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System-Wide Water Resources Program

Development of a Distributed Nutrient Sub-Model (NSM Version 1.0) for Watersheds – Kinetic Process Descriptions

Billy Johnson and Terry Gerald   November 2006

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Environmental Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

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Abstract: Within the System-Wide Water Resources Program (SWWRP), multiple riverine, estuarine, watershed, and subsurface flow models are being modified to address issues of environmental concern. Several integration approaches are either ongoing or proposed to accomplish this task. To have a full system-wide water quality and contaminant capability in SWWRP, the different hydrologic and hydraulic engines must utilize a common water quality and contaminant approach to prevent the arbitrary partitioning of constituents. The goal of this development effort has been to upgrade existing hydrologic and hydraulic models (i.e., water engines) using a common water quality approach in order to facilitate their linkage and application on a system-wide basis.

In keeping with a common water quality approach to model development, a library of water quality kinetics has been developed such that these kinetics can be integrated with a variety of water transport engines. The library of algorithms are able to deal with a multi-species, multi-phase, multi-reaction system, should include both fast (equilibrium-based) and slow (non-equilibrium-based or rate-based) reactions, are easily extensible to new reaction pathways, include both common nutrient and contaminant packages as well as geochemistry, and have a simple, well-defined data interface and calling procedure, making them portable. The modules are developed such that they are data structure independent thus facilitating their integration into a wide range of modeling systems.

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Preface

This report summarizes the development of overland and channel nutrient kinetic modules for linkage with a variety of hydraulic and hydrologic modeling systems. This development effort was performed by the Engineer Research and Development Center (ERDC), Waterways Experiment Station, Vicksburg, Mississippi. Funding was provided under the System-Wide Water Resources Program (SWWRP). Dr. Steven L. Ashby is the program manager for SWWRP. Appreciation is extended to all who assisted in the formulations and review of the kinetics implemented within the nutrient sub-modules (NSM).

Principal Investigators for this study were Dr. Billy E. Johnson of the Water Quality and Contaminant Modeling Branch (WQCMB) and Terry K. Gerald of SpecPro Inc. Mr. Gerald was funded as an onsite contractor under Task Order Contract W912HZ-05-D-0011 on Civil Delivery Order No. 15. Dr. Johnson conducted his portion of the study under the general supervision of Dr. Barry W. Bunch, Chief of WQCMB, and under the general supervision of Dr. Richard E. Price, Chief EPED, and Dr. Beth C. Fleming, Director of EL.

COL. Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

Summary

Nutrient Sub-Model (NSM) version 1.0 consists of Overland and Channel Nutrient Kinetics. These kinetics were initially taken from SWAT formulations; however, modifications were made in an effort to enhance their linkage with USACE hydraulic and hydrologic water engines.

The overland module simulates the nitrogen and phosphorus nutrient cycles with algorithms available for initializing soil concentrations if observed data are not available. The channel module simulates nitrogen and phosphorus in addition to accounting for algal growth, carbonaceous biological oxygen demand, and dissolved oxygen.

Initial integration is currently taking place with the Gridded Surface Sub-surface Hydrologic Analysis (GSSHA) model and the Hydrologic Engineer Center River Analysis System (HEC-RAS) model. GSSHA is a physically based distributed watershed model that will take advantage of all the NSM capabilities. HEC-RAS is a 1-D stream model that will only use the channel kinetic capabilities of NSM.

Future versions of NSM will include: 1) a carbon cycle; 2) plant/soil dynamics; and 3) updated channel kinetics. As these new features are implemented, an updated reference manual will be created and integration into various H&H modeling systems will be done. In addition, as field studies and new understandings of the nutrient and water quality processes are performed and discovered, modifications to the NSM algorithms will take place and be propagated to the appropriate modeling systems. The common framework approach taken in this development effort will ensure that the latest nutrient process descriptions are implemented into the USACE modeling systems in the most efficient manner.

1   Introduction

Background

The concept of watershed planning is not new to the U.S. Army Corps of Engineers. Throughout its history, the Corps has incorporated watershed planning into the process by which it manages water resource systems. Even the Corps' geographic organization, along watershed boundaries rather than State and county lines in most cases, supports the historic understanding of the need to manage water within a watershed context. However, this understanding and organizational concept alone are not sufficient to ensure proper protection and responsible development of the Nation's water resources in the future.

This country is facing a looming water crisis. It is seeing frequent regional droughts, disputes over allocation brought on by growing population demands, environmental degradation due to changing land uses, and widespread disagreement over competing purposes for water resources use. The problems of rapid growth in certain areas are worse because responsibilities to address water needs are distributed among a multitude of government agencies and private companies, so the problem-solving efforts are typically fragmented. The results are predictable: instead of broadly supported regional solutions that address multiple needs, balance competing uses, and can be quickly implemented, solutions are narrowly focused, contentious and slowly implemented, uncertain, expensive, and inferior. For several years, the Nation's priorities and values related to water resources have been changing. This is a natural evolution resulting from advances in scientific knowledge, public reaction to that increase in knowledge, and an unprecedented national prosperity that allows us to consider more than the short-term basics of life.

In the summer and fall of 2000, the Corps of Engineers held a series of 16 "listening sessions" around the Nation to hear what Americans thought were the major water challenges for the 21st Century. The participants provided valuable input for Federal involvement that would best help various levels of government face these challenges. One of the frequently raised topics was the need to address water challenges from a watershed view, highlighting collaboration and integration. Some present-day watershed management efforts, such as the Comprehensive Everglades

Restoration Plan, already promote active participation of all interested parties in the planning and decision-making process. The Corps believes that this concept of integration is the key to reforming America's water development, protection, and restoration. In its recently released *Watershed Perspective for the Civil Works Program*, the Corps describes the foundation for watershed activities and involvement. The nine Watershed Principles outlined there provide the approach the Corps seeks to follow in its water resource management.

- Seeking sustainable water resources management.
- Integrating water and related land management.
- Considering future water demands.
- Coordinating planning and management.
- Promoting cooperation among government agencies at all levels.
- Encouraging public participation.
- Evaluating monetary and non-monetary tradeoffs.
- Establishing interdisciplinary teams.
- Applying adaptive management as changing conditions or objectives warrant.

Unlike the single-purpose, project-driven initiatives that the Corps has been directed to accomplish in the past, the perspective of this new watershed approach is based on multi-purpose, multi-objective management, examining all water needs in the watershed and receiving water bodies. With this broader context, watershed partners would collaborate to simultaneously address multiple objectives - environmental quality, social effects, and national and regional economic development.

In support of the Corps' watershed approach, the System-Wide Water Resources Program (SWWRP) was designed to assemble and integrate the diverse components of water resources management. Products from this program are designed to help users surpass individual project level analysis, and apply current and improved technologies for multi-disciplinary system-wide assessments. The ultimate goal of SWWRP is to provide the Corps, its partners, and stakeholders with the overall technological framework and analytical tools to restore and manage water resources and balance human development activities with natural system requirements.

Within SWWRP, multiple riverine, estuarine, watershed, and subsurface flow models are being modified to address issues of environmental concern. Several integration approaches are either ongoing or proposed to accomplish this task. To have a full system-wide water quality and contaminant capability in SWWRP, the various hydrologic and hydraulic engines must utilize a common water quality and contaminant approach to prevent the arbitrary partitioning of constituents. The goal of this development effort is to upgrade existing hydrologic and hydraulic models (i.e., water engines) using a common water quality approach in order to facilitate their linkage and application on a system-wide basis.

In keeping with a common water quality approach to model development, a library of water quality kinetics will be developed such that they can be integrated with a variety of water transport engines. The library of algorithms will be able to deal with a multi-species, multi-phase, multi-reaction system, should include both fast (equilibrium-based) and slow (non-equilibrium-based or rate-based) reactions, will be easily extensible to new reaction pathways, will include both common nutrient and contaminant packages as well as geochemistry, and will have a simple, well-defined data interface and calling procedure, making them portable. The modules will be developed such that they are data structure independent, thus facilitating their integration into a wide range of modeling systems.

Objectives

The primary purpose of the System-Wide Water Resources Program Nutrient Sub-Model (SWWRP-NSM) is to provide a method of determining the fate of nitrogen, phosphorus, and carbon in watersheds exposed to receiving water. This will be integrated within the distributed watershed model's solute transport component, so the concentrations of the nutrient species are simulated for every watershed grid, and are updated, along with water flow and solute transport, every time-step.

This report describes the current state of the NSM in addition to the nutrient process theory and formulations proposed for future versions of NSM. The NSM simulates three domain processes: soil, overland flow, and stream/channel. Chapter 2 discusses the soil nutrient cycle processes, Chapter 3 discusses the overland flow nutrient transport and transformation processes, and Chapter 4 discusses the in-stream nutrient transport and water quality processes.

As research continues, it is anticipated that improved process descriptions will be developed and as such will be integrated into the NSM. As these development efforts occur, this report will be revised in order to reflect the current options available within the NSM.

2 Soil Nutrient Processes

Nitrogen (N) and phosphorus (P) are essential nutrients for plants and animals; however, excessive accumulation of nutrients can represent too much of a good thing and cause eutrophication, especially in water bodies such as streams, lakes, and estuaries. The problem of eutrophication has drawn attention to the role of watershed management in elevating N and P concentrations within soil leachates and runoff. The main factors influencing watershed nutrient movement can be separated into the transport, nutrient source, and management factors. Transport factors include the mechanism by which nutrients move in runoff and erosion within the landscape. Factors which influence the source and amount of nutrients available to be transported are soil nutrient content and form of nutrient applied. Nutrient management factors include the method of application, timing, and placement in the landscape as influenced by the management of application equipment and tillage. Effective nutrient management, whether directed toward nutrient supply or abatement, requires a working knowledge of N and P cycling that involves a series of transformation and transport processes.

The complexity of nutrient transformations and transport in watershed systems has led to the use of both conceptual and mechanistic models for their description. Modeling of nutrients in the watershed consists of three distinct parts. The first part deals with simulating most of the nutrient transformations and movements in the soil nutrient cycle, whereas the second part focuses on the transport and transformation of nutrients in the overland flow. The third part simulates nutrient in-stream transport and transformation processes. The distribution of soil nutrients within a watershed can provide clues as to how nutrients are transported from soil to stream. The Nutrient Sub-Model (NSM) has been developed such that it simulates the nutrient processes, in soil, overland flow and stream, for multiple species and phases.

Within NSM, soil nutrient cycles will be modeled for N and P. Mathematical models of the soil N and P are generally in the form of storage (pool) accounting procedures; however, in a very limited number of models they have been modeled by a set of partial differential equations derived from the actual physical and chemical laws which describe the transformation

process. This pool conceptual model of N and P in soils is relatively straightforward. In comparison to other nutrient processes models, the soil N and P representation in the SWAT model (Neitsch et al. 2002) offers a fair accounting for most of the variables in the soil N and P cycle and it can provide an adequate estimate of N and P loads transported with the overland flow in dissolved or particulate forms.

Although the dynamics of the soil N and P cycle have been described adequately in the SWAT model, the relations in the model have not been formulated in partial differential form. Nevertheless these relations can be utilized to build a more mathematically sound model to simulate the soil N and P dynamics in a partial differential equation formulation. In NSM the soil nutrient mass balance equations for each state variable define all the inputs, outputs or storage of nutrients in a system, or in a specified region. The mathematical formulations describing the transformation and the biochemical processes of the different soil N and P variables in SWAT were adopted along with recent research findings to develop NSM. The work represented here aims to improve the spatial resolution and the level of physical description in nutrient modeling by the development of a grid-based nutrient modeling component to allow the modeling of nutrients using fully distributed watershed models. All nutrient mass balance equations are based on watershed cells and maintained for multiple soil layers. Most of the possible chemical and physical processes occurring to nutrients in both the soil and the overland flow have been accounted for in the NSM. The hydrological variables required to drive the NSM can be calculated using any physically based distributed model capable of producing a reasonable simulation of the flow and sediment fields in the watershed. Linking a physically based hydrological model with NSM gives a more realistic description of the nutrient dynamics in watersheds. This is especially important for agricultural watersheds where the nutrient plays a more important role and its occurrence is highly variable both in time and space. Hence, nutrient contamination hot-spots are more accurately identified and watershed management changes to reduce nutrient transport can be made more confidently.

In order to better describe the interaction between mineral and organic N/P pools, NSM will include a module that simulates carbon (C) dynamics in the soil-plant system according to a C cycle similar to that used in the EDYS model (Childress et al. 2002). It includes three soil organic matter (SOM) pools: active, slow, and passive. The carbon cycle is fundamental

for simulation of all organic matter dynamics and many nutrient cycling processes. To be effective in real-world applications, NSM also must be connected with models for plant growth, soil temperature, water and solute transport, as well as other factors.

Soil nitrogen module

Nitrogen cycle

Of all the mineral nutrients, N has the most complex nutrient cycle, largely because N can exist as a gas (both ammonia and nitrogen gas), whereas the other mineral nutrients do not exist as gases under normal soil conditions. To help understand the various components of the N cycle, definitions and molecular formulas of the numerous N forms are provided in Table 1.

Table 1. Definitions of each N form.

Nitrogen Form	Molecular Formula	Notes
Nitrogen gas	N_2 (g)	—
Ammonia gas	NH_3 (g)	—
Ammonium	NH_4^+	Plant available, attracted to exchange sites on clay particles
Nitrate	NO_3^-	Very mobile, requires more energy by plant than ammonium
Nitrite	NO_2^-	Mobile, generally low concentrations
Organic N	—	Slowly supplies available N to soil solution

N occurs in several chemical forms. These forms vary greatly not only in their characteristics but also in the way they behave. These forms are classified as either organic or inorganic N. Typically, most N in soils and surficial sediments occurs in organic form. Organic forms of N are found in compounds such as amino acids, protein, and more resistant N compounds (ultimately, humus). Inorganic forms include ammonium (NH_4^+), nitrate (NO_3^-), and with a low concentration of nitrite (NO_2^-). Organic N and NH_4^+ are mostly absorbed by clays. In such forms, it can be considered immobile. Inorganic forms of N are the "available" forms that plants and microorganisms can use or that can move in the soil as water moves

through it. Most N in the soil is in the unavailable organic form. Many forms of N are present in any environment at any point in time, mainly because N readily shifts from one form to another. NO_3^- and NH_4^+ can be converted to organic N (ON) by plants and microorganisms; ON can be converted back to inorganic forms as the organic compounds decompose. N can also shift between inorganic forms. These shifts occur as nature attempts to establish an equilibrium among the various forms as environmental conditions change. N in the soil interacts with the atmosphere, soil particles, soil solution, microorganisms, and plants. If a new source of N is added to alter the balance or if environmental conditions (such as temperature and moisture) change, N transformations take place. Because environmental conditions are constantly changing, N transformations are constantly occurring. This continual movement of N from one form to another is known as the "nitrogen cycle." The N cycle consists of various storage pools of N and processes by which the pools exchange N. Figure 1 shows the major components of the watershed model N cycle.
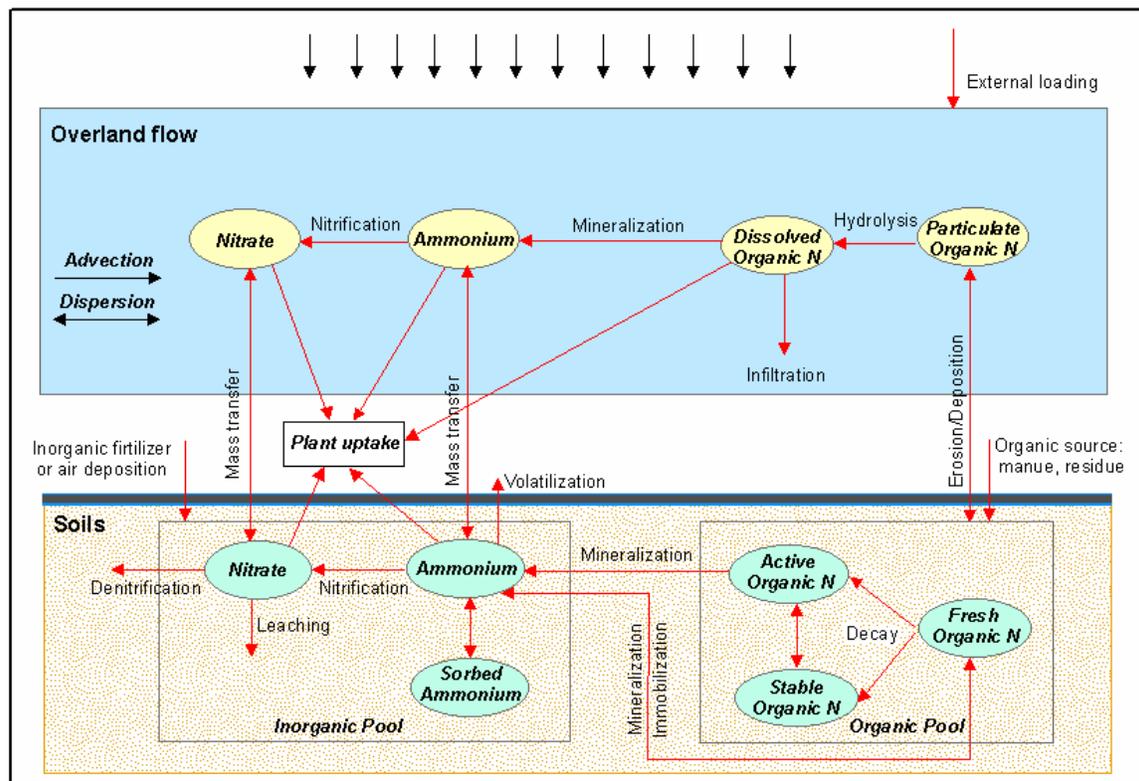

Figure 1. Watershed model nitrogen cycle.

