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MASTER DEGREE IN ENVIRONMENTAL ENGINEERING



MASTER THESIS

Modeling nitrate transport in watersheds using travel time distributions

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1 Introduction

1.1 Nitrate pollution

The inexorable global population growth has led to an increasing need for food and, consequently, to a continuous improvement in farming and agriculture aimed at making the most of the limited available land. Especially during the second half of the 20th century, since the industrial synthesis of ammonia by Haber-Bosch, a significant usage of nitrogen fertilizers took place. The applied nitrogen load was frequently disproportionately high in relation to crops demand [13]. The oversupply of anthropogenic nitrogen intruded the nitrogen natural cycle, perturbing its delicate balance, resulting in an excess of stored nitrate in soils. Over the decades it was transported to surface water bodies by means of groundwater and runoff. The excess of nitrate in surface water may impair the environment through the process of eutrophication but also threaten human health in case of high concentrations.

Eutrophication is caused by high contents of nutrients such as nitrogen and phosphorus, their accumulation enhances the growth of aquatic plants and phytoplankton and boosts the formation of algal blooms on the water surface. Algal coverage prevents solar radiation from penetrating the water column, depriving the plants which grow in depth of the light necessary for the survival. As the plants die, the decomposition of the organic residues depletes the oxygen in the water. The reduction of the oxygen available for organisms reaches a point where life in the aquatic ecosystem is no longer possible. The death of aquatic fauna implies the production of additional organic residues which, in turn, undergo biodegradation, increasing the consumption of oxygen.

The issue of water quality depletion caused by nitrate was brought to the attention of European Commission, which in 1991 enacted the Nitrate Directive 91/676/EEC with the aim of protecting water resources against nitrate pollution . The Directive states that Member States are required to identify the *Nitrate Vulnerable Zones*, lands that drain to waters that are subject or susceptible to nitrate pollution (1.1), and there implement action programmes intended to monitor and limit the applied load of fertilizers. A water resource is designed as polluted, or at risk of pollution, when the concentration of nitrate exceed 50 mg/l or when the condition of the resource shows evidences of eutrophication. The countermeasures proposed by the European Commission include the application of the correct amount

of nutrients needed by each crop type, the definition of suitable climatic conditions to deliver them in order to avoid losses into the environment, and a safe management of animal manure.



Figure 1.1. Nitrate Vulnerable Zones designated areas (2015). Blue striped areas correspond to the Countries who decided to apply the action programmes over the whole territory (Image source: European Commission, Joint Research Centre - Water unit).

In Italy the directive was transposed as the Legislative Decree n.152 of 11 May 1999, afterwards repealed and replaced by the Legislative Decree n.152 of 3 April 2006. In 2007 the areas designed as NVZ almost covered 31,8% of the national SAU (surface used for agricultural purposes) and are mainly concentrated in the Po valley. Figure 1.2 shows the NVZs identified in Piemonte according to the Regional Regulation 9/R of 2002 and further zones added in 2012 with the Regional Regulation 12/R [11].

The establishment of effective strategies to contain nitrate spreading into the environment requires accurate predictions about the fate of the nutrients released on lands. The development of reliable models would allow to estimate, in terms of quality of the surface water, the results of the measures taken and improve them. A tool linking nitrate export to water bodies and hydrological forcing is required, also with a view to deal with climate



Figure 1.2. Nitrate Vulnerable Zones identified in Piemonte, according to DRG 9/R (orange) and 12/R (green) [20].

changes. The recent trend of intense and concentrated precipitation, joined with very dry periods and warm temperatures, affects considerably nitrate transport dynamics in watershed. Nitrate in catchments is, indeed, more prone to be carried by rainwater to the aquifer and finally to the streams.

1.2 Hydrology and water quality

Previously, hydrology and the study of water quality, although sharing the same field of investigation, proceeded independently also for what concern modeling [15]. Actually, these two disciplines are strictly interconnected. The most prominent example is the so-called "old water paradox". It was frequently observed that, despite rainfalls affected the hydrological response of catchments, causing considerable fluctuations in stream discharge, the stream concentration of many solutes remained fairly stable. The reason for that is because the catchment converts the input of the rain in signal of discharge with a certain delay, therefore, the water released to the stream is different from the one that entered the system as precipitation. The observed concentration in the stream is not attributable to the contribution of rain water, but has to be related to the water stored in the catchment before the occurrence of the precipitation event. This example points out the importance of addressing the modeling of solutes hydrological transport with an integrate approach combining catchment hydrology and water quality disciplines.

Travel time distributions (TTDs) allow to track water flow assigning to each water volume its *age*, the time spent within the catchment since its entry as rainwater. The outflow composition in terms of water ages is determined by StorAge Selection functions. Formulating a relationship between water age and the concentration of solute, it is possible to compute the amount of solute transported to the receiving water body.

1.3 Objective of the thesis

The purpose of this thesis is developing a model that could be a tool to understand and predict the fate of agricultural-derived nitrate within watersheds.

Based on the TTDs approach and given the control volume of a catchment, the model would be able to compute non-conservative solutes (nitrate and geogenic solutes) concentration in the draining stream, on the basis of input data of precipitation, evapotranspiration, discharge and anthropogenic activities such as fertilization. The model aims to be used in many catchments with different characteristics, regardless of climate and geology, relying on the possibility of adapting SAS functions to properly represent the catchment response.

A mass-transfer equation would be defined, to regulate solutes exchange between soil and water which allows to compute the concentration in water as a function of the water age. This equation is applicable to both geogenic solutes and nitrate. Geogenic solutes presence in the subsurface could be represented as an infinite storage, which is not depleted by masstransfer with flowing water. Nitrates undergo, instead, a series of bio-geochemical reactions, which can reduce or increase the mass of solute stored in the soil. Therefore, following to a literature research about the modeling of nitrogen cycle in the soil-water system, a nitrate mass-balance would be set out, to define solute availability to hydrological transport.

Once implemented, the model would be tested on a case study catchment, where agriculture and farming are practised and fairly monitored, and a preliminary sensitivity analysis would be carried out. Finally a calibration phase would be conducted, to define the best parameters sets for each solute investigated and to evaluate quantitatively model performances.

The long-term target of future investigations is being able to enlarge the control volume to bigger sets of watersheds and lands.

2 Methods

In this chapter the developed model and the underlying theory are described. First the general approach is introduced, secondly Travel Time Distributions (TTDs) and the concept of water age are outlined and, finally, the modeling of solutes transport is investigated.

2.1 A cacthment-scale approach

2.1.1 Hydrological balance

A catchment, or a watershed, can be defined as all the lands draining to the same outlet. Rainwater falling on a catchment infiltrates in the soil, replenishes groundwater and flows through the porosity of the terrain until it is released to the stream as discharge. Whether they are contained in rainwater or in the solid matrix of the catchment soil, solutes are transported by water until the outlet section. The modeling of stream solute dynamics is therefore linked to the description of water movement within the whole watershed.

If the entire watershed is considered as a control volume, it is possible to set up a water mass balance, stating that all the rain entering the system is either stored in the soil, kept away by evapotranspiration or discharged at the outlet. The storage of water in the control volume is defined as $S(t) = S_0 + V(t)$ where S_0 is the initial storage in the system and V(t)are the storage variations resulting from the hydrological balance (2.1)

$$\frac{dV}{dt} = J(t) - ET(t) - Q(t)$$
(2.1)

where J is the precipitation, ET the evapotranspiration and Q the discharge (figure 2.1).

