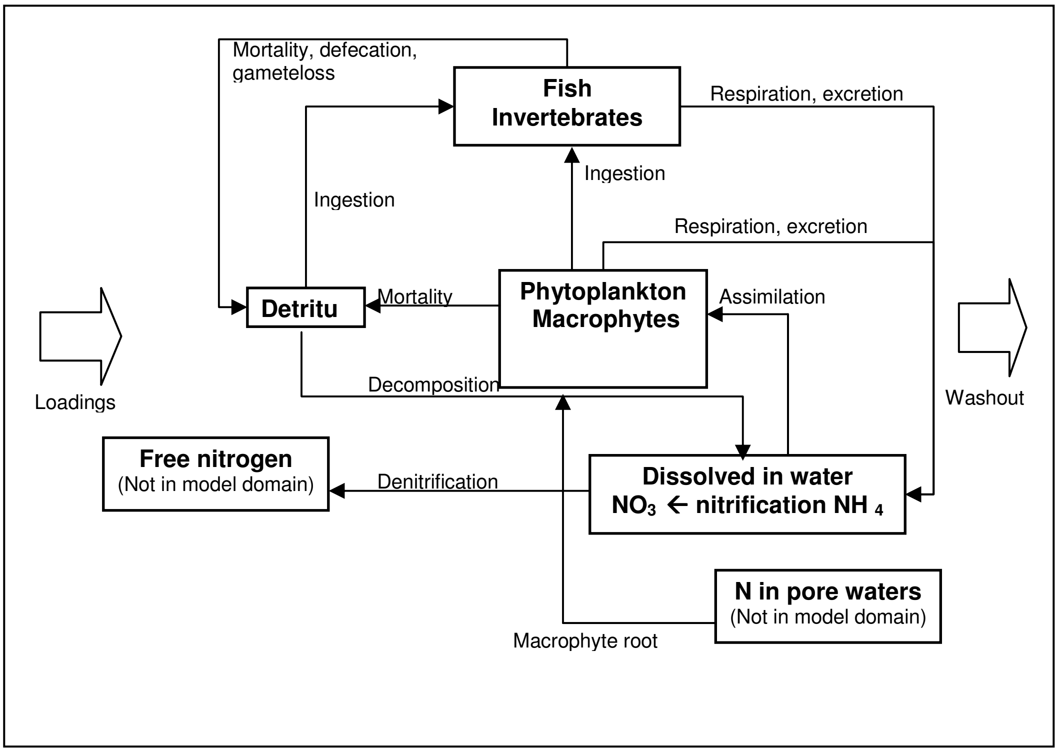

Figure 1. Nitrogen cycle in AQUATOX (Park & Clough 2008).

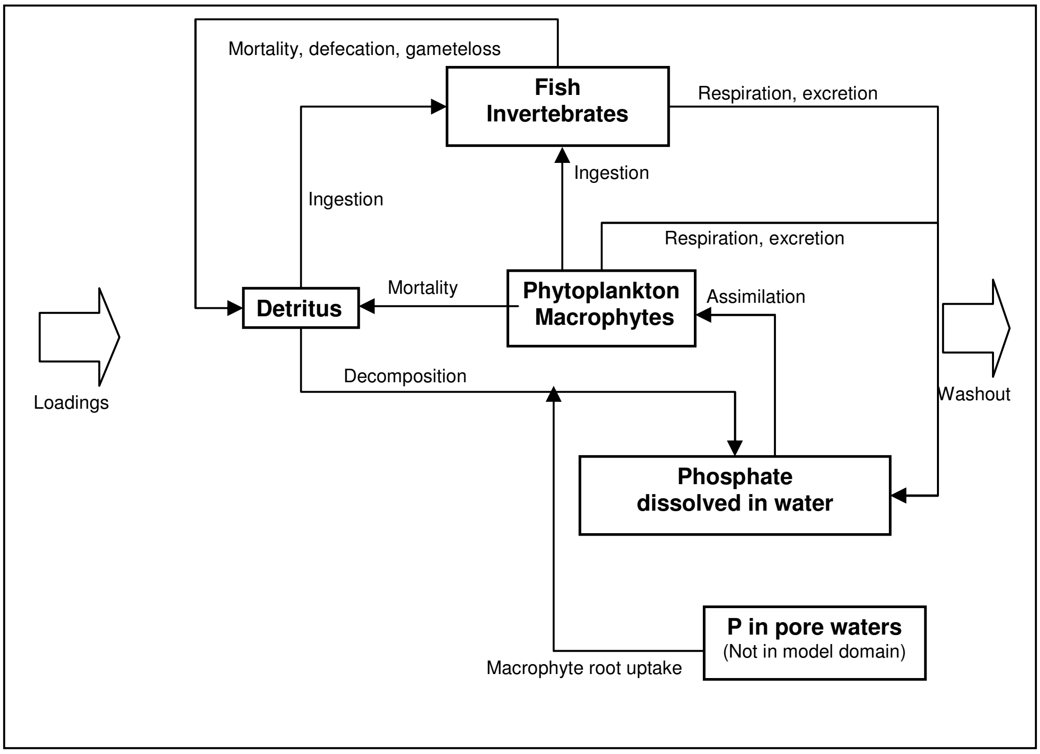

Figure 2. Phosphorus cycle in AQUATOX (Park & Clough 2008).