Soil N cycling consists of nine major processes: mineralization, immobilization, nitrification, denitrification, volatilization, sorption, plant uptake,

leaching, and surface runoff and erosion. Each of these processes is described below.

Soil nitrogen transformations

Nitrogen exists in a number of chemical forms and undergoes chemical and biological reactions. Unlike other nutrients, only a small amount of N is contributed from the mineral part of the soil (i.e., rocks). Most naturally occurring N enters the soil either as NO_3^- or NH_4^+ in rainfall (atmospheric deposition) or by special plants, such as alfalfa, ceanothus, and red alder, that are called "nitrogen fixers." Humans also increase the N in soils by fertilizing with either chemical or organic fertilizers. Once in the soil, the N will transform through the processes of mineralization, immobilization, volatilization, nitrification, denitrification, plant uptake, and sorption. Two of these transformations—volatilization and denitrification—result in losses of N from the soil. N is also lost through leaching and runoff. Because most of the transformations and losses are caused by microbial action, all the processes are slowed down considerably when temperatures are low.

Mineralization and immobilization

Mineralization of N occurs when the organic matter (OM) in biosolids decomposes. The soil microorganisms break organic bonds to obtain energy. When the organic matter is completely broken down (oxidized), carbon dioxide (CO_2), water, and minerals are left. The inorganic (available) form of N resulting from decomposition is NH_4^+.

The rate of decomposition and release of available N depends on the nature of the N compounds, which are greatly influenced by the type of treatment or stabilization process the biosolids receive, the duration of the process, and the type of organic matter in the biosolids. Decomposition is slower when the biosolids are more stable. Mineralization amounts are higher in soils with higher amounts of organic matter; therefore, taking steps to maintain or increase soil OM can help supply a relatively constant amount of available N to the soil. The amount of mineralization is also dependent on the type of organic matter present. Fresh manure or crop residue will break down faster than humus that is the result of years of decomposition. In addition, the ratio between total soil carbon and total

soil N affects how quickly this process occurs, because micro-organisms, like plants, need N to live.

Often N released from biosolids OM may be taken up by soil microorganisms and converted back to organic forms. This process is called "immobilization." N immobilization refers to the process where inorganic N (NO_3^- or NH_4^+) is biologically converted to organic N, and is essentially the reverse of N mineralization. Immobilization generally occurs in nutrient-poor soils, in soils with a lot of matter that is low in N and high in carbon (such as woody material or straw), or in soils where organic amendments (such as sawdust or low-N compost) have been added. NH_4^+ immobilization appeared to be dominant when NO_3^- and NH_4^+ were both present.

It has long been recognized that net N mineralization, the balance between N mineralization or immobilization, is tightly coupled with the C cycle. The carbon-to-nitrogen (C:N) ratio is often used as an indication of whether mineralization or immobilization will occur. The C:N ratio is the total concentration of C divided by the total concentration of N. When surface soil layers have a C:N ratio greater than 30:1, then immobilization is highly likely to occur. This is because microorganisms need N to assimilate the available C. When the C:N ratio is below 20:1, N mineralization is likely to occur. When the C:N ratio is between 20:1 and 30:1, both mineralization and immobilization may occur but they will generally balance.

Volatilization

Ammonia (*NH₃*) volatilization refers to the loss of NH_4^+ as a gas into the atmosphere. The process is increased at high pH because NH_4^+ will more easily convert to *NH₃* at high pH. The potential for loss of *NH₃* gas to the air depends on several equilibrium relationships in the soil. NH_4^+ plays an important role in these relationships. Most of the NH_4^+ is bound to soil surface exchange sites; the remainder is dissolved in soil solution. If some NH_4^+ is removed from the soil solution through plant uptake or other means, NH_4^+ will move from the soil surface sites into the soil solution to reestablish equilibrium.

The amount of NH_3 that volatilizes depends on a number of environmental factors and biosolids management techniques. The important ones, in addition to the pH, include temperature and wind speed, and whether the biosolids are incorporated, injected, or surface applied. As much as 100 percent of the initial NH_3 and NH_4^+ in biosolids that are surface applied to agricultural soils can be lost to volatilization. Even when the biosolids have been mixed in with the soil, the majority of the NH_3 may volatilize if the soil has a high pH (over 8.0). Little volatilization may occur in sites such as forest environments because of the low pH of the forest floor, the low wind speed in the forest stands, and the low amounts of radiation reaching the forest floor.

Nitrification

Soil NH_4^+ can quickly (hours to weeks) be converted into NO_2^- and then into NO_3^-. NO_2^- is an intermediate product in many N transformations. This process, known as nitrification, only occurs in the presence of oxygen, so generally it will be slow or non-existent in waterlogged, anaerobic soils. During the process, the microorganism *Nitrosomonas* oxidizes NH_4^+ to NO_2^-, and the microorganism *Nitrobacter* oxidizes the NO_2^- to NO_3^-. Nitrification rates are highest when soils are warm and moist and the pH is neither strongly acidic nor alkaline. Over-application of inorganic N in arid climates will promote buildup of excess NO_3^- in the soil.

Denitrification

Denitrification refers to the process where NO_3^- becomes nitrogen gas (N_2). It is the opposite of nitrification in that oxygen is removed rather than added. Denitrification requires the absence of oxygen, or 'anaerobic' conditions. Similar to nitrification, microorganisms are responsible for denitrification, and therefore it occurs faster in warm, moist soils. Therefore, denitrification losses of N are most significant when soils alternate between aerobic conditions, which allow NO_3^- to accumulate, and anaerobic conditions.

The amount of denitrification depends on the availability of NO_3^-, soil saturation, soil temperature, and availability of easily decomposable organic matter. When a site within the soil becomes saturated with water,

O_2 can no longer diffuse readily into that site. If microorganisms are active within that site, they will deplete the O_2 and then begin using the NO_3^-. If a soil is too cold for microbial activity or if there is too little food (organic matter) available for the microorganisms, the O_2 will not be depleted and denitrification will not occur.

Plant uptake

Inorganic forms of N (NH_4^+ and NO_3^-) are taken up by plants rooted in the soil or floating in the water. Plant N uptake varies widely, depending on plant type, growing conditions (moisture and temperature), and management practices. In addition, NO_3^- requires more energy by the plant after it is taken up because the NO_3^- must be converted to NH_4^+ in the plant before it is made into proteins. It is increasingly being shown that the uptake of organic N can represent a substantial fraction of total plant N uptake in soil (Bardgett et al. 2003).

Sorption

Most soil profiles are negatively charged and sorption of N in the soil occurs through the process of cation exchange, whereby the NH_4^+ is weakly bound to soil particles by electrostatic attraction. The sorption prevents NH_4^+ from moving very rapidly through the soil. Although it may seem that the NH_4^+ would not be available for plant uptake, NH_4^+ can move away from the soil surface as NH_4^+ levels decrease in soil solution due to the process known as diffusion. Hence, there is an exchange of NH_4^+ between soil and soil solution. More NH_4^+ is held by high pH (neutral to alkaline) soils, and conversely, NH_4^+ moves more readily in low pH (acidic) soils.

The two negatively charged N forms (NO_3^- and NO_2^-) will be repelled from negative charges on the clay surface, and are not attracted very strongly to the fewer positive charges on clay surfaces. Therefore, NO_3^- and NO_2^- both have relatively high mobility, meaning they can move easily through the soil and do not undergo much exchange.

Surface runoff, erosion, and leaching

Nitrogen may be lost from the soil by surface runoff and erosion. Dissolved forms of N can be transferred from surface water to soil solution (pore-water) and vice versa, through the process of diffusion. Erosion losses of N can be significant. NO_3^- is highly mobile as discussed previously and subject to leaching losses when both soil NO_3^- content and water movement are high. Movement of NO_3^- through soil is governed by convection, or mass flow, with the moving soil solution and by diffusion within the soil solution (Jury and Nielson 1989). NO_3^- leaching from field soils must be carefully controlled because of the serious impact that it can have on the groundwater. Leaching of NH_4^+ is usually insignificant.

Soil nitrogen mass balance equations

The basic concept in the soil N module is the mass balance that was employed to formulate mathematical equations for each of the soil N state variables. As classified in the SWAT model, the state variables of the soil N are: the fresh organic nitrogen (*orgN_{frs}*), the active organic nitrogen (*orgN_{act}*), the stable organic nitrogen (*orgN_{sta}*), the ammonium N (NH_4^+), and the nitrate N (NO_3^-). Fresh organic N is associated with crop residue and microbial biomass while the active and stable organic N pools are associated with the soil humus. NH_4^+ is partitioned between the aqueous and sorbed phases. Ion exchange may be an important reaction for NH_4^+ in soils, sediments, and aquifer systems (Drever 1982). However, NO_3^- is very soluble in water, so the corresponding sorption of NO_3^- is rare. Therefore, there are in total six soil N state variables. Figure 2 is a diagram of the soil N transformation module used in NSM.

N transformation processes in the soil are simulated in NSM for the five state variables: *orgN_{frs}*, *orgN_{act}*, *orgN_{sta}*, NH_4^+ and NO_3^- . Exchange of NH_4^+ between the soil solution and adsorbed phase is assumed to be reversible, NH_4^+ on soil particles is not considered as a state variable in this NSM version. All N transformation rates are estimated using first-order kinetic equations taking into account the effect of soil water content and temperature. This section summarizes the mass balance equations used to simulate the N cycle in soils.
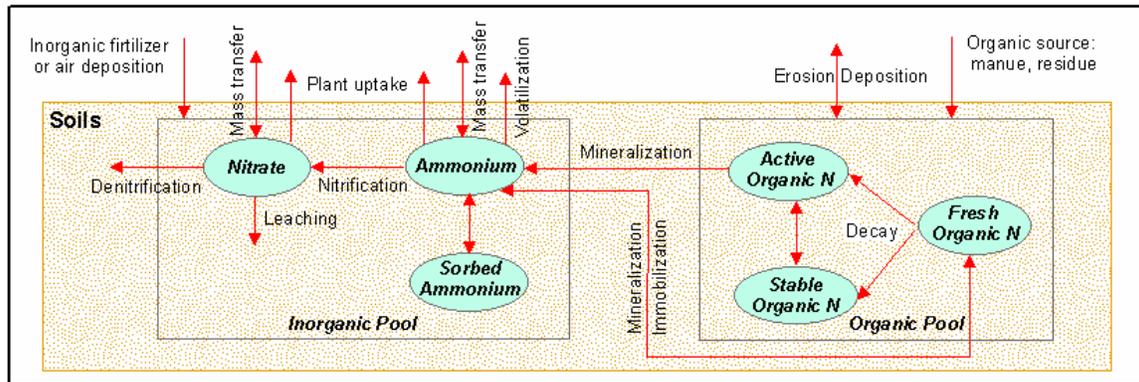
Figure 2. Soil nitrogen transformation module.

Fresh organic nitrogen

This pool contains all the crop N returned to the soil during the growth of the crop. This includes N in dead roots, root exudates, fallen leaves and other plant debris shed during the growing season. Upon decomposition, the N in the crop residues will enter the humus and biomass pools. The mass balance equation for the soil fresh organic N concentration over time is described as:

$$\frac{d(\Delta z \cdot orgN_{frs})}{dt} = -ON_{min|imb} - ON_{dec} - ON_{frs,e} + ON_{frs,s} \tag{1}$$

where

$orgN_{frs}$ = concentration of soil layer fresh organic N pool [M/L³]

Δz = depth of the soil layer [L]

$ON_{min|imb}$ = net mineralization/immobilization rate of soil layer fresh organic N pool [M/L²/T]

ON_{dec} = decomposition rate of soil layer fresh organic N pool [M/L²/T]

$ON_{frs,e}$ = net surface erosion/deposition rate of soil layer fresh organic N pool [M/L²/T]

$ON_{frs,s}$ = external sources added to the soil layer fresh organic N pool [M/L²/T].

Mineralized $orgN_{frsh}$ is added to the NH_4^+ pool while decomposed $orgN_{frsh}$ is added to the humus active organic pool, which is further partitioned into $orgN_{sta}$ and $orgN_{act}$ using partitioning ratios determined for soil organic N. Both transformation equations are adopted from the SWAT model. The N mineralization rates in SWAT are net mineralization rates, which

incorporate immobilization into the equations. N mineralization from the residue fresh organic N is estimated as:

$$ON_{min|imb} = \frac{1}{\Delta z} fr_a \cdot \delta_{ntr} \cdot orgN_{frs} \tag{2}$$

where

fr_a = fraction of soil layer fresh organic N mineralized to the NH_4^+ pool (0.8)

δ_{ntr} = residue decay rate constant [1/T]

The decomposition equation is adopted from the SWAT model. Decomposition from the residue fresh organic N pool to the active organic pool is estimated as:

$$ON_{dec} = \frac{1}{\Delta z} fr_h \cdot \delta_{ntr} \cdot orgN_{frs} \tag{3}$$

where

fr_h = fraction of soil layer fresh organic N decomposed to the humus pool (0.2)

Decomposition and mineralization are controlled by a decay rate constant. The decay rate constant is a function of the C:N ratio, the C:P ratio, and the composition of the crop residue, temperature, and soil water.

$$\delta_{ntr} = \beta_{rsd} \cdot \gamma_{ntr} \left(\gamma_{tmp} \cdot \gamma_{sw} \right)^{1/2} \tag{4}$$

where

β_{rsd} = mineralization rate coefficient of the soil residue fresh organic N pool (0.05 day^{-1}) [1/T]

γ_{ntr} = residue composition correction factor for the soil layer

γ_{tmp} = temperature correction factor for the soil layer ($\geq$ 0.1)

γ_{sw} = water moisture correction factor for the soil layer ($\geq$ 0.05).

The residue composition correction factor is determined by:

$$\gamma_{ntr} = \min\left\{ \begin{array}{c} \exp\left[-0.693\dfrac{\left(\varepsilon_{C:N}-25\right)}{25}\right] \\[2mm] \exp\left[-0.693\dfrac{\left(\varepsilon_{C:P}-200\right)}{200}\right] \\[2mm] 1.0 \end{array} \right\} \qquad (5)$$

where

$\varepsilon_{C:N}$ = C:N ratio of the residue in the soil layer

$\varepsilon_{C:P}$ = C:P ratio of the residue in the soil layer

In future NSM versions, C:N and C:P ratios will be calculated in the carbon cycle module and passes to nutrient cycling residue composition factor equations.