2.1.2 Travel Time Distributions

The trajectories of water flowing in the subsoil are tortuous and influenced by local discontinuities that may create preferential pathways and bypassing. Describing this flow requires the knowledge of the geological and hydraulic properties of the catchment with an adequate level of spatial resolution. In this thesis is pursued a catchment-scale approach, which only



Figure 2.1. Depiction of the fluxes constituting the hydrological balance of a catchment. [4]

accounts for the catchment as a whole, embedding all the heterogeneities and properties of the watershed in the system integrated response at the outlet. This allows to overcome the issue of the detailed characterization of the porous medium as well as any spatially explicit modeling [5, 21].

This approach is based on the analogy which equates water volumes and populations. Indeed, as a group of people progressively grows older till the day of death, similarly, water "parcels" get older within the catchment until when they are released as an outflow and leave the control volume. Identifying the travel time as the time elapsed between water entrance and exit from the system, the definition of its probability distributions allows to describe how catchments respond to hydrological forcing like rainfall, retaining and releasing water and solutes [7].

Water residence time in hydrological systems can be tracked through two different formulations: the forward one and the backward one. The forward formulation focuses on the moment of the injection, when water enters the system through a rain event. At that time, each water parcel has a life expectancy that defines the time it will reach the outlet section. Water movement is thus described by the time remaining for the parcel to exit the system, when the life-expectancy drops to zero. On the contrary, the backward formulation concentrates on the outlet section and refers to each water volume with its residence time [4]. The latter, hereinafter referred to as the water *age*, is defined as the time spent by a water parcel within a catchment from the moment of its injection through precipitation to its exit as discharge or evapotranspiration. Water age and its determination through the observation of time series of hydrological inputs and outputs is the key to the catchment scale approach. At any time *t* the sum of a parcel's age and life-expectancy is the travel time. The two formulations are equivalent only in the case of a stationary system. Forward formulation is particularly useful when working with tracers, to predict the breakthrough curve at the outlet, in order to define how each input of precipitation contributes to the recorded outflow. Since the aim of this study is understanding how streamwater is the result of inputs of different ages, the backward formulation is preferable.

The water storage, at any time *t* is composed by parcels with different ages *T* which entered the catchment at time t_0 . Hence, at any time *t* the storage is characterized by a distribution of ages $p_S(T, t)$. Similarly, the outflows, discharge and evapotranspiration, are characterized by the age distributions $p_Q(T, t)$ and $p_{ET}(T, t)$, respectively. A useful variable is the rank storage S_T which is defined as $S_T(T, t) = S(t) \int_0^T p_S(\tau, t) d\tau$ and represents the volume of stored water which is younger than *T* at any time *t*. The rank storage varies in time depending on the balance between the inflow of precipitation and the outflows, evapotranspiration and discharge.

2.1.3 StorAge Selection functions

The catchment storage and the out-fluxes are characterized by a distribution of ages p_S , p_Q , P_{ET} . StorAge Selection (SAS) functions describe to what extent volumes of different ages contribute to the outflows. In the form of probability density functions (pdf) they correspond to the ratio between the age distribution of the outflow and the age distribution of the storage (2.2).

$$\omega(T,t) = \frac{p_Q(T,t)}{p_S(T,t)}$$
(2.2)

In this thesis SAS functions are expressed in terms of cumulative distribution functions of the rank storage (CDFs). They are indicated as $\Omega(S_T, t)$ and represent the fraction of the total outflow that is produced by the rank storage S_T , namely the water younger than the age *T*.

Is thus possible to express the hydrological balance (2.1) with respect to the rank storage

$$\frac{\partial S_T(T,t)}{\partial t} + \frac{\partial S_T(T,t)}{\partial T} = J(t) - Q(t) \,\Omega_Q(S_T(T,t),t) - ET(t) \,\Omega_{ET}(S_T(T,t),t) \,, \tag{2.3}$$

Equation (2.3) is known as Age Master Equation and requires the following boundary conditions:

$$S_T(T, t = 0) = S_{T_0} \tag{2.4}$$

$$S_T(T=0,t) = 0$$
 (2.5)

(2.4) defines the initial conditions and (2.5) states that in the storage there are no parcels with an age younger that T = 0.

SAS functions can have any shape, the most common one is the power law shape defined as

$$\Omega(S_T, t) = \left[\frac{S_T(T, t)}{S(t)}\right]^k = \left[\frac{S_T(T, t)}{S_0 + V(t)}\right]^k$$
(2.6)

k, the affinity, is the only parameter and, besides the shape, it determines the preference of the catchment to release younger or older water (figure 2.2). When k > 1 the system tends to discharge older water, while when k < 1 the preference moves towards younger water. Taken to extremes, the case when k > 1 describe a condition of *plug flow*, a vertical system where every time there is a new injection, the water released is always the oldest one. An example of the latter could be a lysimeter: a monitored bounded column of soil used to measure evapotranspiration. The case when k = 1 refers to an ideal condition defined "random sampling" where the age distribution of the outflows is representative of the age distribution of the whole storage.



Figure 2.2. Different shapes of SAS functions as a function of the parameter *k*. In blue and red preference towards younger water, in yellow random sampling and in violet, preference towards older water.

Power-law time-variant SAS functions

The parameter k could also be used to express the impacts of catchment wetness conditions on its hydrological response. In dry conditions, indeed, the catchment tends to release older water since there is no younger water injected through precipitation and the discharge is mainly constituted by water that spent long time within the subsoil. Conversely, when rain events are frequent and the water table is fairly shallow, the system preferably releases younger water, also partly because of superficial runoff [15, 6]. The power law time-variant SAS function, adapts the age distribution to reproduce this behaviour: the parameter kvaries linearly over time between two extremes k_{min} and k_{max} as a function of the catchment index of wetness wi (the computation of this index is described in paragraph 2.2).



Figure 2.3. Depiction of the influence of catchment wetness on SAS functions shape. From blue (lower *k* and more humid conditions) to red (higher *k* and dry conditions).

The discharge age distribution $p_Q(T, t)$ is obtained with the relation

$$p_Q(T,t) = \frac{\partial P_Q(T,t)}{\partial T} = \frac{\partial \Omega_Q(S_T(T,t),t)}{\partial T} = \frac{\partial \Omega_Q(S_T,t)}{\partial S_T} \frac{\partial S_T}{\partial T}$$
(2.7)

where $P_Q(T, t) = \Omega(S_T, t)$ is the cumulative distribution of $p_Q(T, t)$.

To each water parcel stored within the control volume is possible to assign a solute

concentration $C_{ST}(T, t)$. Streamflow solute concentration can then be derived from the integration over the age domain of the product of the parcel concentration and the outflow age distribution:

$$C_Q(t) = \int_0^\infty C_{ST}(T,t) p_Q(T,t) \, dT$$
 (2.8)

The same applies for the concentration of the evapotranspiration flux $C_{ET}(T, t)$.

Step SAS function for evapotranspiration

To describe how evapotranspiration fluxes are composed in terms of water age, in the model was introduced a SAS function whit a shape different from the power-law one. The pdf is a



Figure 2.4. Shape of the probability density function and cumulative density function used for evapotranspiration, defined by the sole parameter *u*.

step function characterized by the sole parameter u which varies between the interval [0 1] (figure 2.4). This SAS function allows simultaneously to neglect the tail of the distribution and to uniform the contribution of the youngest fraction of water. The exponential shape, in fact, rises rapidly in the first part of the age distribution, giving major importance to the very youngest volumes of water and leading to also significant differences for close age classes. Moreover, evapotranspiration flux act mainly in the soil between the surface, where air heat and convection flows force water to evaporate, and the maximum depth reached by plants roots. The older water is therefore usually a negligible part of this hydrological outflow.