APPENDIX 2.

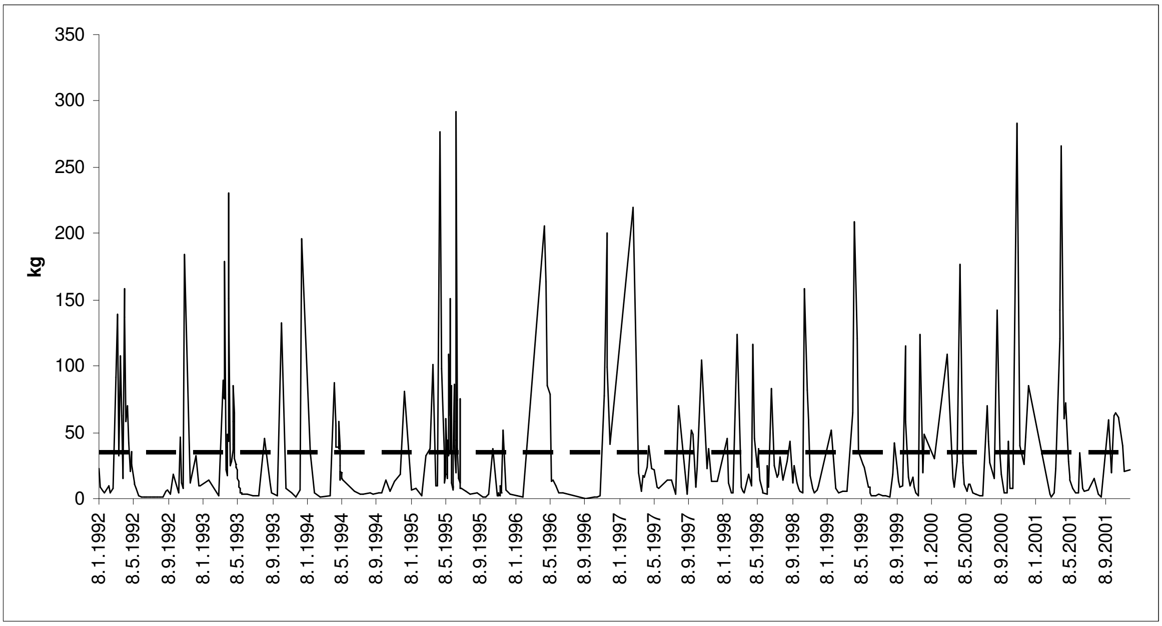

Figure 1. Total phosphorus load from river Ylänejoki and Pyhäjoki to lake Pyhäjärvi. Broken line describes the mean load used in constant conditions and solid line the observed load used in dynamic conditions.

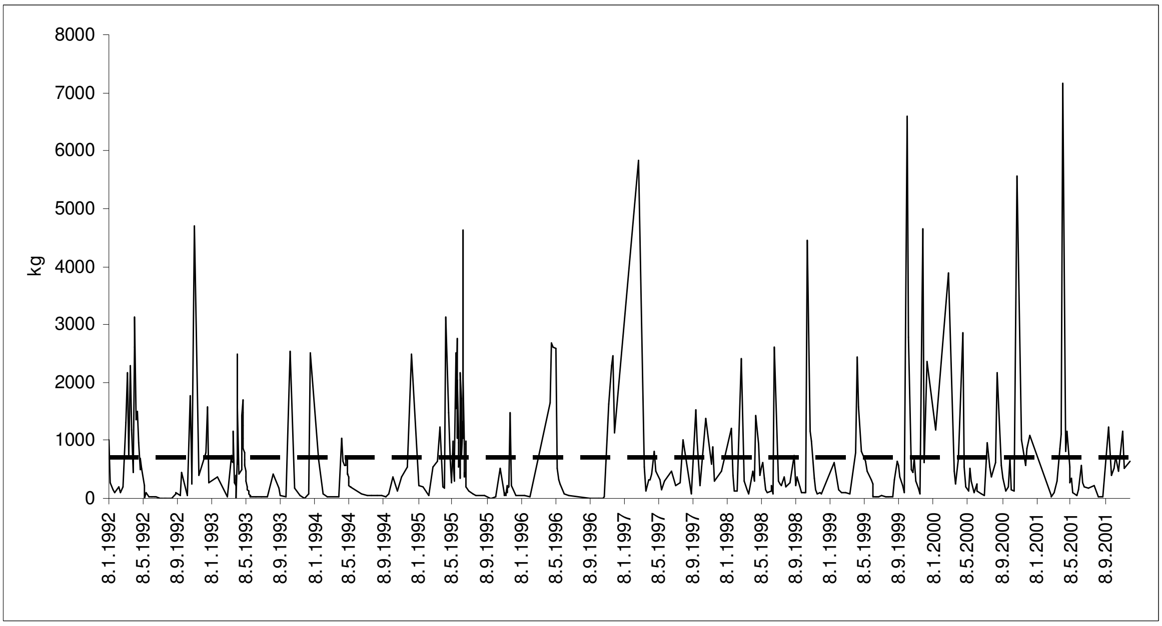

Figure 2. Total nitrogen load from river Ylänejoki and Pyhäjoki to lake Pyhäjärvi. Broken line describes the mean load used in constant conditions and solid line the observed load used in dynamic conditions.