The temperature correction factor is determined by:

$$\gamma_{tmp} = 0.9\frac{T_{soil}}{T_{soil}+\exp\left(9.93-0.312\cdot T_{soil}\right)}+0.1 \qquad (6)$$

where

T_{soil} = temperature of soil layer [°C]

The water moisture correction factor is determined by:

$$\gamma_{sw} = \frac{\theta}{\theta_{FC}} \qquad (7)$$

where

θ = soil water content (mm H_2O)

θ_{FC} = soil water content at field capacity (mm H_2O)

Active organic nitrogen

N enters this pool from crop debris, the soil microbial biomass, and from any applied organic manure. The mass balance equation for the soil active organic N concentration over time is described as:

$$\frac{d(\Delta z \cdot orgN_{act})}{dt} = ON_{dec} - ON_{trn} - ON_{min} - ON_{act,e} + ON_{act,s} \tag{8}$$

where

$orgN_{act}$ = concentration of soil layer active organic N pool [M/L³]

ON_{trn} = rate transferred between the active and stable organic pool [M/L²/T]

ON_{min} = mineralization rate of soil layer active organic N pool [M/L²/T]

$ON_{act,e}$ = net surface erosion/deposition rate of soil layer active organic N pool [M/L²/T]

$ON_{act,s}$ = external sources added to the soil layer active organic N pool [M/L²/T]

The organic N associated with humus is partitioned into two pools (active and stable) to account for the variation in availability of humic substances to mineralization. The active and stable organic N pools are in dynamic equilibrium and are described using a procedure adapted from the SWAT model. Organic N flux between the active and stable pools is estimated as:

$$ON_{trn} = \beta_{trn} \frac{1}{\Delta z} \left[orgN_{act} \left(\frac{1}{fr_{act}} - 1 \right) - orgN_{sta} \right] \tag{9}$$

where

β_{trn} = rate constant (0.00001 day⁻¹) [1/T]

fr_{act} = fraction of soil layer humic organic N in the active organic N pool (0.02)

$orgN_{sta}$ = concentration of soil layer stable organic N pool [M/L³]

In SWAT, N mineralized from the humus active organic pool is added to the NH_4^+ pool in the layer. If the soil water content exceeds field capacity, or soil temperature is less than 0 °C, mineralization from the humus active organic pool (ammonification) does not occur. It is estimated as:

$$ON_{min} = \frac{1}{\Delta z} \beta_{min} \left(\gamma_{tmp} \cdot \gamma_{sw} \right)^{1/2} orgN_{act} \qquad (10)$$

where

β_{min} = mineralization rate coefficient of the soil humus active organic N (0.0003 day⁻¹) [1/T]

Stable organic nitrogen

Most soil N retained in this pool can accumulate rapidly but is not readily accessible to microbial mineralization (Kaye et al. 2003). The mass balance equation for the soil stable organic N concentration over time is described as:

$$\frac{d(\Delta z \cdot orgN_{sta})}{dt} = ON_{dec} + ON_{trn} - ON_{sta,e} + ON_{sta,s} \qquad (11)$$

where

$ON_{sta,e}$ = net surface erosion/deposition rate of soil layer stable organic N pool [M/L²/T]

$ON_{sta,s}$ = external sources added to the soil layer stable organic N pool [M/L²/T]

Ammonium nitrogen

Nitrogen enters the soil NH_4^+ pool by the mineralization of soil organic N (organic manure, humus, soil microbial biomass, and crop debris), by the hydrolysis of urea, from any applied organic manure, and from NH_4^+ fertilizers. NH_4^+ is removed via volatilization, nitrification, and by immobilization. NH_4^+ is available to plants and is not leached to a great extent. Since NH_4^+ is a positively charged ion (cation), it may be attracted to and held by the negatively charged soil clay. The mass balance equation for the soil NH_4^+ concentration over time is described as:

$$\frac{d(\Delta z \cdot NH_4^+)}{dt} = NH_{min} - NH_{nit|vol} - NH_{up} - R_{NH4,e} + NH_s \qquad (12)$$

where

$$NH_4^+ = \text{concentration of soil layer } NH_4^+ \text{ pool [M/L}^3\text{]}$$

NH_{min} = total mineralization processes rate of soil layer organic N pools [M/L²/T]

$NH_{nit|vol}$ = net nitrification/volatilization processes rate in the soil layer [M/L²/T]

NH_{up} = plant uptake rate of soil layer NH_4^+ pool [M/L²/T]

$R_{NH4,e}$ = mass transfer rate of NH_4^+ between the upper soil layer and surface runoff [M/L²/T]

NH_s = external sources added to the soil layer NH_4^+ pool [M/L²/T]

Based on Equations 2 and 10, the total mineralization rate to the NH_4^+ pool is calculated as:

$$NH_{min} = \frac{1}{\Delta z} fr_a \cdot \delta_{ntr} \cdot orgN_{frs} + \frac{1}{\Delta z} \beta_{min} \left(\gamma_{tmp} \cdot \gamma_{sw} \right)^{1/2} orgN_{act} \qquad (13)$$

Nitrification and volatilization equations are adopted from the SWAT model. The total rate of NH_4^+ lost to nitrification and volatilization is calculated using a first-order kinetic rate equation (Reddy et al. 1979):

$$NH_{nit|vol} = \frac{1}{\Delta z} NH_4^+ \left[1 - \exp\left(-\eta_{nit} - \eta_{vol} \right) \right] \qquad (14)$$

where

η_{nit} = nitrification regulator

η_{vol} = volatilization regulator

To partition $NH_{nit|vol}$ between nitrification and volatilization, the expression by which NH_4^+ is multiplied in Equation 14, is solved using each regulator individually to obtain a fraction of each process. The rate of N removed from the NH_4^+ pool by nitrification is then calculated as:

$$NH_{nit} = \frac{fr_{nit}}{\left(fr_{nit} + fr_{vol} \right)} NH_{nit|vol} \qquad (15)$$

and the rate of N removed from the NH_4^+ pool by volatilization becomes:

$$NH_{vol} = \frac{fr_{vol}}{\left(fr_{nit} + fr_{vol}\right)} NH_{nit|vol} \tag{16}$$

where

NH_{nit} = nitrification processes rate in the soil layer [M/L²/T]
NH_{vol} = volatilization processes rate in the soil layer [M/L²/T]
fr_{nit} = 1-exp($-\eta_{nit}$) (estimated fraction of N lost by nitrification)
fr_{vol} = 1-exp($-\eta_{vol}$) (estimated fraction of N lost by volatilization)

The impact of environmental factors on nitrification and ammonia volatilization is defined by the nitrification regulator and volatilization regulator. The nitrification regulator is determined by:

$$\eta_{nit} = \eta_{tmp} \cdot \eta_{sw} \tag{17}$$

and the volatilization regulator is determined by:

$$\eta_{vol} = \eta_{tmp} \cdot \eta_{volz} \tag{18}$$

where

η_{tmp} = nitrification/volatilization temperature correction factor
η_{sw} = nitrification soil water correction factor
η_{volz} = volatilization depth correction factor

The nitrification/volatilization temperature correction factor is estimated as:

$$\eta_{tmp} = 0.41 \frac{\left(T_{soil} - 5\right)}{10} \quad \text{if} \quad T_{soil} > 5 \tag{19}$$

The nitrification soil water correction factor is estimated as:

$$\eta_{sw} = \frac{\theta - \theta_{WP}}{0.25\left(\theta_{FC} - \theta_{WP}\right)} \quad \text{if} \quad \theta - \theta_{WP} < 0.25\left(\theta_{FC} - \theta_{WP}\right) \tag{20}$$

$$\eta_{sw} = 1.0 \quad \text{if} \quad \theta - \theta_{WP} \geq 0.25 \left(\theta_{FC} - \theta_{WP} \right) \tag{21}$$

where

θ_{WP} = soil water content at wilting point (mm H₂O)

The volatilization depth correction factor is estimated as:

$$\eta_{volz} = 1 - \frac{z}{z + \exp\left(4.706 - 0.305 \cdot z\right)} \tag{22}$$

where

z = depth from the soil surface to the middle of the layer [L]

Plant uptake is a very complicated process, involving crop, environment, and cultivation factors. The uptake rate is known to depend both on a plant's requirements and the availability of N in the soil to meet those requirements. The crop N uptake is limited by the inorganic N available in the soil layer. Adopted from the NITS model (Birkinshaw and Ewen 2000), the rate of plant uptakes from NH_4^+ is estimated as:

$$NH_{up} = \min \left\{ \begin{array}{l} NH_{up}^* \dfrac{NH_4^+}{NH_4^+ + NO_3^-} \\[2mm] k_{up} NH_4^+ \end{array} \right\} \tag{23}$$

where

NH_{up}^* = potential plant uptake rate of soil layer NH_4^+ [M/L²/T]

k_{up} = maximum plant uptake rate of soil layer NH_4^+ [T⁻¹]

Nitrate nitrogen

N enters the soil NO_3^- pool from NO_3^- fertilizers, inputs from the atmosphere, and from the nitrification of NH_4^+. NO_3^- is one of the principal forms of N used by plants. Unlike NH_4^+, NO_3^- exists only in the dissolved phase and is very soluble, being subject to only dissolved transport, and moves through the soil profile with percolating water. In modeling NO_3^-,

the partition coefficient equals zero. The mass balance equation for the soil NO_3^- concentration over time is described as:

$$\frac{d(\Delta z \cdot NO_3^-)}{dt} = NH_{nit} - NO_{dnit} - NO_{up} - R_{NO3,f} - R_{NO3,e} + NO_s \qquad (24)$$

where

NO_3^- = concentration of soil layer NO_3^- pool [M/L³]

NO_{dnit} = denitrification processes rate in the soil layer [M/L²/T]

NO_{up} = plant uptake rate of soil layer NO_3^- pool [M/L²/T]

$R_{NO3,e}$ = mass transfer rate of NO_3^- between the upper soil layer and surface runoff [M/L²/T]

$R_{NO3,f}$ = infiltration rate of soil layer NO_3^- pool [M/L²/T]

NO_s = external sources added to the soil layer NO_3^- pool [M/L²/T].

The NO_3^- form of N is a major concern in groundwater pollution. Leaching of NO_3^- from the soil layers is modeled as:

$$R_{NO3,f} = f \cdot NO_3^- \qquad (25)$$

Denitrification of NO_3^- to N_2 is assumed to occur when soil water exceeds field capacity. Based on the SWAT model, the denitrification rate of NO_3^- is estimated as:

$$NO_{dnit} = NO_3^- \left[1 - \exp\left(-1.4 \cdot \gamma_{tmp} \cdot orgC \right) \right] \quad \text{if} \quad \gamma_{sw} \geq 0.95 \qquad (26)$$

$$NO_{dnit} = 0.0 \quad \text{if} \quad \gamma_{sw} < 0.95 \qquad (27)$$

Adopted from the NITS model (Birkinshaw and Ewen 2000), the rate of plant uptakes from NO_3^- is estimated as:

$$NO_{up} = \min \left\{ \begin{array}{c} NO_{up}^* \dfrac{NO_3^-}{NO_3^- + NH_4^+} \\[2ex] k_{up} NO_3^- \end{array} \right\} \qquad (28)$$

where

NO_{up}^{*} = potential plant uptake rate of soil layer NO_3^- [M/L²/T]

k_{up} = maximum plant uptake rate of soil layer NO_3^- [1/T]

In future NSM versions, plant uptake of N will be calculated in the plant dynamic module and passed to the inorganic N mass balance equations described above.

Initialization of nitrogen levels

In addition to the appropriate transport fields given by hydrologic and sediment transport simulations, the user must define the initial N levels for the state variables within the watershed. The following is provided as an empirical reference if measured data are not available.

Nitrogen in rainfall

Lightning discharge converts atmospheric N_2 to nitric acid, which can then be transferred to the soil with precipitation. It has been estimated that rainfall adds about 10 lb of N to the soil per acre per year. More N will be added to the soil with rainfall in areas with a high amount of lightning activity than in areas with little lightning. In SWAT, the N in rainfall is added to the nitrate pool in the top 10 mm of soil. The concentration of nitrate added to the soil in rainfall is calculated as:

$$NO_{rain} = \frac{R_{NO3} \cdot R}{h} \qquad (29)$$

where

NO_{rain} = concentration of NO_3^- added by rainfall [M/L³/T]

R_{NO3} = concentration of N in the rain [M/L³]

R = precipitation intensity (mm H_2O) [L/T]

h = precipitation depth [L]

Nitrogen in soils

The user will be able to either define the initial N levels or use model defaults to initialize the levels of N in the different pools. If the user allows

the model to initialize the N levels, then the method as described below will be followed.

Inorganic forms of N are usually added to the soil by precipitation (i.e., rain or snowfall), or as fertilizers. Microorganisms in the soil convert organic forms of N into inorganic forms that are then usable by plants. The ammonium N pool for the soil NH_4^+ is initialized to 0 ppm. Initial nitrate levels in the soil are varied by depth using the following relationship:

$$NO_{3,z}^- = 7 \cdot \exp\left(\frac{-z}{1000}\right) \tag{30}$$

where

z = depth from the soil surface [L]

$NO_{3,z}^-$ = concentration of NO_3^- in the soil at depth z [M/M or ppm], the NO_3^- concentration for a layer is calculated by solving Equation 30 for the soil horizon's lower boundary depth.

Nitrogen enters the soil in organic forms such as plant roots, leaves, and other plant materials, in addition to dead animals, insects, and microorganisms, manure, compost, and sewage sludge. Organic N levels will be assigned assuming that the initial C:N ratio for humic materials is 14:1. The concentration of humic organic N, in a soil layer, is calculated as:

$$orgN_{hum} = 10^4 \left(\frac{orgC}{14}\right) \tag{31}$$

where

$orgC$ = concentration of organic carbon in the soil layer (%)

$orgN_{hum}$ = concentration of soil humic organic N [M/M or ppm]

The humic organic N is partitioned between the active and stable pools using the following equations:

$$orgN_{act} = orgN_{hum} \cdot fr_{act} \tag{32}$$

$$orgN_{sta} = orgN_{hum} \left(1 - fr_{act}\right) \tag{33}$$

In SWAT, the fraction of humic N (fr_{act}) in the active N pool is set to 0.02. N in the fresh organic pool will be set to zero in all layers except the top 10 mm of soil. In the top 10 mm, the fresh organic N pool will be set to 0.0015 of the initial concentration of residue on the soil surface.

$$orgN_{frs} = 0.0015 \cdot rsd \qquad (34)$$

where

rsd = concentration of residue in the soil layer [M/L^3]

Soil phosphorus module

Phosphorus cycle

Phosphorus can exist in the soil as phosphate (HPO_4^{-2} or $H_2PO_4^-$), particulate P, organic P, or in P minerals. Phosphate is the only form that plants can take up, yet in most agricultural soils there is less than 1 mg/L (ppm) of phosphate in solution, which represents much less than 1 percent of the total soil P. Organic P, which is P bound in organic matter, has been found to represent between about 25 percent and 65 percent of total P in surface soils, with mineral P (such as calcium phosphate minerals) and sorbed P representing the remainder (Brady 1984).