2.2 Model implementation

The model was implemented in MATLAB, integrating the preexisting model *tran*-SAS package [3], which was designed to compute the concentration in streamwater of a tracer, solving the age Master Equation by means of StorAge Selection functions.

The Age Master Equation (2.3) has an exact solution only in the case of random sampling. Therefore, a numerical implementation is required. In the model the equation is converted into a set of ordinary differential equations using the method of characteristics, writing the variable t as $T + t_0$:

$$\frac{dS_T(T, T+t_0)}{dT} = J(T+t_0) - Q(T+t_0)\Omega_Q(S_T, T+t_0) - ET(T+t_0)\Omega_{ET}(S_T, T+t_0)$$
(2.9)

with the initial condition $S_T(0, t_0) = 0$. t_0 is the moment when the water entered the system and *T*, the only variable of the differential equation, is the water age.

The (2.9) is solved by means of a forward Euler scheme, once time and age are discretized using the same time step: $\Delta T = \Delta t = h$. Thus, $T_i = i \cdot h$ and $t_j = j \cdot h$. The fluxes are considered as an average over the interval *h* which refers to its beginning. The same applies for the storage variations resulting from the hydrological balance. The discretized form of equation (2.9) becomes

$$S_T[i+1,j+1] = S_T[i,j] + h \cdot (J[j]\Omega_Q^*[i,j] - ET[j]\Omega_{ET}^*[i,j])$$
(2.10)

for $i, j \in [0, N]$, being N the number of total time steps in the simulation, and with the boundary condition $S_T[0, j] = 0$. [i, j] indicates the numerical evaluation of the function in (T_i, t_j) . $\Omega^*[i, j]$ corresponds to $\Omega(S_T[i, j], t_j)$ and is calculated in order to take into account also the water input carried by the rain event occurring at the same time step:

$$\Omega^*[i,j] = \Omega(S_T[i,j] + e[j], t_j)$$
(2.11)

where

$$e[j] = max(0, J[j] - Q[j]\Omega_Q[0, j-1])$$
(2.12)

is an estimation of the youngest water stored in the system at the end of the time step j [3]. The (2.12) is, indeed, an hydrological balance computed with reference to the SAS function related to the previous time step (j - 1).

The numerical routine starts with the computation of $\Omega^*_{Q,ET}[i, j]$, then the rank storage S_T is determined using equation (2.10) for $i \in [1, n_i]$. To determine the model output, at

each time step the storage concentration C_{ST} is updated according to the chosen formulation. For conservative solutes, for instance, $C_{ST}[i, j]$ corresponds to the precipitation input $C_I[i - j]$. The definition of C_S for non-conservative solutes is investigated in the following paragraph (2.4). Finally, the model computes solute concentration in streamwater: $C_Q[j] = \sum_{i=1}^{n_j} C_{ST}[i, j] \cdot p_Q[i, j] \cdot h.$

Since the age distributions are defined over the domain $[0, +\infty)$, the rank storage is composed by an infinite number of water parcels, among them, the oldest usually represent a negligible contribution with respect to the total stored volume. To perform the calculations over a finite number of elements, the model merges the tail of the age distribution p_Q into a pool of older water to which is assigned a single value of age.

The model also computes at each time step the wetness index wi as the storage variations normalized to the interval [0,1]. This variable gives a general idea of the catchment wetness conditions and is essential when using a power-law time-variant SAS function, but should not be confused with the soil moisture or the soil water content.

2.3 Application to conservative solutes

To better understand the operation and the potential of the model, some results related to the transport of conservative solutes are reported and discussed. Once they enter the system, the amount of conservative solutes dissolved in water is constant since they do not undergo any chemical reaction or degradation process while crossing the watershed. A typical example is deuterium, a stable isotope of hydrogen contained in rainwater, which was used as a tracer for previous studies on this subject [6].

In the reverse of how it happens for non-conservative solutes, streamflow concentration of conservative ones is directly proportional to the amount of younger water released. Indeed, since no mass-transfer phenomena are occurring, parcels' solute concentration is not influenced by water age. Figure 2.5 shows the outcome of a simulation, run setting a constant content of conservative solute in rainwater. Precipitation input is modeled with a sinusoidal shape as it follows a seasonal pattern. Streamflow concentration reproduces the same trend, but the signal is delayed and its amplitude dampened. This is due to the time elapsed between solute's entry in the system through precipitation and the moment when it is released at the outlet. SAS functions modulate this retention time. Indeed, as emphasized in the figure, the more the catchment presents an affinity for younger water, the quicker and reactive is the response in terms of solute concentration (orange line). An higher value of affinity k_Q implies, instead, mitigated fluctuations, since concentrated water is released later. It is also highlighted in figure how to each strong precipitation event, and hence high discharge, corresponds a rise in the streamflow concentration.



Figure 2.5. Example of modeled streamflow concentration of conservative solute, with catchment affinity for younger water (orange line) and older water (blue line).



Figure 2.6. Modeled streamflow concentration of a conservative solute, in the case of an input which instantaneously rises and is suddenly interrupted after about one year, for different values of affinity k_Q .

Figure 2.6 displays how streamflow concentration reflects a step reduction up to 0 of a constant input of conservative solute. When discharge affinity k_Q is higher and the catchment tends to release younger water, system responsiveness is appreciably higher than with a lower k_Q . Indeed, streamwater concentration rises quicker in response to the solute supply and similarly returns earlier to the initial condition.

2.4 Non-conservative solutes transport

2.4.1 Mass transfer equation

Non-conservative solutes, contrary to isotopes, do not preserve their concentration along the path through the soil: they can be already present in the soil and being mobilized by the flowing water and can undergo biochemical reactions. Geogenic solutes, like magnesium and silicon, derive from the weathering of rocks and minerals; nitrate and chloride, on the other hand, are mainly a result of anthropogenic activities such as agriculture, farming or wastewater treatments. Independently of the kind of solute, its transfer between soil and



Figure 2.7. Graphical representation of mass-exchange between mobile water and soil matrix, with an high concentration of solute.

water flowing throughout the watershed can be expressed with the equation

$$\frac{\partial C_{ST}(T,t)}{\partial T} = k \cdot (C_{lim} - C_{ST}(T,t))$$
(2.13)

k is a first order kinetic constant which regulates the mass exchange between the solid phase, which has an high concentration of solute, and the liquid phase, with a lower concentration (C_{ST}) . C_{lim} is the limit concentration: the maximum concentration that the liquid phase can achieve once at the equilibrium with the solid phase [5]. Theoretically, the equation is valid



Figure 2.8. Trend of the storage solute concentration C_{ST} , normalized with respect to the limit concentration C_{lim} , as a function of time and of the kinetic constant *k*.

also in the case of an higher concentration of solute in the liquid phase. In these circumstances, the transfer of solute would occur in the opposite direction, i.e from the mobile water to the soil matrix.

The solute concentration of the water in contact with the soil matrix, assuming a residence time high enough for the equilibrium to be achieved, would follow a trend like the one depicted in figure 2.8. The concentration would rise, from an initial value C_0 which could be zero or could coincide with the concentration in rainwater, to the limit concentration C_{lim} at the equilibrium. The speed at which C_{lim} is reached, is function of the kinetic constant: the higher k, the lower the time required. Thus, the longer the time spent by the water in contact with the soil matrix, the more considerable the mass exchange, and, the older the age of the water, the higher its solute concentration. Moreover, the transfer of solute is more important the bigger is the concentration gradient between C_{lim} and $C_{ST}(t)$. In usual conditions, rainwater enters the system with a low concentration and is enriched in solute by leaching.