Phosphorus is generally much less mobile than N, being strongly adsorbed to soil particles as well as organic matter. Figure 3 shows the major components of the watershed model P cycle. Soil P is divided into an organic and mineral component that can receive inputs via inorganic fertilizers, organic manure, waste, and sludge. Organic P in the soil is divided into three pools: the fresh organic P pool ($orgP_{frs}$), the active organic P pool ($orgP_{act}$) and the stable organic P pool ($orgP_{sta}$). The $orgP_{frs}$ represents the organic matter that can be easily mineralized (e.g. manures, decayed plants, and microbial biomass). The $orgP_{act}$ constitutes materials with a slower rate of mineralization, whereas $orgP_{sta}$ is composed of P in stable organic matter (i.e., humus). Organic pools are differentiated on the basis of C:P ratios. Inorganic P is divided into labile (soluble) inorganic P (P_{sol}), active inorganic P ($minP_{act}$), and stable inorganic P ($minP_{sta}$) pools. P_{sol} is in rapid equilibrium with $minP_{act}$, which in return is in slow equilibrium with $minP_{sta}$. When inorganic fertilizer P is added, it rapidly equilibrates between P_{sol} and $minP_{act}$. The slow reaction between $minP_{act}$ and $minP_{sta}$ then follows.
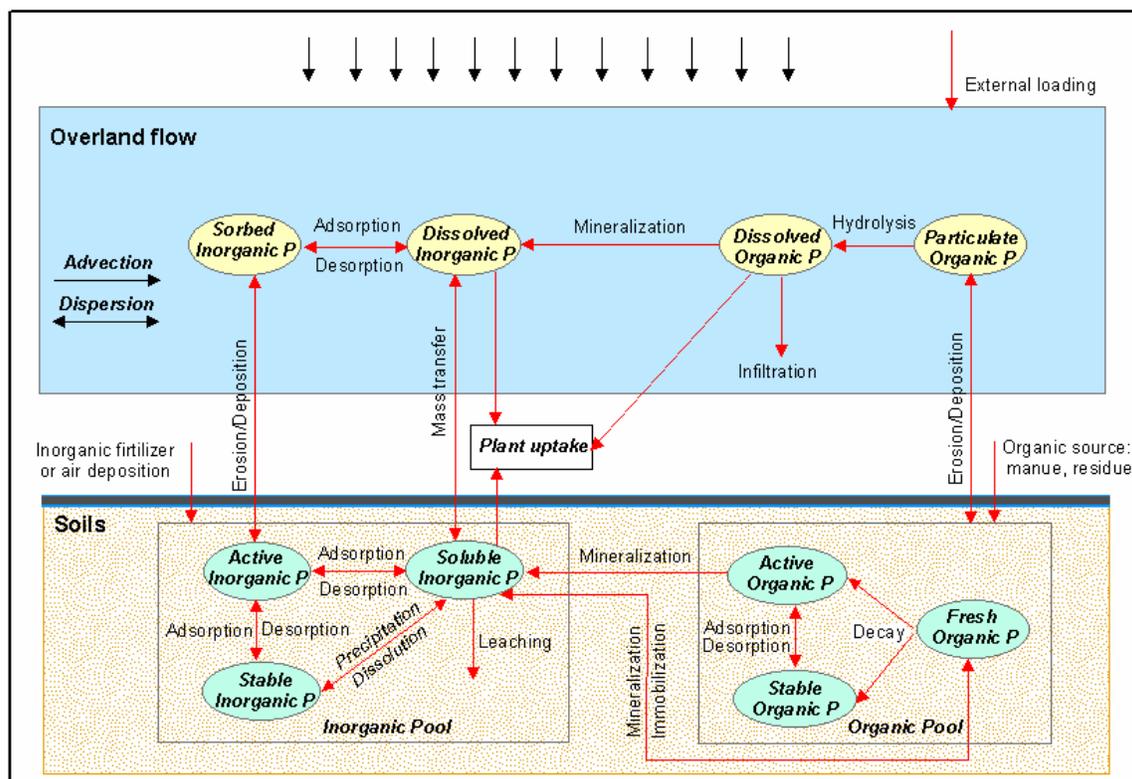
Figure 3. Watershed model phosphorus cycle.

P transformation processes in NSM are simulated for organic and inorganic P in the soil. The processes that control the concentration of available P in the soil are: mineralization, immobilization, precipitation, dissolution, adsorption, desorption, plant uptake, surface runoff, and erosion. Each of these processes is described below.

Soil phosphorus transformations

The P transformations in soils involve complex mineralogical, chemical, and biological processes. P transformations in the soil include decomposition and mineralization of organic P, immobilization of labile P, and sorption of labile P to/from soil particles. P dissolved in soil water and P adsorbed to soil particles can be transported to surface water. Microorganisms deeply affect soil P transformation through mineralization–immobilization processes. Knowledge of P transformations is essential to understanding P behavior in soils.

Mineralization and immobilization

In general, P mineralization and immobilization are similar to those of N in that both reactions or processes occur simultaneously in soils and can be depicted as follows:

$$\text{Organic P} \underset{\text{Immobilization}}{\overset{\text{Mineralization}}{\rightleftarrows}} \text{Inorganic P} \left(HPO_4^{-2} \text{ or } H_2PO_4^- \right) \qquad (35)$$
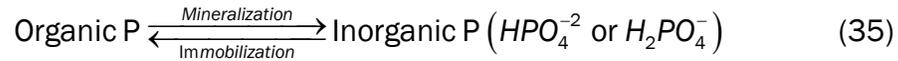
Mineralization converts organic P to inorganic, plant-available P. Immobilization is the reverse process of mineralization where inorganic P is converted back to plant unavailable organic P. The C:P ratio of the decomposing residues regulates the predominance of P mineralization over immobilization, just as the C:N ratio regulates N mineralization over immobilization. The following guidelines have been suggested: mineralization occurs most readily when the C:P ratio is less than 200:1, and immobilization occurs when that ratio is greater than 300:1 (Havlin et al. 1999). Mineralization and immobilization of P are affected by temperature, moisture, aeration, and pH in similar ways as N mineralization and immobilization, because they involve the same microbial processes.

Adsorption and desorption

Adsorption refers to the binding of P to soil particles. Because phosphate has a negative charge, it is attracted to, and binds strongly to, positively charged minerals, such as aluminum (Al) and iron (Fe) hydroxides and oxides. Like other soil particles, these minerals become more positively charged at lower pH; therefore, more phosphate is sorbed at a lower pH. Finer textured soils generally can adsorb more P because they have more surface area.

Adsorption is decreased, and hence available P levels are increased, when the soil solution contains high levels of other anions such as bicarbonate, carbonate, silicate, sulfate, or molybdate that compete for sorption 'sites.' In addition, dissolved organic compounds associated with organic matter can increase P availability by competing for phosphate sorption sites or coating Fe/Al oxides. Adsorption of P generally increases with increased temperatures in P fertilized soils, but there is no correlation with temperature in soils that have not had P added (Havlin et al. 1999). Desorption is the opposite of adsorption. P desorption generally increases as solution P

decreases, or under flooded conditions due to dissolution of Fe hydroxides and oxides, that release adsorbed P.

Precipitation and dissolution

Precipitation is the process through which soluble P is converted to part of mineral P. Available P concentrations are largely controlled by the solubility of P minerals that are dominated by calcium phosphates (Ca-P) in neutral to high pH soils, and by Al and Fe phosphates (Al-P and Fe-P) at pH levels below about 6.5. There are numerous forms of calcium phosphates in soil, ranging from the very soluble monocalcium phosphate (MCP) to the very insoluble fluorapatite. After fertilizing with P in a neutral or high pH soil, MCP will form first, followed by the other calcium phosphates in order from high to low solubility. The time for each mineral to form is highly dependent on temperature. If a soil has a mixture of the various Ca-P solids, the more soluble forms will dissolve more readily as phosphate levels in solution decrease during the growing season. Decreasing pH would take large quantities of acid, or acid-producing substances such as elemental S, Fe^{+3}, or manure. As may be expected, soils with higher levels of calcium carbonate (lime) will tie up more P due to precipitation of Ca phosphates, and thus lower the soil test P.

Al phosphates and Fe phosphates are the predominant P minerals in soils with pH levels below about 6.5 (Havlin et al. 1999). The solubility of these minerals decreases at lower pH, directly opposite of the solubility for calcium phosphates. Therefore, P is most available around pH 6.5, because at lower pH levels, P retention is high due to Al-P and Fe-P precipitation, and at higher pH levels, Ca-P minerals precipitate. Precipitation and dissolution are not depicted within the current NSM soil P module.

Plant uptake

Despite low concentrations of phosphate in soil solution, plants can take up substantial amounts of P due to P desorption and dissolution, followed by P diffusion to the plant root (Foth and Ellis 1997). By taking up large amounts of P, a strong 'diffusion gradient' is created, which moves P toward the plant root at much higher rates than water is moving via transpiration. Plant dynamic modules are currently under development and will be available in future releases of NSM.

Erosion and surface runoff

Erosion represents a loss of P from soils and can occur from water or wind because P is generally bound so tightly to the soil. Dissolved P in runoff can represent another loss of P. However, the concentration of dissolved P in runoff is generally low due to the high amount of sorption and precipitation of P minerals. One exception to this general rule is animal manure stockpiles or manure application sites, where P is concentrated and sorption sites in the manure and surrounding soil may be approaching saturation. It is important to realize that the general perception that P binds strongly to soil is true only to a certain soil P level or application amount. A large amount of research has correlated soil test P levels with dissolved P in soil solution, drainage water, or runoff. One of these studies found that P in solution began to significantly increase only when Olsen P levels were above 60 ppm (Heckrath et al. 1995).

Soil phosphorus mass balance equations

Simulation of soil P dynamics is taken from the SWAT model in which six pools (state variables) of P are identified. They are: the fresh organic P ($orgP_{frs}$), the active organic P ($orgP_{act}$), the stable organic P ($orgP_{sta}$), the active inorganic P ($minP_{act}$), the stable or insoluble inorganic P ($minP_{sta}$), and the labile (soluble) P (P_{sol}). Figure 4 is a diagram of the soil P transformation module used in NSM.
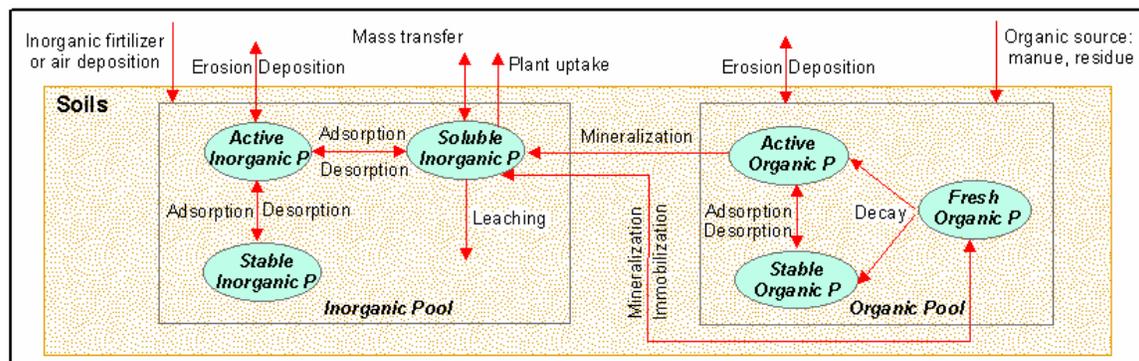

Figure 4. Soil phosphorus transformation module.

P transformation processes in the soil are simulated by NSM for the six pool state variables: $orgP_{frs}$, $orgP_{act}$, $orgP_{sta}$, P_{sol}, $minP_{act}$, and $minP_{sta}$. All P transformation rates are estimated using first-order kinetic equations taking into account the effect of soil water content and temperature. This

section summarizes the mass balance equations used to simulate the P cycle in soils.

Fresh organic phosphorus

This pool consists of P in undecomposed plant residues, livestock excretion, manure and microbes. The mass balance equation for the soil fresh organic P concentration over time is described as:

$$\frac{d(\Delta z \cdot orgP_{frs})}{dt} = -OP_{min|imb} - OP_{dec} - OP_{frs,e} + OP_{frs,s} \tag{36}$$

where

$orgP_{frs}$ = concentration of soil layer fresh organic P pool [M/L³]

OP_{dec} = decomposition rate of soil layer fresh organic P pool [M/L²/T]

$OP_{min|imb}$ = net mineralization/immobilization rate of soil layer fresh organic P pool [M/L²/T]

$OP_{frs,e}$ = net surface erosion/deposition rate of soil fresh organic P pool [M/L²/T]

$OP_{frs,s}$ = external sources added to the soil layer fresh organic P pool [M/L²/T]

Mineralized $orgP_{frsh}$ is added to soluble P while decomposed $orgP_{frsh}$ is added to humus organic pool ($orgP_{hum}$). The $orgP_{hum}$ is further partitioned into $orgP_{sta}$ and $orgP_{act}$ using partitioning ratios determined for soil organic P. Both transformation equations are adopted from the SWAT model. The P mineralization rates are net mineralization rates that incorporate immobilization into the equations. P mineralized from the fresh organic pool is added to the soluble P pool and is estimated as:

$$OP_{min|imb} = \frac{1}{\Delta z} fr_a \cdot \delta_{ntr} \cdot orgP_{frs} \tag{37}$$

Phosphorus decomposed from the fresh organic pool is added to the humus organic pool. It is estimated as:

$$OP_{dec} = \frac{1}{\Delta z} fr_h \cdot \delta_{ntr} \cdot orgP_{frs} \tag{38}$$

Active organic phosphorus

This pool is P in the solid phase, which is relatively easily transformed to the soil solution. The mass balance equation for the soil humic active organic P concentration over time is described as:

$$\frac{d(\Delta z \cdot orgP_{act})}{dt} = OP_{dec} - OP_{min} - OP_{trn} - OP_{act,e} + OP_{act,s} \tag{39}$$

where

$orgP_{act}$ = concentration of soil layer active organic P pool [M/L^3]

OP_{min} = mineralization rate of soil humic active organic P pool [M/L^2/T]

OP_{trn} = rate transferred between the active and stable organic P pools [M/L^2/T]

$OP_{act,e}$ = net surface erosion/deposition rate of soil humic active organic P pool [M/L^2/T]

$OP_{act,s}$ = external sources added to the soil layer active organic P pool [M/L^2/T]

P mineralized from the humus active organic pool is added to the soluble P pool in the layer. It is estimated as:

$$OP_{min} = 1.4 \frac{1}{\Delta z} \cdot \beta_{min} \left(\gamma_{tmp} \cdot \gamma_{sw} \right)^{1/2} orgP_{act} \tag{40}$$

Stable organic phosphorus

The soil stable organic P is relatively inert to transformation. The mass balance equation for the soil stable organic P concentration over time is described as:

$$\frac{d(\Delta z \cdot orgP_{sta})}{dt} = OP_{dec} + OP_{trn} - OP_{sta,e} + OP_{sta,s} \tag{41}$$

where

$orgP_{sta}$ = concentration of soil layer stable organic P pool [M/L^3]

$OP_{sta,e}$ = net surface erosion/deposition rate of soil humic stable organic P pool [M/L^2/T]

$OP_{sta,s}$ = external sources added to the soil layer stable organic P pool [M/L²/T].

Soluble phosphorus

The soil soluble P pool is very small and will usually contain only a fraction of a pound of P per acre. The soluble P usually is in the inorganic form, but small amounts of organic P may exist as well. Of total soluble P, organic P is more labile than inorganic P since it is not easily bound to soil particles. Inorganic P is a preferred form for plant growth although organic P is also uptaken. The inorganic P in solution not uptaken by plants or immobilized by microorganisms can be adsorbed to mineral surface or precipitated as secondary P compounds. With low soluble P concentrations, adsorption appears to dominate, while precipitation reactions proceed when the concentration of P and associated cations in the soil solution exceeds that of the solubility product of the mineral. The mass balance equation for the soil-soluble P concentration over time is described as:

$$\frac{d(\Delta z \cdot P_{sol})}{dt} = IP_{min} - IP_{sol|act} - IP_{up} - R_{DIP,e} + IP_{s} \tag{42}$$

where

P_{sol} = concentration of soil layer soluble P pool [M/L³]

IP_{min} = total mineralization processes rate of soil layer organic P pools [M/L²/T]

$IP_{sol|act}$ = net sorption/desorption rate transferred between the soluble P pool and active inorganic P pool [M/L²/T]

IP_{up} = plant uptake rate of soil layer soluble P pool [M/L²/T]

$R_{DIP,e}$ = mass transfer rate of soluble P between the upper soil layer and surface runoff [M/L²/T]

IP_{s} = external sources added to the soil layer soluble P pool [M/L²/T]

Based on Equations 37 and 40, the total mineralization rate to the soluble P is calculated as:

$$IP_{min} = 1.4 \frac{1}{\Delta z} \cdot \beta_{min} \left(\gamma_{tmp} \cdot \gamma_{sw} \right)^{1/2} orgP_{act} + \frac{1}{\Delta z} fr_{a} \cdot \delta_{ntr} \cdot orgP_{frs} \tag{43}$$

Equilibrium sorption between the solution and active inorganic P pool is governed by the P availability index (PAI). Sharpley et al. (1984) have estimated values of the PAI for different soils based on regression analyses. PAI is the P sorption coefficient defined as the fraction of fertilizer P remaining in the labile pool after the initial rapid phase of P sorption is complete. The PAI is determined by:

$$PAI = \frac{P_{sol,f} - P_{sol,i}}{P_{sol,frt}} \tag{44}$$

where

$P_{sol,f}$ = concentration of P in solution after fertilization and incubation [M/L³]

$P_{sol,I}$ = concentration of P in solution before fertilization [M/L³]

$P_{sol,frt}$ = concentration of soluble P fertilizer added to the soil [M/L³]

SWAT simulates P sorption by assuming the soluble inorganic P pool is in rapid equilibrium with the active inorganic P pool. The transformation of P between the solution and active inorganic pools is determined by the following equations:

$$IP_{sol|act} = \frac{1}{\Delta z}\left[P_{sol} - minP_{act}\left(\frac{PAI}{1-PAI}\right)\right] \quad \text{If} \quad P_{sol} > minP_{act}\left(\frac{PAI}{1-PAI}\right) \tag{45}$$

$$IP_{sol|act} = \frac{1}{\Delta z}\beta_{trn}\left[P_{sol} - minP_{act}\left(\frac{PAI}{1-PAI}\right)\right] \quad \text{If} \quad P_{sol} < minP_{act}\left(\frac{PAI}{1-PAI}\right) \tag{46}$$

where

β_{trn} = first order rate constant for optimal temperature and moisture conditions (0.1 day⁻¹)

Uptake of P (mainly in the form of $H_2PO_4^-$) by plant roots is assumed to follow Michaelis-Menten kinetics (Barber 1980) and is limited by soil water availability:

$$IP_{up} = U_{max}\mu\frac{P_{sol}}{M\mu + P_{sol}}k_{\varphi} \tag{47}$$

where

U_{max} = maximum rate of P uptake by the given plant [M/L²/T]

μ = ratio of potential crop coefficient for a given time-step to the maximum crop coefficient (=$K_{co}/K_{co(max)}$)

M = Michaelis-Menten's half-saturation constant of soluble P concentration for the given plant [M/L³]

k_{φ} = soil water stress factor

The soil water stress factor is applied to limit the P uptake rate according to soil water availability. There is no limitation when the soil water content exceeds the field capacity, but P uptake decreases linearly as the soil water content decreases from field capacity to wilting point and no uptake occurs when the soil water content is below the wilting point. Thus, Equation 47 reflects both the P demand and availability in the root zone. In future NSM versions, crop uptake P will be calculated in the plant dynamic module and passed to the inorganic P mass balance equation.

Active inorganic phosphorus

Active inorganic P, which is assumed to be adsorbed on soil particles, represents more stable P that is not easily desorbable but is in equilibrium with soluble inorganic P. As plants take up phosphate, the concentration of phosphate in solution is decreased and some phosphate from the active inorganic P pool is released. Because the soluble P pool is very small, the active inorganic P pool is the main source of available P for crops. The mass balance equation for the soil active inorganic P concentration over time is described as:

$$\frac{d(\Delta z \cdot minP_{act})}{dt} = IP_{sol|act} - IP_{act|sta} - IP_{act,e} + IP_{act,s} \qquad (48)$$

where

$minP_{act}$ = concentration of soil layer active inorganic P pool [M/L³]

$IP_{act|sta}$ = net slow sorption/desorption transfer rate between the active inorganic P pool and the stable inorganic P pool [M/L²/T]

$IP_{act,e}$ = surface erosion/deposition rate of soil active inorganic P detachment [M/L²/T]

$IP_{act,s}$ = external sources added to the soil layer active inorganic P pool [M/L²/T]

The active and stable inorganic P pools are dynamic and are assumed to exist at a slow equilibrium with the stable mineral P pool. At equilibrium, the stable inorganic pool is four times the size of the active inorganic pool. The transformation of P between the active and stable inorganic pools is determined by the following equations:

$$IP_{act|sta} = \frac{1}{\Delta z} \beta_{eqs} \left(4 \cdot minP_{act} - minP_{sta} \right) \quad \text{If} \quad minP_{sta} < 4 \cdot minP_{act} \qquad (49)$$

$$IP_{act|sta} = \frac{1}{\Delta z} \beta_{trn} \cdot \beta_{eqs} \left(4 \cdot minP_{act} - minP_{sta} \right) \quad \text{If} \quad minP_{sta} > 4 \cdot minP_{act} \quad (50)$$

where

β_{eqs} = slow equilibrium rate constant (0.0006 day^{-1}) [1/T]

Stable inorganic phosphorus

This pool comprises stable forms of inorganic P adsorbed on the soil in equilibrium with the active pool of inorganic P. The inorganic phosphate compounds in this pool are more crystalline in their structure and less soluble than those compounds considered to be in the active inorganic P pool. Some slow conversion between the stable P pool and the active P pool does occur in soils. The mass balance equation for the soil stable inorganic P concentration over time is described as:

$$\frac{d(\Delta z \cdot minP_{sta})}{dt} = IP_{act|sta} - IP_{sta,e} + IP_{sta,s} \qquad (51)$$

where

$minP_{sta}$ = concentration of soil layer stable inorganic P [M/L^3]
$IP_{sta,e}$ = surface erosion/deposition rate of soil stable inorganic P detachment [M/L^2/T]
$IP_{sta,s}$ = external sources added to the soil layer stable inorganic P pool [M/L^2/T]

Initialization of soil phosphorus levels

Users can define the concentration of inorganic and organic P in all soil layers at the beginning of the simulation. If such information is not

available, the following default values will be used to initialize levels of P in the different pools.

Initial soluble P pool for the soil is set at 5 mg/kg to simulate unmanaged conditions. A concentration of 25 mg/kg is considered representative of cropland. Organic P decreases quickly with soil depth, paralleling decreases in organic matter. The distribution of organic P with depth also varies among soils. The concentrations of P in the active inorganic pool and the stable inorganic pool are initialized, respectively, to (Jones et al. 1984):

$$\min P_{act} = P_{sol} \frac{1 - PAI}{PAI} \tag{52}$$

$$\min P_{sta} = 4 \cdot \min P_{act} \tag{53}$$

Organic P levels are assigned assuming that the N:P ratio for humic materials is 8:1. The concentration of humic organic P in a soil layer is calculated as:

$$orgP_{hum} = 0.125 \cdot orgN_{hum} \tag{54}$$

P in the fresh organic pool is set to zero in all layers except the top 10 mm of soil. In the top 10 mm, the fresh organic P pool will be set to 0.0003 of the initial concentration of residue on the soil surface.

$$orgP_{frs} = 0.0003 \cdot rsd \tag{55}$$

3   Overland Flow Nutrient Processes

Nutrient storage in the soil occurs primarily in the uppermost few centimeters where it is accessible to shallow-rooted vegetation. Surface water fluxes interact with this layer and can dissolve some of the soluble nutrient stores, as well as cause erosion of the organic and adsorbed stores. Water serves as a solvent and physical/chemical transport medium for dissolved and particulate materials and thus overland flow can be an important mechanism of nutrient transport from soils to streams (Sharpley et al. 1992, Goulding et al. 1996). Loading of nutrients from watersheds to surface waters causes changes in ecological function, and often has undesirable environmental and economic consequences. Indeed, non-point runoff of N and P from agricultural landscapes is viewed as one of the most important factors causing impaired water quality in freshwater and estuarine ecosystems (Correll 1998, Carpenter et al. 1998, Daniel et al. 1998, Downing et al. 1999, Hessen et al. 1997, Puckett 1995, Sims et al. 1998). Ammonium, nitrate and orthophosphate are the principal nonpoint source forms of N and P. A major source for these elements is the soil nutrient pools. Overland flow transport of these chemicals is vital for quantifying a nonpoint source. The growing concern about the environmental impact of nutrients has enhanced the desire to predict the transport and transformation of nitrogen in overland flow more accurately.

Surface runoff can remove large quantities of nutrients from the soil in both dissolved and particulate forms. In the case of N, the dissolved inorganic component is further discriminated into NO_3^- and NH_4^+. The loss of dissolved nutrients in surface runoff is the result of rainfall mixing with the dissolved nutrients in the upper portion of the soil. These dissolved nutrients interact with surface runoff and once in water, they are transported. Suspended nutrients, which are assumed to be either organic or adsorbed inorganic components, attach to eroded sediment material derived from erosion or from bed erosion in the stream channel, and are transported with water. The concentration of suspended nutrients in overland flow is largely determined by soil texture, infiltration rate, rainfall intensity, slope, and ground cover. However, the high degree of temporal and spatial variability in the distribution of surface runoff makes it difficult to conduct studies on nutrient transport by this process. Some of the challenges in conducting nutrient mass balance studies are in determining

the unmeasured amounts of nutrients removed from the water and stored in aquatic organisms and sediments, and nutrients added to the water from resuspension, erosion, and dissolution processes.

Nutrient routing in overland flow is described by a two-dimensional (2D) advection-dispersion equation, which is based on the principle of conservation of mass and Fick's law. The forms of nutrient govern the transport process and the pathway the nutrient is carried through. The mass balance for each nutrient species in overland flow in two directions is written as:

$$\frac{\partial (h \cdot C_j)}{\partial t} + \nabla C_j - \nabla \cdot \nabla C_j = \sum R_{j,k} + S_j \qquad (56)$$

$$\underset{1}{} \qquad \underset{2}{} \qquad \underset{3}{} \qquad \underset{4}{}$$

where

C_j = concentration of species j in overland flow [M/L³]

$\nabla C_j = \partial(q_x \cdot C_j)/\partial x + \partial(q_y \cdot C_j)/\partial y$ is total advection transport flux of species j in the x- and y-direction [M/L²/T]

$\nabla \cdot \nabla C_j = \dfrac{\partial}{\partial x}\left(h \cdot D_x \dfrac{\partial C_j}{\partial x}\right) + \dfrac{\partial}{\partial y}\left(h \cdot D_y \dfrac{\partial C_j}{\partial y}\right)$ is total dispersion flux of species j in the x- and y-direction [M/L²/T]

q_x and q_y = unit discharge of overland flow in the x- and y-direction [L²/T]

D_x and D_y = dispersion coefficient of species j in the x- and y-direction [L²/T]

$R_{j,k}$ = transformation rate of disappearance or generation of species j in reaction k [M/L²/T]

S_j = load of species j in the external source or sink [M/L²/T]

In Equation 56, term 1 represents advection transport, the major transport process in overland flow. Term 2 is the mass transfer by diffusion or dispersion. The third term is the sum of internal mass change due to kinetic or equilibrium biological and chemical transformation processes and interaction with the upper soil layer. All these processes consider the effect on N and P cycles. The last term represents the external addition or loss of mass. The dissolved substance differs from the particulate substance in overland flow. Within the model, hydrolysis is defined as the process by which particulate organic nutrients are converted to dissolved organic form. Mineralization is defined as the process by which dissolved organic nutrients are converted to dissolved inorganic form. Direct mineralization

of particulate organic nutrients does not occur. The mass balance equations for each nutrient variable are presented below in detail.

Equation 56 cannot be solved alone in itself but requires the application of a hydrologic model as an input. With the flow field computed by the hydrologic model, the flow results can be used to compute the fate and transport of nutrient quantities, i.e., species concentration and load.

Overland flow nitrogen module

The dominant N species in waters are dissolved inorganic N (DIN) - NH_4^+, NO_2^-, NO_3^-, dissolved organic N (DON), and particulate organic N (PON) and inorganic N (PIN) (Burt et al. 1993). There are substantial differences in chemical properties among the N species. Total dissolved N (TDN) consists of DIN and DON, and is readily available for plant uptake. DIN mainly comprises $NO_3^- + NH_4^+$. NH_4^+ is the form of N taken up most readily by phytoplankton because NO_3^- must first be reduced to NH_4^+ before it is assimilated into amino acids in organisms. Organic N includes all substances in which N is bonded to C. The largest fraction is made up of amino acids and peptides and is often called amino N. It occurs in both particulate and soluble forms. DON is found in a wide range of complex chemical forms such as amino acids, proteins, urea and humic acids. The particulate N consists of PON and NH_4^+ adsorbed onto mineral particles. Particulate N can be found in suspension or on the sediment. Some portion of the particulate N is subject to rapid mineralization, and is biologically available. Total nitrogen (TN) is a measure of all forms of dissolved and particulate N present in waters.

In NSM, N transport processes are simulated for dissolved NO_3^-, dissolved NH_4^+, DON and PON. Figure 5 is a diagram of the overland flow N transport and transformation module used in NSM. This section summarizes the governing equations used to simulate N transport and transformation in the overland flow.
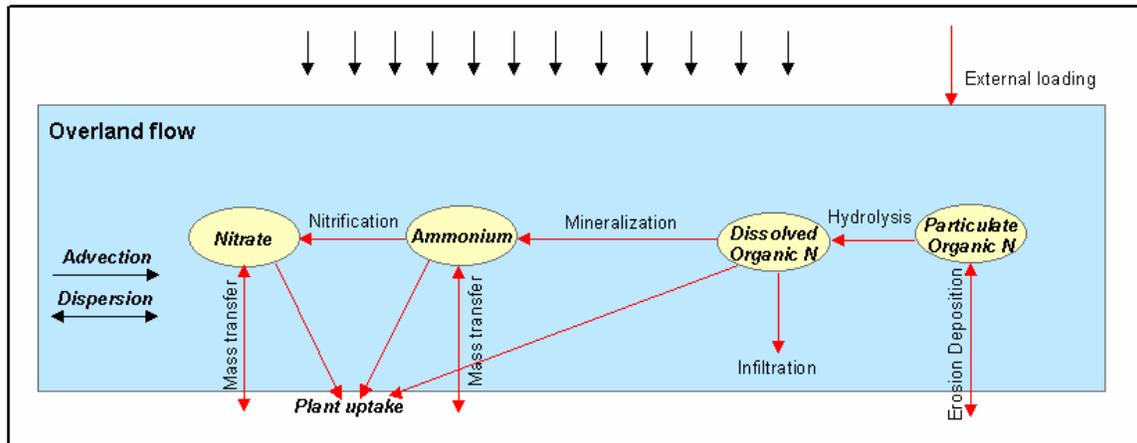
Figure 5. Overland flow nitrogen transport and transformation module.

Particulate organic nitrogen

Organic N may exist in waters in particulate form. This phase includes
small organisms (algae, bacteria, …), both living and dead, and fragments
of organisms. As such, PON particles are carried by runoff and transported
through erosion and deposition processes. The sediment transport equa-
tion assumes the types of "particles" variables are conservative, which
indicates that no kinetic functions are applicable. Therefore, mineraliza-
tion, dissolution, or other transformation processes need to be considered
and applied to PON. Simulations may consider PON as a single variable,
or, alternately, represent from one to many particle types or fractions. The
mass balance equation of PON transport in 2D overland flow is written for
the total PON concentration:

$$\frac{\partial(h \cdot PON_{ov})}{\partial t} + \nabla PON_{ov} + \nabla \cdot \nabla PON_{ov} = R_{PON,e} - R_{PON,d} - R_{PON,hyd} + S_{PON} \qquad (57)$$

where

PON_{ov} = concentration of the overland flow PON [M/L^3]
$R_{PON,d}$ = deposition rate of the overland flow PON [M/L^2/T]
$R_{PON,e}$ = erosion rate of the upper soil layer organic N [M/L^2/T]
$R_{PON,hyd}$ = hydrolysis rate of the overland flow PON [M/L^2/T]
S_{PON} = external sources added to the overland flow PON [M/L^2/T]

PON is subsequently entrained into surface runoff as these particles are
eroded by the moving water. The concentration of PON available for trans-

port is calculated as the sum of *orgP~sta~*, *orgP~act~*, and *orgP~frsh~* in the upper soil layer. The erosion flux of PON due to runoff is computed by:

$$R_{PON,e} = \sum_1^N f_{pn} \cdot v_r \cdot orgN_t \qquad (58)$$

where

f_{pn} = fraction of the PON associated with particle "n"
v_r = resuspension (erosion) velocity [L/T]
$orgN_t$ = total concentration of organic N in the upper soil layer [M/L³]

When the sediment transport capacity is lower than the sediment load, sediment deposition occurs. PON particles in the runoff may deposit on the upper soil layer with suspended sediments. The deposition flux of PON in overland flow is computed by:

$$R_{PON,d} = \sum_1^N f_{pn} \cdot v_{se} \cdot PON_{ov} \qquad (59)$$

where

v_{se} = effective settling (deposition) velocity [L/T]

A portion of the PON hydrolyzes to DON. Hydrolysis of PON is modeled as a first order decay process:

$$R_{PON,hyd} = k_{hyd} \cdot PON_{ov} \qquad (60)$$

where

k_{hyd} = hydrolysis rate constant [1/T]

Dissolved organic nitrogen

While much research has studied the role of DIN in leachates, the contribution of DON has been largely ignored or considered to be insignificant. However, recent research demonstrated that DON made up the majority of TDN in stream exports in areas with large anthropogenic inputs of DIN.