The evolution of C_{ST} over time, follows the trend of a sorption/desorption isotherm. Conceptually C_{lim} coincides with the equilibrium concentration, but it is called differently to avoid misinterpretation, since it is appropriate to mention the equilibrium only in the case of the achievement of a steady state. The value of the limit concentration depends on the amount of solute contained in the immobile phase and varies with temperature, pH and other parameters which influences the dissolution process. At the catchment-scale, significantly larger than the scale of spatial heterogeneities, it is possible to identify spatially uniform limit concentration [5]. In this study C_{lim} is assumed as constant for geogenic solute and time-variant for nitrate, as described in paragraph 2.4.3.

2.4.2 Geogenic solutes

The most common geogenic solutes are magnesium, silicon, and sodium. Their presence in streamwater is mainly due to erosion of rocks and minerals by groundwater. To model how mobile water is enriched of this kind of solutes, equation (2.13) is used, where C_{lim} is set as constant. An inexhaustible source of solute is assumed to be located in the soil: the amount mobilized by water does not impoverish the total mass available (figure 2.9). Accounting



Figure 2.9. Scheme of mass-transfer of geogenic solutes between mobile water and soil.

also for the solute concentration in rainwater C_J , the equation describing the mass-exchange becomes $\frac{\partial C_{ex}(T, t)}{\partial C_{ex}(T, t)}$

$$\frac{\partial C_{ST}(T,t)}{\partial T} = C_J(t) + k \cdot (C_{lim} - C_{ST}(T,t))$$
(2.14)

The concentration at the outlet C_Q , according to (2.8) is calculated with the equation

$$C_Q(t) = \int_0^T C_{ST}(T, t) \cdot p_Q(T, t) \, dT$$
(2.15)

An example of the age distribution of the discharge p_Q is presented in figure 2.10. The oldest water parcels present an higher concentration of solute since they spent a longer time in contact with the source. The youngest, instead, have a lower concentration being released earlier than the abovementioned.



Figure 2.10. Example of age distribution and its link with geogenic solutes concentration in water.

2.4.3 Nitrate

Compared to geogenic solutes, nitrate follows a much more articulated path in the soil-water system. The formulation of the mass transfer between immobile and mobile phase is the same, the difference is in the definition of the limit concentration C_{lim} . In its expression lies the complexity of the nitrogen cycle and all the mass fluxes that make the nitrate stored in the soil vary appreciably over time. A brief review of the literature concerning the modeling of nitrogen cycle was necessary to develop the model.

Nitrogen cycle

Nitrogen cycle in the soil-water system (figure 2.11) consists in several processes both biological and physical. The cycle is linked to the one of carbon, since many reactions are carried out by microorganisms and is significantly influenced by soil moisture dynamics.

Nitrogen in soils is mainly present in the organic form, which is the least available for plant uptake and losses through leaching. Organic nitrogen is part of the Soil Organic Matter (SOM), which can be subdivided into three different pools: litter, humus and biomass.

Inputs from the atmosphere such as atmospheric deposition and biological fixation are negligible when considering the catchment scale, since their contribute becomes significant at a wider spatial and temporal scale. Natural nitrogen inflows in the system are then mainly composed by plant residues that enter the litter pool. The organic matter of the litter is biodegraded by biomass, the less complex compounds are metabolized for microorganisms' subsistence and growth, whereas the most complex ones constitute the humus pool and take longer to be degraded.



Figure 2.11. Nitrogen cycle in soil-water systems. Arrows represent mass fluxes. Dashed lines indicates fluxes that can be neglected at a catchment scale under the assumption of an agricultural soil.

Mineral nitrogen consists in ammonium NH_4^+ and nitrate NO_3^- . In this form nitrogen is soluble in water and can be absorbed by vegetation or flushed by water flowing within the porosity of the soil. Mineralization and immobilization are two biological processes which represent the connection between mineral and organic pools. Their occurrence and rates depend on nitrogen availability. In fact, biomass has a fixed nitrogen requirement in order to keep constant its carbon to nitrogen ratio. Whenever there is nitrogen abundance, biomass tends to release the excess of nutrient in the form of ammonium through mineralization. Instead, when organic nitrogen is insufficient for their survival, bacteria immobilizes mineral nitrogen into their cells. In agricultural soils there are usually high nutrients concentrations, as a result of fertilization, therefore we can assume that the biomass nitrogen demand is met with organic matter degradation and only mineralization takes place. Ammonium undergoes nitrification, an oxidation reaction carried out by microorganisms resulting in nitrate. Nitrite is an harmful reaction intermediate of nitrification, but in warm climates its transformation in nitrate is so fast that its presence can be neglected. Ammonium can additionally leave the system through ammonia volatilization, plant uptake, leaching or interaction phenomena with the soil matrix.

Plant uptake is the process through which crops get nutrients from the terrain during the growing season. It can be passive, exploiting transpiration fluxes or, when the latter is not enough to meet the nitrogen demand, active, by the creation of a concentration gradient between roots surface and soil. When soil is particularly rich in nitrogen, the active uptake can be neglected.

Leaching is solute displacement, carried out by water, from the superficial layers of soil to the aquifer and finally to the receiving water body. Is the flux which deserves the greatest attention, constituting a significant nutrients loss and a threat for freshwater resources.

Nitrate also undergoes plant uptake and leaching, with the addition of denitrification. Denitrification is the process of nitrate reduction, performed by anaerobic bacteria, which use the bonded oxygen for their respiration. It results in molecular nitrogen N_2 and other gaseous products *NO* and N_2O .

Besides all the natural occurring phenomena described above, nitrogen cycle at our latitudes is strongly affected by anthropogenic impacts. Inflows due to chemical fertilizers and livestock manure are substantially larger compared to the ones due to natural cycling.

The influence of soil moisture on nitrogen cycle must be mentioned despite being neglected in the implementation of the model both for the sake of simplicity and because the case study catchment didn't provide reliable measurements of that variable. High level of soil moisture leads to the creation of anaerobic or anoxic conditions which prevents biological organic matter degradation. On the other hand, also low water contents reduce the activity of microorganisms due to cells dehydration and decreased mobility. Moreover, a lower soil moisture precludes vegetation growth and hence the decrease of plant residues supplying the litter pool with organic nitrogen. Finally, denitrification, being a process that requires an anoxic environment, is enhanced when soil moisture is high [19].

Nitrate mass balance

With a view to simplify the modeling, this thesis focuses only on the processes directly involving nitrate: fertilization, plant uptake, denitrification, leaching and nitrification (figure 2.12).



Figure 2.12. Scheme of the reactions involving nitrate, in blue the fluxes which will be the subject of the modeling.



Figure 2.13. Fluxes composing nitrate mass balance.

A mass-balance (2.16) can be applied to the nitrate contained within the soil (figure 2.13), hereinafter referred to as M_{NO_3} , or stored mass of nitrate.

$$\frac{dM_{NO_3}}{dt} = \Phi_{NIT}(t) + \Phi_F(t) - \Phi_{PU}(t) - \Phi_{DENIT}(t) - \Phi_{LE}(t)$$
(2.16)

All the terms appearing in the balance are mass fluxes averaged over the whole catchment surface $[ML^{-2}T^{-1}]$.

Nitrification is the connection between nitrate and the rest of the cycle and implies all the reactions and degradation processes regarding the organic pool and held by microorganisms. Describing adequately the processes involving biomass requires a detailed modeling of the carbon cycle and of the catchment's soil properties. Therefore, Φ_{NIT} is here set as a constant flux.

The modeling of fertilization (Φ_F) is detailed in paragraph 2.4.3.