The mass balance equation of DON transport in 2D overland flow is written for the DON concentration:

$$\frac{\partial\left(h \cdot DON_{ov}\right)}{\partial t} + \nabla DON_{ov} - \nabla \cdot \nabla DON_{ov}$$
$$= R_{PON,hyd} - R_{DON,f} - R_{DON,min} - R_{DON,up} + S_{DON} \tag{61}$$

where

DON_{ov} = concentration of DON in the overland flow [M/L³]

$R_{DON,f}$ = infiltration rate of the overland flow DON [M/L²/T]

$R_{DON,min}$ = mineralization hydrolysis rate of the overland flow DON to NH_4^+ [M/L²/T]

$R_{DON,up}$ = plant uptake rate of the overland flow DON [M/L²/T]

S_{DON} = external sources added to the overland flow DON [M/L²/T]

The DON infiltration flux can be computed from the water infiltration:

$$R_{DON,f} = f \cdot DON_{ov} \tag{62}$$

DON is mineralized to NH_4^+. Mineralization of DON is modeled as a first order decay process:

$$R_{DON,min} = k_{min} \cdot DON_{ov} \tag{63}$$

where

k_{min} = mineralization rate constant [1/T]

Ammonium nitrogen

The mass balance equation of NH_4^+ transport in 2D overland flow is written for the dissolved NH_4^+ concentration:

$$\frac{\partial(h \cdot NH_{4\,ov}^+)}{\partial t} + \nabla NH_{4\,ov}^+ - \nabla \cdot \nabla NH_{4\,ov}^+$$
$$= R_{DON,min} - R_{NH4,f} + R_{NH4,e} - R_{NH4,nit} - R_{NH4,up} + S_{NH4} \tag{64}$$

where

$NH_{4\,ov}^{+}$ = concentration of NH_4^+ in the overland flow [M/L³]

$R_{NH4,f}$ = infiltration rate of the overland flow NH_4^+ [M/L²/T]

$R_{NH4,e}$ = mass transfer rate between the upper soil layer and surface runoff [M/L²/T]

$R_{NH4,nit}$ = nitrification rate of the overland flow NH_4^+ to NO_3^- [M/L²/T]

$R_{NH4,up}$ = plant uptake rate of the overland flow NH_4^+ [M/L²/T]

S_{NH4} = external sources added to the overland flow NH_4^+ [M/L²/T]

The mass transfer flux of the dissolved NH_4^+ between the soil water and the overland flow can be expressed as:

$$R_{NH4,e} = k_e \cdot \left(NH_4^- - NH_{4\,ov}^- \right) \tag{65}$$

where

k_e = effective mass transfer rate constant [L/T]

The dissolved NH_4^+ infiltration flux can be computed from the water infiltration:

$$R_{NH4,f} = f \cdot NH_{4\,ov}^- \tag{66}$$

Nitrification is represented as a two-stage process with NH_4^+ being converted to NO_2^- followed by conversion to NO_3^-. NO_2^- concentrations are usually much less than NO_3^-, and for modeling purposes, NO_2^- is combined with NO_3^-. The nitrification rate is therefore calculated by:

$$R_{NH4,nit} = k_{nit} \cdot NH_{4\,ov}^- \tag{67}$$

where

k_{nit} = nitrification rate constant [1/T]

Nitrate nitrogen

Nitrate concentration increases with nitrification but decreases through denitrification. The mass balance equation of NO_3^- transport in 2D overland flow is written for the dissolved NO_3^- concentration:

$$\frac{\partial(h \cdot NO_{3ov}^-)}{\partial t} + \nabla NO_{3ov}^- - \nabla \cdot \nabla NO_{3ov}^-$$
$$= R_{NH4,nit} - R_{NO3,f} + R_{RO3,e} - R_{NO3,up} + S_{NO3} \tag{68}$$

where

NO_{3ov}^- = concentration of NO_3^- in the overland flow [M/L³]

$R_{NO3,e}$ = mass transfer rate of NO_3^- between the upper soil layer and surface runoff [M/L²/T]

$R_{NO3,f}$ = infiltration rate of the overland flow NO_3^- [M/L²/T]

$R_{NO3,up}$ = plant uptake rate of the overland flow NO_3^- [M/L²/T]

S_{NO3} = external sources added to the overland flow NO_3^- [M/L²/T]

The mass transfer flux of the NO_3^- between the overland flow and the soil water can be expressed as:

$$R_{NO3,e} = k_e \cdot \left(NO_3^- - NO_{3ov}^- \right) \tag{69}$$

where

k_e = effective mass transfer rate constant [L/T]

Dissolved chemicals in the runoff will enter the upper soil if the water transporting those chemicals infiltrates. To account for this process, the NO_3^- infiltration flux can be computed from the water infiltration:

$$R_{NO3,f} = f \cdot NO_{3ov}^- \tag{70}$$

Overland flow phosphorus module

Unlike N, which is highly mobile, P solubility is limited in most environments. P combines with other ions to form a number of insoluble com-

pounds that precipitate out of solution. These characteristics contribute to a buildup of P near the soil surface that is readily available for transport in surface runoff. In addition to precipitating, P adsorbs to soil particles and can be transported via soil erosion. Sharpley and Syers (1979) observed that surface runoff is the primary mechanism by which P is exported from most watersheds. P movement in runoff occurs as particulate P and dissolved P. Particulate P is attached to mineral and organic sediment as it moves with the runoff. Dissolved P is in the water solution. In terms of their impact on eutrophication of water bodies, particulate P becomes less available to algae and plant uptake than dissolved P because of the chemical form it has with the mineral (particularly iron, aluminum, and calcium) and organic compounds. Dissolved P is readily available for plants, and consists of inorganic orthophosphate ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) and organic phosphorus-containing compounds. The movement of dissolved P begins with the sorption, dissolution, and extraction of P from the soil, plant, and organic material. These processes occur when rain and runoff water interact with the upper soil layer. Some water infiltrates into the soil and percolates through the profile where desorption of P will result in a low dissolved concentration in subsurface and return flow. High dissolved P concentration can be expected in the water percolating through organic, coarse-textured, and oxygen-depleted, waterlogged soils. The particulate P consists of organic P (POP), mineral P, and phosphate adsorbed on mineral surfaces. Particulate P can be found in suspension or on the sediment. The adsorption and desorption of phosphate from mineral surfaces forms a buffering mechanism that regulates dissolved phosphate concentrations in water bodies. Total P (TP) is a measure of all the various forms of P found in waters. In NSM, P transport processes are simulated for DIP, DOP, and POP. Sediment sorbed inorganic P (SIP) will be added in future versions of NSM. Figure 6 is a diagram of the overland flow P transport and transformation module used in NSM.

Phosphorus is most commonly assumed to be transported predominantly in particulate forms through soil erosion by surface runoff (Walling et al. 1997, Bowes et al. 2003). However, where soil erosion is limited, the majority of P transported by surface runoff may be in dissolved forms (Haygarth and Jarvis 1997, Heathwaite and Dils 2000). Transfer of soil P to runoff water is controlled by physical and chemical processes such as desorption, dissolution, and diffusion. The interaction between particulate and dissolved P in the runoff is very dynamic and the mechanism of transport is complex. Important processes related to P transport in the runoff

include: detachment and deposition of sediment particles; adsorption and desorption of soluble P to/from sediment particles (House et al. 1995); coprecipitation of P with calcite in hardwaters (House and Donaldson 1986, Jarvie et al. 2002); formation of the ferrous phosphate mineral vivianite in anoxic sediments (Woodruff et al. 1999); and P uptake by aquatic plants through either root or shoot. The combination of all of these processes, in tandem with variations in overland flow and other environmental factors, drives the following mass balance equations of P transport and transformation processes. This section summarizes the governing equations used to simulate P transport and transformation in the overland flow.
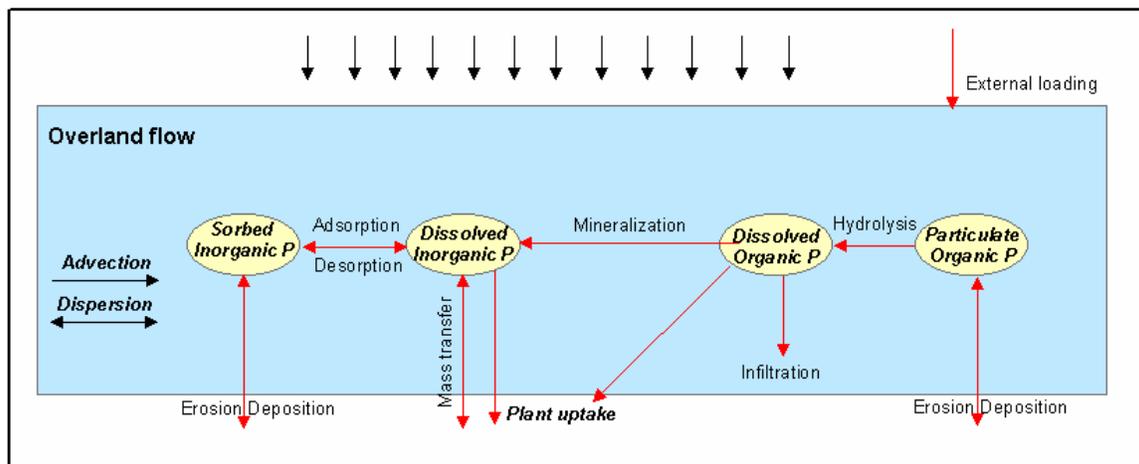

Figure 6. Overland flow phosphorus transport and transformation module.

Particulate organic phosphorus

Sources and sinks for DOP included in the model are: hydrolysis to DIP, erosion, deposition, and external loads. The mass balance equation of POP transport in 2D overland flow is written for the POP concentration:

$$\frac{\partial(h \cdot POP_{ov})}{\partial t} + \nabla POP_{ov} - \nabla \cdot \nabla POP_{ov}$$
$$= R_{POP,e} - R_{POP,d} - R_{POP,hyd} + S_{POP} \tag{71}$$

where

POP_{ov} = concentration of POP in the overland flow [M/L³]
$R_{POP,d}$ = deposition rate of the overland flow POP [M/L²/T]
$R_{POP,e}$ = total erosion rate from the upper soil layer organic P [M/L²/T]

$R_{POP,hyd}$ = hydrolysis rate of the overland flow POP [M/L²/T]

S_{POP} = external sources added to the overland flow POP [M/L²/T]

Erosion of organic and adsorbed phosphorus occurs in conjunction with surface sediment erosion and is dependent on the presence of surface run-off. The concentration of POP available for transport is calculated as the sum of $orgP_{sta}$, $orgP_{act}$, and $orgP_{frsh}$ in the upper soil. The erosion flux of POP due to runoff is computed by:

$$R_{POP,e} = \sum_{1}^{N} f_{pn} \cdot v_r \cdot orgP_t \tag{72}$$

where

$orgP_t$ = total concentration of organic P in the upper soil layer [M/L³].

The deposition flux of POP in overland flow is computed by:

$$R_{POP,d} = \sum_{1}^{N} f_{pn} \cdot v_{se} \cdot POP_{ov} \tag{73}$$

A portion of the POP hydrolyzes to DOP. Hydrolysis of POP is modeled similarly as:

$$R_{POP,hyd} = k_{hyd} \cdot POP_{ov} \tag{74}$$

Dissolved organic phosphorus

Sources and sinks for DOP included in the model are: hydrolysis from PON, mineralization to DIP, infiltration into soil, and external loads. The mass balance equation of DOP transport in 2D overland flow is written for the DOP concentration:

$$\frac{\partial(h \cdot DOP_{ov})}{\partial t} + \nabla DOP_{ov} - \nabla \cdot \nabla DOP_{ov}$$
$$= R_{POP,hyd} - R_{DOP,f} - R_{DOP,min} + S_{DOP} \tag{75}$$

where

DOP_{ov} = concentration of DOP in the overland flow [M/L³]

$R_{DOP,f}$ = infiltration rate of the overland flow DOP [M/L²/T]
$R_{DOP,min}$ = mineralization rate of the overland flow DOP [M/L²/T]
S_{DOP} = external loadings added to the overland flow DOP [M/L²/T]

The dissolved organic P infiltration flux can be computed from the water infiltration:

$$R_{DOP,f} = f \cdot DOP_{ov} \qquad (76)$$

DOP is mineralized to phosphate. Mineralization of DOP is modeled similarly as:

$$R_{DOP,min} = k_{min} \cdot DOP_{ov} \qquad (77)$$

Dissolved inorganic phosphorus

Inorganic P is mainly transported into the waters via surface runoff, either as particulate P bounded to sediment particles in connection with erosion or as dissolved P. Once P is in solution, the transition between dissolved and sorbed forms during overland flow can change, mediated by sorption–desorption properties of the sediments. A linear relationship exists between the concentration of PIP in sediment and the concentration of DIP in water at equilibrium. Equilibrium partition coefficients are used to distribute the total between the two states. The mass balance equation of DIP transport in 2D overland flow is written for the DIP concentration:

$$\frac{\partial(h \cdot DIP_{ov})}{\partial t} + \nabla DIP_{ov} - \nabla \cdot \nabla DIP_{ov}$$
$$= R_{DOP,min} - R_{DIP,f} - R_{DIP,e} - R_{DIP,up} + S_{DIP} \qquad (78)$$

where

DIP_{ov} = concentration of DIP in the overland flow [M/L³]
$R_{DIP,f}$ = infiltration rate of the overland flow DIP [M/L²/T]
$R_{DIP,e}$ = mass transfer rate between the upper soil layer and overland flow [M/L²/T]
$R_{DIP,up}$ = plant uptake rate of the overland flow DIP [M/L³]
S_{DIP} = external loadings added to the overland flow DIP [M/L²/T]

The mass transfer flux of the dissolved inorganic P between the soil water and the overland flow can be expressed as:

$$R_{DIP,e} = k_e \cdot \left(P_{sol} - DIP_{ov} \right) \tag{79}$$

The dissolved inorganic P infiltration flux can be computed from the water infiltration:

$$R_{DIP,f} = f \cdot DIP_{ov} \tag{80}$$

4   In-Stream Nutrient Processes

Water quality in estuaries, lakes and reservoirs depends upon the quantity and quality of inflows from the upstream watershed, which is usually the most significant source of pollutants. Streamflow is therefore of primary importance to the health of receiving waters and its quantification is crucial to our ability to manage those systems in an environmentally healthy manner. In order to understand or predict nutrient pollution, the transport and the transformations of nutrients within the channel network are accounted for in NSM. Parameters that affect stream water quality and can be considered pollution indicators include N, P, and C. The in-stream nutrient transformation processes formulations that follow are adapted, in part, from the QUAL2E and CE-QUAL-RIV1 (RIV1) models. Both QUAL2E and RIV1 are 1D comprehensive stream water quality models. In-stream internal sources or sinks are correlated to temperature, which governs kinetic rates of biological or chemical reactions as well as the equilibrium speciation. Water quality constituents that can be simulated in the current NSM version are:

- Algae as Chlorophyll *a*
- Organic Nitrogen (*orgN*)
- Ammonia Nitrogen (NH_4^+)
- Nitrate Nitrogen (NO_3^-)
- Organic Phosphorus (*orgP*)
- Inorganic Phosphorus (*irgP*)
- Carbonaceous Biological Oxygen Demand (*CBOD*)
- Dissolved Oxygen (*DO*)