As stated above, in agricultural soils, where the nitrate is abundant, the passive plant uptake can be assumed as the only one occurring. Φ_{PU} can thus be expressed as a function of the transpiration rate [8]. Botter et al., 2006, suggest a formulation of plant uptake rate: $\Phi_{PU}(t) = Tr(t) \cdot \frac{[NO_3]}{k_1}$, where Tr(t) is the transpiration rate $[L^3][T^{-1}]$, $[NO_3]$ is the nitrate concentration in the soil $[M][L^{-3}]$ and k_1 is a coefficient embedding nitrate water solubility and the impact of soil moisture. With regard to this expression, the formula for plant uptake was defined as

$$\Phi_{PU}(t) = ET(t) \cdot \alpha \cdot C_{ET}(t)$$
(2.17)

Evapotranspiration rate is multiplied by the reduction coefficient α to account for the fact that the only flux that plants can exploit is transpiration, nevertheless, ET(t) easier to record at the catchment-scale. C_{ET} is the concentration of nitrate in the water composing the evapotranspiration outflow, calculated with the (2.15).

The same paper expresses the denitrification rate as follows, as a function of soil moisture *s* and the average daily temperature:

$$\Phi_{DENIT}(t) = \begin{cases} \frac{\mu_D \cdot s(t)}{s_{FC}} \beta^{\frac{Temp(t) - 25}{10}} \cdot [NO_3] & \text{if } s(t) \ge s_{FC} \\ 0 & \text{if } s(t) < s_{FC} \end{cases}$$
(2.18)

where μ_D is the maximum denitrification rate per unit concentration of nitrate, achievable at the optimum temperature of 25°C, and s_{FC} is the field capacity, the greatest water content the soil can held before the formation of superficial runoff. For the sake of simplicity, denitrification is here expressed just as a function of the limit concentration:

$$\Phi_{DENIT}(t) = k_{DENIT} \cdot C_{lim}(t) \tag{2.19}$$

Denitrification, indeed, operates on the dissolved fraction of nitrate.

Nitrate losses by leaching are modelled, as for geogenic solutes, as the product of discharge and its nitrate concentration:

$$\Phi_{LE}(t) = Q(t) \cdot C_Q(t) \tag{2.20}$$

Modeling of nitrate transport

Following the same scheme used for geogenic solute, nitrate mass-transfer between the soil and the mobile water is regulated by the equation

$$\frac{\partial C_{ST}(T,t)}{\partial T} = k \cdot (C_{lim}(t) - C_{ST}(T,t))$$
(2.21)

equivalent to the (2.13) except for the time-variant C_{lim} . For nitrate, indeed, the limit concentration achievable by the water flowing through the catchment depends on the total mass of nitrate stored in the soil, which in turns results from the mass balance 2.16.

 k_d is the partitioning coefficient defining the distribution of nitrate between the solid phase and the liquid phase at the equilibrium:

$$k_d = \frac{\frac{M_{NO_3}}{M_{dry}}}{C_{lim}}$$
(2.22)

where M_{dry} is the dry mass of soil contained within the control volume and calculated as $M_{dry} = c_1 \cdot S_{NO_3}$, where c_1 is a constant embedding soil bulk density and S_{NO_3} is a measure of the height of the soil volume involved by the storage of nitrate. This last variable could coincide with the water storage S_0 or, more appropriately, could be smaller, according to the assumption that the presence of nitrate in the undissolved form interests only a superficial fraction of the catchment's soil.

The limit concentration can, thus, be expressed as a function of the mass of nitrate stored in the soil:

$$C_{lim(t)} = \frac{M_{NO_3}(t)}{M_{dry} \cdot k_d} = \frac{M_{NO_3}(t)}{c_1 \cdot S_{NO_3} \cdot k_d}$$
(2.23)

Combining into one the two constants in the denominator, $c = c_1 \cdot k_d$, the 2.23 becomes

$$C_{lim(t)} = \frac{M_{NO_3}(t)}{c \cdot S_{NO_3}}$$
(2.24)

The equation to compute nitrate concentration in the outflows is equivalent to the one for geogenic solutes (2.8):

$$C_{Q,ET(t)} = \int_0^\infty C_{ST}(T,t) \cdot p_{Q,ET}(T,t) \, dT$$
(2.25)

The computation of the nitrate mas balance to evaluate M_{NO_3} is subordinated to the solving of equation (2.25) which defines the amount of solute brought away from the system by hydrological outflows. Therefore, to deal with this linkage, the model numerical routine to compute streamflow concentration starts with an assigned value of C_{lim} for the time t_1 . By means of the latter, it calculates the current concentration of the stored water (2.13) and hence the concentration in the outflows (2.25) required to compute nitrate losses. Known these values, the model solves the nitrate mass balance (2.13), obtaining a value of M_{NO_3} corresponding to the following timestep t_2 . The first value given to C_{lim} is arbitrarily set according to the mean trend of streamflow concentration, taking into account that for sufficiently long simulation interval, the choice of this value does not affect the results of the simulation. The same should apply for the fact that the mass balance of a given time t is actually calculated on the basis of fluxes related to a previous timestep t - 1. Indeed, up to t = 24h, this is still a reasonable approximation.

Modeling of fertilization

Fertilizers can be applied on fields either in the liquid form through irrigation or in the solid form, when they are organic and animal-derived. Especially in the second case, they are spread over lands where they accumulate mainly in the first layers of the subsoil and are afterwards carried in depth by rain water. Since the application in the liquid form is hard to model when the irrigation inputs are unknown, and the case study catchment chosen to test the model is highly exploited for animal breeding (paragraph 3.2), the fertilization was modeled as follows.

The nitrate injected when the fertilization occurs is collected in a subset of the total storage of nitrate, the *fertilizer pool* (figure 2.14). At the time of a rain event, the latter is emptied all the accumulated mass enters the nitrate mass balance (2.16).

The model provides different configurations for what concerns the distribution in time of fertilizer application: constant over the all simulation length, constant over some months or by means of impulses on a regular basis. The second type allows to better reproduce the seasonality of fertilization and is the most precautionary option when the actual application dates are unknown. Even if the composition of fertilizers varies considerably, in this model



Figure 2.14. Scheme of the modeling nitrate input by fertilization.

nitrate supply is considered as a constant value. Organic nitrate introduced by animalderived fertilizers, afterwards transformed in mineral by mineralization, is factored into Φ_{NIT} .

2.4.4 Summary of model parameters and required input data

The model requires input data of hydrological fluxes acting within the control volume defined by the catchment: precipitation rate, rainfall concentration of solute (when relevant) and evapotranspiration rate. The model can compute discharge solving the hydrological balance (equation 2.1), but it is also possible to use measured data of discharge, when available.

To run the model is first necessary to set the desired timestep, which determines the level of detail of the produced outcome. Secondarily it is required to assign a value to the following parameters:

- initial storage $S_0(mm)$
- kinetic constant $k(d^{-1})$
- limit concentration $C_{lim} (mg/l)$
- coefficient $c \left(\frac{l}{mm \cdot ha}\right)$ in the case of nitrate

• SAS functions parameters for evapotranspiration, k_{ET} or u, and discharge, $k_{Q,min}$ and $k_{Q,max}$.

These parameters vary widely according to the catchment and the solute under consideration and thus require to be calibrated by means of experimental data.

As regards nitrate, some additional constants come into play, i.e. coefficient α , related to plant uptake, annual nitrate load supplied by fertilization $(\frac{kg_{NO_3}}{ha \cdot y})$, denitrification rate μ_D (d^{-1}), storage available for nitrate S_{NO_3} (mm) and nitrification flux ϕ_{NIT} ($\frac{kg_{NO_3}}{ha \cdot h}$). The value of these parameters can be either calibrated, as for the ones listed above, or derived by literature or previous investigations on site.