Figure 7 shows the stream water quality state variables and interaction.
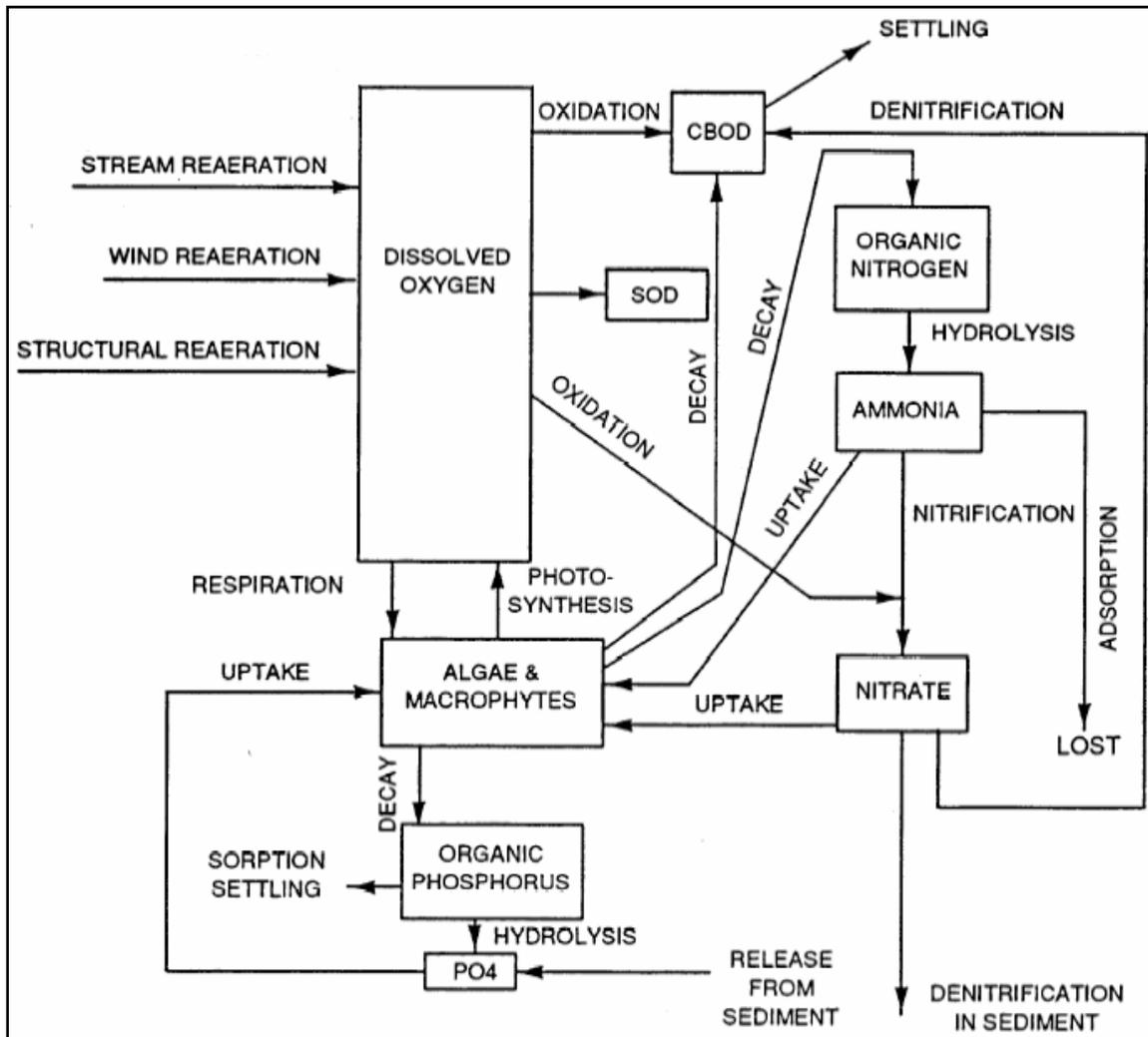
Figure 7. Schematic of in-stream water quality state variables and interaction.

In-stream algae

During the day, algae increases the stream's dissolved oxygen concentration via photosynthesis. At night, algae reduce the concentration via respiration. As algae grow and die, they form part of the in-stream nutrient cycle.

Chlorophyll *a*

Chlorophyll *a* is assumed to be directly proportional to the concentration of phytoplanktonic algal biomass.

$$chla_{ch} = \alpha_o \cdot alg_{ch} \qquad (81)$$

where

$chla_{ch}$ = chlorophyll a concentration [M/V]
a_o = ratio of chlorophyll a to algal biomass [M/M]
alg_{ch} = algae biomass concentration [M/V]

Algal growth

Growth and decay of algae/chlorophyll a are calculated as a function of the growth rate, the respiration rate, the settling rate, and the amount of algae present in the stream. The change in algal biomass is given as:

$$\frac{dalg_{ch}}{dt} = \mu_a \cdot alg_{ch} - \rho_a \cdot alg_{ch} - \frac{\sigma_1}{D} \cdot alg_{ch} \qquad (82)$$

where
μ_a = local specific growth rate of algae [1/T]
ρ_a = local respiration or death rate of algae [1/T]
σ_1 = local settling rate for algae [L/T]
D = the depth of water in the channel [L]

Local specific growth rate of algae

The local specific growth rate of algae is a function of the availability of required nutrients, light, and temperature. A variety of mathematical equations for calculating multiple nutrient-light limitations on algae growth rate has been reported. In QUAL2E, the user has three options for calculating the specific algal growth rate: 1) multiplicative; 2) limiting nutrient; and 3) harmonic mean.

Multiplicative option

The multiplicative option multiplies the growth factors for light, N, and P together to determine their net effect on the local algal growth rate. This option has its biological basis in the multiplicative effects of enzymatic processes involved in photosynthesis:

$$\mu_{a,20} = \mu_{max} \cdot FL \cdot FN \cdot FP \qquad (83)$$

where
$\mu_{a,20}$ = local specific algal growth rate at 20 °C [1/T]

μ_{max} = maximum specific algal growth rate [1/T]
FL = algal growth attention factor for light
FN = algal growth limitation factor for N
FP = algal growth limitation factor for P

Limiting nutrient option

The limiting nutrient option calculates the local algal growth rate as limited by light and either N or P. The nutrient/light effects are multiplicative, but the nutrient/nutrient effects are alternate. The algal growth rate is controlled by the nutrient with the smaller growth limitation factor. This approach mimics Liebig's law of the minimum:

$$\mu_{a,20} = \mu_{max} \cdot FL \cdot \min(FN, FP) \tag{84}$$

Harmonic mean option

The harmonic mean is mathematically analogous to the total resistance of two resistors in parallel and can be considered a compromise between the previous two equations. The algal growth rate is controlled by a multiplicative relation between light and nutrients, while the nutrient/nutrient interactions are represented by a harmonic mean.

$$\mu_{a,20} = \mu_{max} \cdot FL \cdot \frac{2}{\left(\dfrac{1}{FN} + \dfrac{1}{FP}\right)} \tag{85}$$

Algal growth limiting factor for light

A number of mathematical relationships between photosynthesis and light have been developed. All relationships show an increase in photosynthesis rate with increasing light intensity up to a maximum or saturation value. The algal growth limiting factor for light is calculated using a Monod half-saturation method. In this option, the algal growth limitation factor for light is defined by a Monod expression:

$$FL_z = \frac{I_{pht,z}}{K_L + I_{pht,z}} \tag{86}$$

where
FL_z = algal growth attenuation factor for light at depth z

$I_{pht,z}$ = photosynthetically active light intensity at a depth z below the water surface [W/L²-T], which is radiation with a wavelength between 400 and 700 nm

K_L = half-saturation coefficient for light [W/L²-T], which is defined as the light intensity at which the algal growth rate is 50 percent of the maximum growth rate

Photosynthesis is assumed to occur throughout the depth of the water column. The variation in light intensity with depth is defined by Beer's Law:

$$I_{pht,z} = I_{pht,hr} \exp\left(-k_l \cdot z\right) \tag{87}$$

where

$I_{pht,hr}$ = photosynthetically active solar radiation reaching the ground/water surface during a specific hour on a given day [W/L²-T]

k_l = light extinction coefficient [1/L]

z = depth from the water surface [L]

Substituting Equation 86 into 87 and integrating over the depth of flow gives:

$$FL = \left(\frac{1}{k_l \cdot D}\right) \cdot \ln\left[\frac{K_L + I_{pht,hr}}{K_L + I_{pht,hr} \exp\left(-k_l \cdot D\right)}\right] \tag{88}$$

The photosynthetically active solar radiation is calculated as:

$$I_{pht,hr} = I_{hr} \cdot fr_{pht} \tag{89}$$

where

I_{hr} = solar radiation reaching the ground during a specific time on the current day of simulation [W/L²-T]

fr_{pht} = fraction of solar radiation that is photosynthetically active

Algal growth limiting factor for nutrients

The algal growth limiting factor for N will be defined by a Monod expression. Algae are assumed to use both ammonia and nitrate as a source of inorganic N.

$$FN = \frac{NO_{3\,ch}^- + NH_{4\,ch}^+}{\left(NO_{3\,ch}^- + NH_{4\,ch}^+\right) + K_N} \qquad (90)$$

where

$NO_{3\,ch}^-$ = nitrate concentration in the stream [M/V]

$NH_{4\,ch}^+$ = ammonium concentration in the stream [M/V]

K_N = Michaelis-Menton half-saturation constant for N [M/V]

The algal growth limiting factor for P is defined as a Monod expression.

$$FP = \frac{DP_{ch}}{DP_{ch} + K_P} \qquad (91)$$

where

DP_{ch} = concentration of dissolved P in the stream [M/V]

K_P = Michaelis-Menton half-saturation constant for P [M/V]

The Michaelis-Menton half-saturation constant for N and P defines the concentration of N and P at which algal growth is limited to 50 percent of the maximum growth rate. Users are allowed to set these values. Typical values of K_N range from 0.01 to 0.30 mg N/L while K_P will range from 0.001 to 0.05 mg P/L.

Temperature factors affecting algae growth

Algal growth and death rates are temperature dependent. If the algal growth rate at 20 °C is calculated, the rate coefficient is then adjusted for temperature effects using a Streeter-Phelps type formulation:

$$\mu_a = \mu_{a,20} \cdot 1.047^{(T_{wat} - 20)} \qquad (92)$$

where

T_{wat} = average water temperature for the day [T]

The local respiration or death rate of algae represents the net effect of three processes: 1) the endogenous respiration of algae, 2) the conversion of algal P to organic P, and 3) the conversion of algal N to organic N. The respiration rate is adjusted to the local water temperature using the relationship:

$$\rho_a = \rho_{a,20} \cdot 1.047^{(T_{wat}-20)} \tag{93}$$

The local settling rate of algae represents the net removal of algae due to settling. The settling rate of algae is adjusted to the local water temperature using the relationship:

$$\sigma_l = \sigma_{l,20} \cdot 1.024^{(T_{wat}-20)} \tag{94}$$

where
$\sigma_{l,20}$ = local algal settling rate at 20 °C [L/T]

Chlorophyll *a* in surface runoff

The algal biomass loading to the stream can be estimated as the chlorophyll *a* loading from the land area. The chlorophyll *a* concentration in surface runoff is calculated using a simplified version of Cluis et al.'s exponential function (1988):

$$chla_{ov} = 0 \quad \text{if} \left(Q_{ov} < 10^{-5}\, m^3/s\right) \text{or} \left(TP \text{ and } TN < 10^{-6}\right) \tag{95}$$

$$chla_{ov} = \frac{0.5 \cdot 10^{2.7}}{Q_{ov}} \quad \text{if} \left(Q_{ov} > 10^{-5}\, m^3/s\right) \text{or} \left(TP \text{ and } TN > 10^{-6}\right) \tag{96}$$

$$chla_{ov} = \frac{0.5 \cdot 10^{0.5}}{Q_{ov}} \quad \text{if} \left(Q_{ov} > 10^{-5}\, m^3/s\right) \text{or} \left(TP < 10^{-6} \text{ and } TN >< 10^{-6}\right) \tag{97}$$

where
$chla_{ov}$ = chlorophyll *a* concentration in the surface runoff [M/V]
Q_{ov} = surface runoff [L]
TN = total Kjeldahl N load (kmoles)
TP = total P load (kmoles)

In-stream nitrogen

In aerobic water, there is a stepwise transformation from organic N to ammonia, to nitrite, and finally to nitrate. The forms of N simulated by the model are organic N, ammonium, and nitrate. Nitrite is not considered because the overall rate of nitrification is ammonia-limited (Parker et al. 1975), and stream surveys do not exhibit significant increases in nitrite in

nitrifying reaches (Garland 1978, Miller and Jennings 1979). This section summarizes the equations used to simulate the N cycle in the stream.

Organic nitrogen

The amount of organic N in the stream may be increased by the conversion of algal biomass N to organic N. Organic N concentration in the stream may be decreased by the conversion of organic N to ammonia or the settling of organic N with sediment. The change in organic N concentration is calculated as:

$$\frac{\partial orgN_{ch}}{\partial t} + \frac{\partial N_{ch,org}}{\partial x} = \alpha_l \cdot \rho_a \cdot alg_{ch} - \beta_{N,3} \cdot orgN_{ch} - \sigma_4 \cdot orgN_{ch} \tag{98}$$

where

$orgN_{ch}$ = organic N concentration in the stream [M/V]

α_l = fraction of algal biomass that is N

$\beta_{N,3}$ = rate constant for hydrolysis of organic N to NH_4^+ [1/T]

σ_4 = organic N settling rate [1/T]

$N_{ch,org}$ is the total organic N transport flux in the channel direction (has two components, advective and dispersive):

$$N_{ch,org} = u_x \cdot orgN_{ov} - D_x \frac{\partial orgN_{ov}}{\partial x} \tag{99}$$

Ammonium nitrogen

The amount of ammonium in the stream may be increased by the mineralization of organic N and diffusion of ammonium from the streambed sediments. The ammonium concentration in the stream may be decreased by the conversion of NH_4^+ to NO_3^- or the uptake of NH_4^+ by algae. The change in ammonium concentration is calculated as:

$$\frac{\partial NH_{4ch}^+}{\partial t} + \frac{\partial N_{ch,NH}}{\partial x}$$

$$= \beta_{N,3} \cdot orgN_{ch} - \beta_{N,1} \cdot NH_{4ch}^+ + \frac{\sigma_3}{1000 \cdot D} - fr_{NH_4^+} \cdot \alpha_l \cdot \mu_a \cdot alg_{ch} \tag{100}$$

where

$\beta_{N,1}$ = nitrification rate constant of NH_4^+ [1/T]

σ_3 = benthos (sediment) source rate for NH_4^+ [M/L²-T]

$fr_{NH_4^+}$ = fraction of algal N uptake from the NH_4^+ pool, and calculated as:

$$fr_{NH_4^+} = \frac{f_{NH_4^+} \cdot NH_{4\,ch}^+}{\left(f_{NH_4^+} \cdot NH_{4\,ch}^+ + \left(1 - f_{NH_4^+}\right) \cdot NO_{3\,ch}^-\right)} \tag{101}$$

where

$f_{NH_4^+}$ = preference factor for NH_4^+

Nitrate nitrogen

The amount of nitrate (NO_3^-) in the stream may be increased by the oxidation of NO_2^-. The conversion of NO_2^- to NO_3^- occurs more rapidly than the conversion of NH_4^+ to NO_2^-, so the amount of nitrite present in the stream is usually very small and not considered in NSM. The nitrate concentration in the stream may be decreased by the uptake of NO_3^- by algae. The change in nitrate concentration is calculated as:

$$\begin{aligned}
&\frac{\partial NO_{3\,ch}^-}{\partial t} + \frac{\partial N_{ch,NO}}{\partial x} \\
&= \beta_{N,1} \cdot NH_{4\,ch}^+ - \beta_{N,2} \cdot NO_{3\,ch}^- - \left(1 - fr_{NH_4^+}\right) \cdot \alpha_l \cdot \mu_a \cdot alg_{ch}
\end{aligned} \tag{102}$$

where

$\beta_{N,2}$ = denitrification rate constant [1/T]