3 Case study

The model was tested and calibrated using data collected on a real catchment in France, for a long time subject of research and, thus, about which many information and published literature are available. In this chapter the case study catchment is described, with particular reference to agricultural practices and nitrate transport.

3.1 The site

The basin of Kervidy-Naizin (figure 3.1) sub-catchment of the Naizin catchment, it is located in Brittany, France (latitude: 48 °, longitude: 357° 10′) and has an area of 4.9 km². It is a second order catchment draining to the Coët-Dan stream, which flows in the Ével river further downstream. The elevation varies between 93 and 135 m above sea level. The geology of the site has been characterized by previous studies: the soil is mainly composed by silt, clay and sandstone materials, the bedrock is composed by fairly fractured schist. The upland areas present a well-drained soil, whereas the one of the bottomland is poorly-drained, with wetlands occurring near the stream channel [18]. The stream is fed by a shallow aquifer, with a marked seasonality and an highly fluctuating water table, which develops in the soil of the bottomlands and in the weathered layer of the hillslopes. The climate can be defined as temperate humid, mean monthly air temperature ranges from 8.4 ° C in winter to 22.9 ° C in summer. The stream reaches the maximum flows in winter and almost dries up during summer (figure 3.2). The values of discharge can overcome $1m^3/s$ in winter [22].

3.2 Land use and fertilization

The catchment is mainly devoted to farming and agriculture, approximatively 30% of the surface is grassland (figure 3.1).

According to Durand, 2004, the catchment revealed an overall excess nitrogen of around 150 kg N ha⁻¹ yr⁻¹. It also reports that previous monitoring showed that "more than 95% of the nitrogen fluxes occur as nitrate", which justifies the focusing on only this form.



Figure 3.1. Location and land use of Naizin catchment. The main cultivation are wheat (orange) and corn (brown). Grassland are indicated in yellow. Blue dots indicate the location of piezometers, the light-blue one the outlet section and the red one the meteorological station. (Image source: AgrHys Environment Research Observatory)

In the years between 1988 and 2001, *Centre d'étude du machinisme agricole, des eaux et des forets* (CEMAGREF) tried to outline the agricultural practices held in the catchment, submitting surveys to the farmers and carrying out field observations. The heterogeneity of the farming in the catchment is such that prevents an exhaustive monitoring and leaves big uncertainties about the applied loads of fertilizers, their nature and the date of injection [12].

According to a study carried out on the catchment [10], crops types are alternated over different fields performing a rotation that optimize fertilizer loads and nitrogen plant uptake in order to make the most of land fertility. Each plant, indeed, has a different demand of nutrients and uptake dynamics. Depending on the crop type, the nitrogen requirement ranges from 150 to 350 kg N ha⁻¹ yr⁻¹ [10]. The breeding of pigs is particularly developed, for that reason too, animal manure and other kinds of organic fertilizers are believed to be applied regularly on fields.

Modeling this complex scheme of fertilization over several years is challenging, therefore, to a first approximation, it is chosen a single value of applied nitrogen load, sufficiently representative of the whole catchment.

3.3 Available data

The site has been monitored since 1992 by the French institution *Institute National de la Recherche Agronomique* (INRA), for what concerns water quality and agricultural impacts on the transport of solutes. These years of research leaded to a remarkably high data availability, which, coupled with abundant published literature, has been useful for the purpose of this thesis. All the data used are provided by the Environment Research Observatory AgrHys, made publicly available for use in education and research [2, 1].

A meteorological station records time series of precipitation, potential evapotranspiration (Penman), temperature solar radiation and other parameters related to climate. Discharge is measured regularly at the outlet by means of a rectangular weir and a water level data logger [10]. Streamwater is monitored at the outlet recording the concentration of more than 40 different solutes. Several piezometers are located on the site to collect data about groundwater.

The period of time where most of the data are available lasts about 12 years between 2000 and 2012. However, except for nitrate, streamflow solutes concentration is only available for the period between 2000 and 2002. All the daily measurements were arbitrarily set as made at 9:00 am to harmonize the dataset and make easier for the model to switch between different time steps.

The dataset included potential evapotranspiration, evaluated with Penman method, (PPET). However, PPET doesn't take into account the constraint of the water availability in the soil, therefore, the amount of water removed by this flux is overestimated. To compute a correct water balance which would not deplete the total storage, it was necessary to commute potential evapotranspiration in evapotranspiration 3.2. The timeseries of *PPET* was multiplied for $\frac{S(t)}{V_0}$ where V_0 is a constant value [L], such as to ensure that the hydrological balance is closed, means that over a certain period of time the storage is able to get back to the initial value S_0 .

The seasonality in the stream discharge repeats itself every year as shown in figure 3.3: the peaks take place in winter and spring whereas between May and November a very low discharge is observed. As can be seen from the second plot of the same figure, in 2001 occurred the highest cumulative discharge over the period 2000-2011.



Figure 3.2. Discharge and evapotranspiration fluxes related to the catchment of Kervidy-Naizin.



Figure 3.3. Discharge recorded over the period 2000-2011 in the stream and cumulative annual discharge.

4 Results

Model performances were tested on the extensive dataset of Naizin catchment. Besides demonstrating the robustness of the implementation, preliminary simulations exposed the influence on the final output of the various parameters involved in the modeling. At this stage differences in solutes transport behaviour have emerged. Subsequently the model was calibrated by means of the same dataset. In this chapter the main results and findings are outlined, as well as the issues raised throughout the calibration process.

4.1 Dynamics of solutes streamflow concentration

For the solutes investigated in this thesis, not deriving by rainwater, the mechanism regulating streamflow concentration is diametrically opposed to the one of conservative solutes. In response to the high flow caused by a rain event, the concentration drops, due to the big amount of younger water with a low solute concentration which has entered the catchment. To each peak in the discharge is thus associated a sudden decrease in streamflow solute concentration. This occurrence is hereinafter referred to as *dilution* effect. On the contrary, when the flow is particularly low, the prevalence of old water leads to higher concentrations, resulting in a signal rather like the mirror-image of the discharge trend. Figure 4.1 reports magnesium streamflow concentration recorded in the case study catchment over the period 2000-2002, as an example of the phenomenon described above.

To expose any difference or analogy among them, streamflow concentrations of several solutes recorded at the outlet of the stream draining the Naizin catchment were compared. Figure 4.2 reports, indeed, the time series of streamflow concentration of sodium, magnesium, silicon, nitrate and chloride, conveniently rescaled to be comparable. It is remarkable how solutes behaviour is extremely similar and follows the same dynamics of dilutions upon the occurrence of a rain event.

However, the plot underlines how nitrate behaves differently in comparison to the other solutes when the discharge is particularly low, such as between July 2001 and January 2002. Over those periods, highlighted in yellow in the figure, nitrate presents a decrease in the



Figure 4.1. Timeseries of magnesium streamflow concentration recorded in Naizin catchment.



Figure 4.2. Normalized streamflow concentration $((C(t) - \overline{C})/\sigma_C)$ of different solutes monitored at Naizin catchment. Yellow bands indicate periods where is noticeable a deviation of nitrate trend from the general one followed by the other analyzed solutes.



Figure 4.3. Detail of figure 4.2

concentration which fades away when the discharge rises, during winter and spring. According to the approach used to set up the model, in periods when flow is low, precipitation is scarce and catchment's conditions are rather dry, the preference would be tending towards the release of older water. Hence, solute streamflow concentration should be higher than in the rest of the hydrological year. In contrast, recorded nitrate concentration is especially low over those intervals of time, departing from the general trend observed for the other solutes.

The calibration phase was designed in such a way as to assess the implications of this particular behaviour on SAS functions and TTDs formulation. Exclusively for nitrate, in addition to the calibrations foreseen also for other solutes over the whole dataset, a supplementary one was planned. The latter covers the interval of the years 2000-2012, with reference to the sole periods of high flow. Excluding the periods where nitrate shows a behaviour in contrast with the other solutes, the calibration is expected to report results consistent with the formulation of the model and comparable to the ones obtained for geogenic solutes.

High flow periods were identified imposing a selection criterion on discharge: measured data of concentration were taken into account only if the logarithm of the corresponding recorded value of discharge was higher than -4. This criterion leads to the exclusion of several days, identified in grey in figure 4.4, constituting more than half of the whole dataset extent. This selection allows to disregard the biggest concentration drops attributable to considerably dry conditions of the catchment.



Figure 4.4. Nitrate streamflow concentration and highlighting of the periods characterized by a scarce flow rate.

4.2 Preliminary testing and sensitivity analysis

The sensitivity analysis consists in inducing variations of the input to understand their impact on the outcome of the model. It makes possible to identify the role of the different parameters and boundary conditions and gives insights on the model dynamics and their relation with the system. Operationally, the model was run several times, manually varying the value of one parameter at a time and examining the fluctuations of the output.

All the simulation were run , both for geogenic solutes and nitrate, always using a time step of 24 hours, given that most of the data have been recorded daily. Inputs from precipitation, negligible in most cases, were set to zero both for nitrate and for geogenic solutes, to draw attention to the mechanism occurring within the catchment.

4.2.1 Initial storage *S*₀

The value of the variable S_0 has a strong impact on the output. The initial storage, indeed, determines the size of the water storage, which represents the volume available for mixing and dispersion mechanisms, affecting thus the age distributions. The higher S_0 , the bigger the storage volume, the older the median age of stored water and the more dumped the catchment response at the outlet (figure 4.5). The contribution of younger water is, indeed, more mitigated in a bigger storage rather than in a smaller one, more reactive and with smaller lag times in the response appearance at the outlet, in terms of water composition. The first plot of figure 4.5, shows how a bigger initial storage implies an higher streamflow



Figure 4.5. Streamflow nitrate concentration as a function of different initial storage S_0 (first plot) and median water ages of the storage (second plot).

concentration of solute and a smoothed dilution effect due to precipitation events. Variable S_0 is impossible to estimate accurately in real catchments which present a pronounced geomorphological heterogeneity, but needs to be derived from a calibration process.

4.2.2 Affinity k_Q

The affinity of discharge outflow k_Q defines SAS functions shape, which influences streamflow solute concentration, affecting the age composition of the water discharged in the receiving water body. The higher k_Q , the more pronounced the preference towards older water, the higher the concentration measured at the outlet section (figure 4.6). High values of k_Q implies, moreover, an output which presents less pronounced fluctuations (red line) compared to the one corresponding to a lower k_Q (yellow line).

The choice of a time-varying power law shape, with a value of k_Q ranging between two extremes, moulding catchment response according to its wetness conditions, allows to better capture solute dynamics providing an improved better fitting. As outlined by the orange line in figure 4.6, indeed, when the discharge is higher, in wetter periods, magnesium streamflow concentration is well described by a low k_Q , whereas in dry periods, an higher value is preferable.



Figure 4.6. Simulation of magnesium streamflow concentration using different values of affinity k_Q . The simulation was run with the following parameters set: $k = 0.1 d^{-1}$, C_{lim} , $S_0 = 1000$ mm.

On the contrary, the impact of k_{ET} on stream concentration C_Q is not as relevant, since evapotranspiration becomes significant only during warm periods when it removes a fraction of the youngest water, also the least charged in solute.

4.2.3 Kinetic constant k

k is a catchment-scale kinetic constant, it regulates the speed of the mass-exchange between solute and the subsurface and, hence, defines how quickly stored water tends to the equilibrium with the immobile phase (2.13). It is an inherent feature of each solute, related to its water solubility and partitioning behaviour. The higher *k*, the higher the solute concentration, at the same contact time. The main evidence of the impact of this variable on the model output is noticeable after a spike in the discharge: *k*, in fact, determines the speed with which the streamflow concentration goes back to ordinary values after the dilution. Figure 4.7 shows how, for sufficiently high values of *k*, water parcels' concentration reaches the limit concentration and this is reflected in streamwater concentration, which after a drop rises asymptotically. On the contrary, for lower *k*, C_{lim} is never achieved since the mass-exchange is not fast enough.

4.2.4 Coefficient c

Coefficient *c* is specific to nitrate and affects the limit concentration C_{lim} , as shown in figure 4.8. Solid lines indicates limit concentration in the different cases: lower values of *c* imply a



Figure 4.7. Magnesium streamflow concentration as a function of different kinetic constants. C_{lim} was set equal to 16.5 mg/l

lower C_{lim} , according to equation (2.24). For sufficiently high values of c, the limit concentration stabilizes at the upper bound, i.e. the value assigned to it at the first timestep t_1 to start the computation. In the simulation plotted in figure this value is 100 mg/l.



Figure 4.8. Nitrate streamflow concentration as a function of different *c*. ($k = 0.1 d^{-1}$, $k_Q = [0.2 0.8]$, u = 0.2, $S_0 = 1000 mm$, $S_{NO_3} = 300 mm$, $k_{denit} = 1.5 \cdot 10^{-3} d^{-1}$, $\alpha = 0.5$)

4.3 Calibration

As mentioned in paragraph 2.4.4, most of the parameters constituting the model differ according to the catchment and the solute under investigation. They clearly can not be determined directly for reasons of time and available technologies. Their values have to be defined with a calibration, by means of a comparison with the data from the case study catchment.

The calibration was run by means of the $DREAM_{ZS}$ software package [24] based on the Markov Chain Monte Carlo method (MCMC), often used for the calibration of hydrological models. The DREAM algorithm compares the outputs of the model obtained evaluating different combinations of the parameters, sampled by the space of possible values by means of a *random walk*, and the concentration measured in the stream. At the end of the process, it reports the posterior distributions of the calibrated parameters, meaning the probability distributions indicating the most probable values that could be assumed by those parameters. Moreover, the model returns the best parameter set between the tested ones: the Maximum A Posteriori values (MAP). The number of iterations was set in order to satisfy a convergence criterion, guarantying a sufficient accuracy in the result. Usually this number ranged between 10^4 and $3 \cdot 10^5$ iterations.

A posterior simulation is the outcome of a set of simulations, run using a certain number of parameters combinations (here 400), sampled from the posterior distributions, so that their distribution is representative of the original one. It is thus possible to use the result of a calibration to evaluate the outcome over a different or longer period of time. Posterior simulations were run including a spinup period, of one year for the interval 2000-2002 and of four years for the interval 2000-2012.