Temperature factors affecting nitrogen transformation

Nitrogen transformation rates are temperature dependent. If the user defines the local rate constant for hydrolysis of organic N to ammonia at 20 °C, the organic N hydrolysis rate will be adjusted to the local water temperature using the relationship:

$$\beta_{N,3} = \beta_{N,3,20} \cdot 1.047^{(T_{wat} - 20)} \tag{103}$$

If the user defines the rate coefficient for organic N settling at 20 °C, the organic N settling rate will be adjusted to the local water temperature using the relationship:

$$\sigma_4 = \sigma_{4,20} \cdot 1.024^{(T_{wat}-20)} \tag{104}$$

The rate constant for biological oxidation of ammonia N will vary as a function of in-stream oxygen concentration and temperature. The rate constant is calculated as:

$$\beta_{N,1} = \beta_{N,1,20} \cdot \left[1 - \exp\left(-0.6 \cdot DO_{ch}\right)\right] \cdot 1.083^{(T_{wat}-20)} \tag{105}$$

where
$\quad \beta_{N,1,20}$ = rate constant for biological oxidation of ammonia N at
$\qquad\qquad$ 20 °C (1/s)
$\quad DO_{ch}$ = DO concentration in the stream [M/V]

If the user defines the benthos source rate for ammonium at 20 °C, the benthos source rate for ammonium N is adjusted to the local water temperature using the relationship:

$$\sigma_3 = \sigma_{3,20} \cdot 1.074^{(T_{wat}-20)} \tag{106}$$

The rate constant for biological oxidation of nitrite to nitrate varies as a function of in-stream oxygen concentration and temperature. The rate constant is calculated as:

$$\beta_{N,2} = \beta_{N,2,20} \cdot \left[1 - \exp\left(-0.6 \cdot DO_{ch}\right)\right] \cdot 1.047^{(T_{wat}-20)} \tag{107}$$

where
$\quad \beta_{N,2,20}$ = rate constant for biological oxidation of nitrite to nitrate at
$\qquad\qquad$ 20 °C

In-stream phosphorus

Although P is not directly toxic in freshwater systems, it is often the limiting nutrient for aquatic growth and high levels can lead to excessive algal or other plant growth. This can result in nuisance issues, as well as contribute to eutrophication. Within the river system, P undergoes numerous

transformation processes in the course of transport. Important processes related to P transformation within the river system include, amongst others, detachment and deposition of sediment particles, and adsorption and desorption of soluble P to/from sediment particles both in suspension and in the riverbed (House et al. 1995).

The P cycle is similar to the N cycle. The death of algae transforms algal P into organic P. Organic P is mineralized to soluble P, which is available for uptake by algae. Organic P may also be removed from the stream by settling. This section summarizes the equations to be used in simulating the P cycle in the stream.

Organic phosphorus

The amount of organic P in the stream may be increased by the conversion of algal biomass to organic P. Organic P concentration in the stream may be decreased by the conversion of organic P to soluble inorganic P or the settling of organic P with the sediment. The change in organic P concentration is calculated as:

$$\frac{\partial orgP_{ch}}{\partial t} + \frac{\partial P_{ch,org}}{\partial x} = \alpha_2 \cdot \rho_a \cdot alg_{ch} - \beta_{P,4} \cdot orgP_{ch} - \sigma_5 \cdot orgP_{ch} \qquad (108)$$

where
$\quad orgP_{ch}$ = dissolved organic P concentration [M/V]
$\qquad \alpha_2$ = fraction of algal biomass that is P [M/M]
$\qquad \beta_{P,4}$ = rate constant for mineralization of organic P [1/T]
$\qquad \sigma_5$ = rate coefficient for organic P settling [1/T]

Inorganic phosphorus

The amount of soluble, inorganic P in the stream may be increased by the mineralization of organic P and diffusion of inorganic P from the streambed sediments. The soluble P concentration in the stream may be decreased by the uptake of inorganic P by algae. The change in soluble P concentration is calculated as:

$$\frac{\partial irgP_{ch}}{\partial t} + \frac{\partial P_{ch,irg}}{\partial x} = \beta_{P,4} \cdot orgP_{ch} + \frac{\sigma_2}{1000 \cdot D} - \alpha_2 \cdot \mu_a \cdot alg_{ch} \qquad (109)$$

where

$irgP_{ch}$ = soluble inorganic P concentration [M/V]
σ_2 = benthos (sediment) source rate for soluble P [M/L²-T]

Temperature factors affecting phosphorus transformation

Phosphorus transformation rates are temperature dependent. If the user defines the local rate constant for mineralization of organic P at 20 °C, the organic P mineralization rate is adjusted to the local water temperature using the relationship:

$$\beta_{P,4} = \beta_{P,4,20} \cdot 1.047^{(T_{wat}-20)} \qquad (110)$$

If the user defines the rate coefficient for organic P settling at 20 °C, the organic P settling rate is adjusted to the local water temperature using the relationship:

$$\sigma_5 = \sigma_{5,20} \cdot 1.024^{(T_{wat}-20)} \qquad (111)$$

If the user defines the benthos source rate for soluble P at 20 °C, the benthos source rate for soluble P is adjusted to the local water temperature using the relationship:

$$\sigma_2 = \sigma_{2,20} \cdot 1.074^{(T_{wat}-20)} \qquad (112)$$

In-stream carbonaceous biological oxygen demand (CBOD)

The CBOD of the water is the amount of oxygen required to decompose the organic material in the water. CBOD is added to the stream with loadings from surface runoff or point sources. Within the stream, two processes are modeled that impact CBOD levels, both of which serve to reduce the carbonaceous biological oxygen demand as the water moves downstream. The change in CBOD concentration within the stream can be calculated as:

$$\frac{d\left(CBOD_{ch}\right)}{dt} = -\kappa_1 \cdot CBOD_{ch} - \kappa_3 \cdot CBOD_{ch} \qquad (113)$$

where
κ_1 = CBOD deoxygenation rate [1/T]
κ_3 = settling loss rate of CBOD [1/T]

Temperature factors affecting CBOD

CBOD rate constants are temperature dependent. If the user defines the carbonaceous deoxygenation rate at 20 °C, the CBOD deoxygenation rate will be adjusted to the local water temperature using the relationship:

$$\kappa_1 = \kappa_{1,20} \cdot 1.047^{(T_{wat}-20)} \tag{114}$$

If the user defines the settling loss rate of CBOD at 20 °C, the settling loss rate is adjusted to the local water temperature using the relationship:

$$\kappa_3 = \kappa_{3,20} \cdot 1.024^{(T_{wat}-20)} \tag{115}$$

CBOD in surface runoff

The loading function for the ultimate CBOD from the surface runoff is calculated based on a relationship given by Thomann and Mueller (1987):

$$CBOD_{ov} = 0.001 \cdot \frac{2.7 \cdot orgC_{ov}}{Q_{ov} \cdot area} \tag{116}$$

where
$CBOD_{ov}$ = CBOD concentration in surface runoff [M/V]
$orgC_{ov}$ = organic carbon in surface runoff [M]
$area$ = area of a grid cell [L²]

In-stream dissolved oxygen

An adequate dissolved oxygen concentration is a basic requirement for a healthy aquatic ecosystem. Dissolved oxygen concentrations in streams are a function of atmospheric reaeration, photosynthesis, plant and animal respiration, benthic (sediment) demand, biochemical oxygen demand, nitrification, salinity, and temperature. The change in dissolved oxygen concentration is calculated as:

$$\frac{dDO_{ch}}{dt} = \kappa_2 \cdot \left(DO_{sat} - DO_{ch}\right) + \left(\alpha_3 \cdot \mu_a - \alpha_4 \cdot \rho_a\right) \cdot alg_{ch} - \kappa_1 \cdot CBOD_{ch}$$
$$-\frac{\kappa_4}{1000 \cdot D} - \alpha_5 \cdot \beta_{N,1} \cdot NH_{4\,ch}^+ - \alpha_6 \cdot \beta_{N,2} \cdot NO_{3\,ch}^- \tag{117}$$

where

κ_2 = reaeration rate for Fickian diffusion [1/T]

α_3 = rate of oxygen production per unit of algal photosynthesis [M/M]

α_4 = rate of oxygen uptake per unit of algae respired [M/M]

κ_4 = sediment oxygen demand rate [M/L²-T]

α_5 = rate of oxygen uptake per unit NH_4^+ oxidation [M/M]

α_6 = rate of oxygen uptake per unit NO_3^- oxidation [M/M]

DO_{sat} = DO saturation concentration [M/V]

An equation developed by the American Public Health Association (APHA) (1985) is used to calculate the saturation of dissolved oxygen in freshwater:

$$DO_{sat} = \exp\left[\begin{array}{c} -139.34410 + \dfrac{1.575701 \times 10^5}{T_{wat,K}} - \dfrac{6.642308 \times 10^7}{\left(T_{wat,K}\right)^2} \\[3mm] + \dfrac{1.243800 \times 10^{10}}{\left(T_{wat,K}\right)^3} - \dfrac{8.621949 \times 10^{11}}{\left(T_{wat,K}\right)^4} \end{array}\right] \tag{118}$$

where

$T_{wat,K}$ = water temperature in Kelvin (273.15 + °C)

Reaeration

Reaeration occurs by diffusion of oxygen from the atmosphere into the stream and by the mixing of water and air that occurs during turbulent flow.

Reaeration by Fickian diffusion

Numerous methods have been developed to calculate the reaeration rate at 20 °C. A few of the methods are listed below.

Using field measurements, Churchill et al. (1962) derived the relationship:

$$\kappa_{2,20} = \left(5.03 \cdot v_c^{0.969} \cdot D^{-1.673}\right) \cdot \frac{1}{86400} \tag{119}$$

where

v_c = average stream velocity [L/T]

O'Connor and Dobbins (1958) incorporated stream turbulence characteristics into the equations they developed. For streams with low velocities and isotropic conditions:

$$\kappa_{2,20} = \left(294 \cdot \frac{(D_m \cdot v_c)^{0.5}}{D^{1.5}} \right) \cdot \frac{1}{86400} \tag{120}$$

where
$\quad D_m$ = molecular diffusion coefficient [L²/T], D_m can be calculated:

$$D_m = 177 \cdot 1.037^{(T_{wat} - 20)} \tag{121}$$

For streams with high velocities and nonisotropic conditions:

$$\kappa_{2,20} = \left(2703 \cdot \frac{D_m^{0.5} \cdot slp^{0.25}}{D^{1.25}} \right) \cdot \frac{1}{86400} \tag{122}$$

where
$\quad slp$ = slope of the streambed [L/L]

Owens et al. (1964) developed an equation to determine the reaeration rate for shallow, fast-moving streams where the stream depth is 0.1 to 3.4 m and the velocity is 0.03 to 1.5 m/s.

$$\kappa_{2,20} = \left(5.34 \cdot \frac{v_c^{0.67}}{D^{1.85}} \right) \cdot \frac{1}{86400} \tag{123}$$

Reaeration by turbulent flow over a dam

Reaeration will occur when water falls over a dam, weir, or other structure in the stream. The amount of reaeration that occurs is a function of the oxygen deficit above the structure and a reaeration coefficient:

$$\Delta DO_{ch} = D_a - D_b = D_a \left(1 - \frac{1}{rea} \right) \tag{124}$$

where
$\quad \Delta DO_{ch}$ = change in dissolved oxygen concentration [M/V]
$\quad\quad D_a$ = oxygen deficit above the structure [M/V]

D_b = oxygen deficit below the structure [M/V]
Rea = reaeration coefficient

The oxygen deficit above the structure D_a is calculated as:

$$D_a = DO_{sat} - DO_{str} \qquad (125)$$

Butts and Evans (1983) document the following relationship that can be used to estimate the reaeration coefficient:

$$rea = 1 + 0.38 \cdot coef_a \cdot coef_b \cdot h_{fall} \cdot \left(1 - 0.11 \cdot h_{fall}\right) \cdot \left(1 + 0.046 \cdot \overline{T}_{wat}\right) \qquad (126)$$

where
$coef_a$ = an empirical water quality factor
$coef_b$ = an empirical dam aeration coefficient
h_{fall} = height through which the water falls [L]
$\overline{T}_{wat}$ = average water temperature [T]

The empirical water quality factor is assigned a value based on the condition of the stream, as shown in Table 2.

Table 2. Empirical water quality factor.

Water Quality Description	$Coef_a$
Clean Water	1.80
Slightly Polluted Water	1.60
Moderately Polluted Water	1.00
Grossly Polluted Water	0.65

The empirical dam aeration coefficient is assigned a value based on the type of structure, as shown in Table 3.

Table 3. Empirical dam aeration coefficient.

Structure Type	$Coef_b$
Flat Broad Crested Weir	0.70 to 0.90
Sharp Crested Weir with Straight Slope Face	1.05
Sharp Crested Weir with Vertical Face	0.80
Sluice Gates with Submerged Discharge	0.05

Temperature factors affecting dissolved oxygen

Dissolved oxygen rates are temperature dependent. If the user defines the sediment oxygen demand rate at 20 °C, the sediment oxygen demand rate is then adjusted to the local water temperature using the relationship:

$$\kappa_4 = \kappa_{4,20} \cdot 1.060^{(T_{wat}-20)}$$
(127)

If the user defines the reaeration rate at 20 °C, the reaeration rate is adjusted to the local water temperature using the relationship:

$$\kappa_2 = \kappa_{2,20} \cdot 1.024^{(T_{wat}-20)}$$
(128)

where
$\quad \kappa_{2,20}$ = reaeration rate at 20 °C [1/T]

Dissolved oxygen in surface runoff

Rainfall is assumed to be saturated with oxygen. To determine the dissolved oxygen concentration of surface runoff, the oxygen uptake by the oxygen-demanding substance in runoff is subtracted from the saturation oxygen concentration.

$$DO_{ov} = DO_{sat} - \kappa_1 \cdot CBOD_{ov} \cdot \frac{\Delta t}{24}$$
(129)

where
$\quad DO_{ov}$ = DO concentration in surface runoff [M/V]
$\quad \kappa_1$ = assumed to be 1.047 day^{-1} for this formulation

QUAL2E and similar 1D models lack a clear operational definition of water quality parameters within the model. For example, it is known that many forms of organic N are present in natural waters. QUAL2E combines them all under 'organic N' and does not specify further whether it is TON, Kjeldahl N, particulate, dissolved, or other. In contrast, the CE-QUAL-ICM (ICM) description contains a precise specification of the N, P, and C variables. ICM is a finite volume eutrophication model that can be used to simulate 1-, 2-, 3-dimensional water quality variables including multiple forms of algae, carbon, nitrogen, phosphorus, and silica; and dissolved oxygen (Cerco and Cole 1995). Since ICM contains more processes, it also

contains more state variables. Future versions of NSM will include additional state variables in addition to revised process descriptions to better reflect current understandings of in-stream nutrient processes.

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14. ABSTRACT

Within the System-Wide Water Resources Program (SWWRP), multiple riverine, estuarine, watershed, and subsurface flow models are being modified to address issues of environmental concern. Several integration approaches are either ongoing or proposed to accomplish this task. To have a full system-wide water quality and contaminant capability in SWWRP, the different hydrologic and hydraulic engines must utilize a common water quality and contaminant approach to prevent the arbitrary partitioning of constituents. The goal of this development effort has been to upgrade existing hydrologic and hydraulic models (i.e., water engines) using a common water quality approach in order to facilitate their linkage and application on a system-wide basis.

In keeping with a common water quality approach to model development, a library of water quality kinetics has been developed such that these kinetics can be integrated with a variety of water transport engines. The library of algorithms are able to deal with a multi-species, multi-phase, multi-reaction system, should include both fast (equilibrium-based) and slow (non-equilibrium-based or rate-based) reactions, are easily extensible to new reaction pathways, include both common nutrient and contaminant packages as well as geochemistry, and have a simple, well-defined data interface and calling procedure, making them portable. The modules are developed such that they are data structure independent, thus facilitating their integration into a wide range of modeling systems.

15. SUBJECT TERMS		
Nutrients Nutrient sub-module	NSM Water quality Kinetics	

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