To evaluate the goodness of the fitting, Nash-Sutcliffe efficiency coefficient (NSE) was calculated for the best output of each performed calibration. It is defined as one minus the sum of the squared differences between the predicted and observed values, normalized by the variance of the observed values during the period under investigation:

$$NSE = 1 - \frac{\sum_{t=1}^{N} (x_{modeled}^{t} - x_{obs}^{t})^{2}}{\sum_{t=1}^{N} (x_{obs}^{t} - \overline{x_{obs}})^{2}}$$
(4.1)

where *x* indicates the general variable for which you want to evaluate the match with observed data and *N* is the total number of observations. NSE is usually used to asses the predictive power of hydrological models, thus, applied to values of discharge, but it can also be employed for other variables. In this case it is applied to streamflow concentration C_Q . NSE ranges from $-\infty$ to 1, the higher its value, the better the fit. A NSE lower than 0

		symbol	unit	prior range
	k _Q min	(-)	[0.2 3]	
SAS functions	k _Q max	(-)	[0.2 3]	
SAS functions parameters		k_{ET}	(-)	[0.2 3]
		S_0	(<i>mm</i>)	[500 3000]
	geogenic solutes	k	(d^{-1})	[0.01 0.5]
specific parameters		C_{lim}	(mg/l)	[1 20]
specific parameters	nitrate	k	(d^{-1})	[0.01 0.5]
		С	$(1/(mm \cdot ha))$	[0.01 1]

Table 4.1.	Summary of the	calibration param	eters and	selected	prior	parameter
ranges.						

Table 4.2. Values assigned to the constants of the model

constant	unit	value
denitrification rate μ_D	d^{-1}	$1.5 \cdot 10^{-3}$
nitrification flux ϕ_{NIT}	kg _{NO3} /(ha∙h)	0.04
plant uptake reduction coefficient α	-	0.5
nitrogen annual load	$kg_{NO_3}/(ha\cdot y)$	150
storage available for nitrate S_{NO_3}	mm	300

means that the simulated timeseries has a fit poorer than the one we could get describing the observed values by their simple mean.

4.3.1 2000-2002

A first set of calibrations was run for magnesium, as an example of geogenic solute, and nitrate over the period between 2000 and 2002, since it is the only interval were measured data are available for both solutes. Power law time-varying SAS functions are used for both discharge and evapotranspiration outflows. As regards nitrate, the fertilizer application is modeled as constant over the month between February and September and nil for the rest of the year. Calibration parameters and related prior variation ranges are summarized in table 4.1

The values chosen for each of the other constants forming part of the model are listed in table 4.2.

Magnesium



Figure 4.9. Best output of the posterior simulation of magnesium streamflow concentration. The two coloured dots identify an example of dry and wet day.

Figure 4.9 shows the best output of the posterior simulation run using the MAP obtained for magnesium ($k_{Q,min} = 0.2$, $k_{Q,max} = 0.81$, $k_{ET} = 0.208$, $S_0 = 2811 \text{ mm}$, $k = 0.37 d^{-1}$, $C_{lim} = 15.4 \text{ mg/l}$). The fitting to the measured time series of concentration is rather good, the main dynamics are captured although some of the dilutions are generally underestimated. It is particularly clear how the power law time-variant SAS function shapes the output according to wetness conditions. Indeed, in the period between October 2000 and May 2001, coincident with a period of abundant flow, dilutions are more marked than in the rest of the simulation. By contrast, when discharge is low or absent, fluctuations in the streamwater concentration are weaker. The model output never overcomes the defined value of limit concentration, which behaves like an upper bound. This is a direct result of how the equation describing the solute mass-exchange has been formulated (2.13). The fitting to the observed concentration curve could be further refined adding an exponent to C_{lim} .

Posterior distributions of the calibrated parameters, reported in figure 4.10, show that the values of SAS functions parameters $k_{Q,min}$ and $k_{Q,max}$ are clearly defined. Indeed, the more the distribution shape looks like a bell curve, the fewer the uncertainties around the allocation of the most probable value to the parameter. The same applies to k and C_{lim} . The calibration of S_0 produced a worst result: the shape of the posterior distribution presents an asymptote. This is due to the fact that any value of the initial storage higher than a certain threshold does not lead to any variation in the model output. This phenomenon arises since the very oldest water parcels represent a negligible contribution to the outflow and thus to its chemical composition. Such an issue is typically encountered when dealing with hydrological transport processes, signal carried by older water components is rather uniform and such as to make it difficult to trace the actual age [6]. Additionally, in this



Figure 4.10. Posterior distributions of the calibrated parameters for magnesium. The y-axis represent therelative number per x-axis unit.

case, the tail of the discharge age distribution p_Q is merged by the model, which assigns the same age to every parcel older than a set threshold. As regards k_{ET} , being the posterior distribution rather flat, this parameter has probably a minor influence on the final result.

Nitrate

A calibration was run over the same period for nitrate, in order to compare the results. It is necessary to point out that observed data present some measurement errors in the period between November 2000 and January 2001, where in several days the lowest concentration values are all recorded as 38.6 mg/l. In this calibration was used the SAS function for evap-otranspiration described in paragraph 2.1.3.

Recorded MAP are: $k_{Q,min} = 0.52$, $k_{Q,max} = 0.28$, u = 0.2, $S_0 = 703$, k = 0.086, c = 0.1. The posterior simulations reported a good fitting to measured data, as shown in figure 4.11. The fluctuations are well captured along the whole interval of simulation, in particular in the period until October 2001. Thereafter are noticeable some discrepancies between modeled and observed data, which are stronger in the summer of the year 2001.

Based on the premise that SAS function parameters are expected to be similar for both magnesium and nitrate over the same interval of time, MAP and posterior distributions



Figure 4.11. Best output of the posterior simulations of nitrate streamflow concentration.

revealed some inconsistencies which may be bring to light unforeseen catchment dynamics. As also displayed in figure 4.12, indeed, affinity k_Q presents a minimum value which is higher than the maximum one. Moreover, besides not having the same distribution shape, the value of the initial storage S_0 resulting from the calibration for nitrate is substantially lower compared to the one indicated for magnesium. Kinetic constant k and parameter c seem to be clearly defined. A value of $k = 0.086 d^{-1}$ indicates that water flowing throughout the catchment needs around 11 days to reach the limit concentration C_{lim} .

4.3.2 2000-2012

A second set of calibration was performed with a particular focus on nitrate over the whole period in which data are available: twelve years between 2000 and 2012. The calibration run over the entire dataset did not produce a fully satisfactory outcome, as shown in figure 4.13 which reports the best output among posterior simulations. Indeed, despite correctly reproduced, fluctuations in the concentration are generally underestimated by the model. Moreover, the concentration returned by the model best output is in general lower than the observed one, up to 5-10 mg/l of difference. What just stated is particularly apparent in figure 4.14, which represents an enlargement of figure 4.13.

For what concerns calibrated parameters, resulting MAP are: $k_{Q,min} = 0.39$, $k_{Q,max} = 0.3$, u = 0.997, $S_0 = 2999$, k = 0.078, c = 0.123. The inaccuracy regarding the maximum and minimum affinity persists, although less pronounced. The calibration reported approximately the same values of kinetic constant and parameter *c* obtained with the calibration run over only two years. The value assigned to storage S_0 is very close to the upper end



Figure 4.12. Posterior distributions of the calibrated parameters for nitrate. The y-axis represent the relative number per x-axis unit.



Figure 4.13. Best output of posterior simulations of nitrate streamflow concentration.



Figure 4.14. Detail of figure 4.13.

of the set range. The same applies for parameter u defining SAS function for evapotranspiration outflow, in contrast with what results from previous calibration. For their part, parameters k and c are well defined and reports values very similar to the ones obtained with the previous calibration.

Figure 4.15 reports the posterior simulations, in red is shown the output of the best parameter set identified by the calibration run over the sorted periods, subsequently extended to the whole interval for which measured data are available. Figure 4.16 displays a detail from the aforementioned, showing the period approximately between November 2006 and June 2010. The fitting to observed data is truly remarkable. The fitting is significantly improved, especially with regards to the comparison between figure 4.14 and figure 4.16. Some offsets persist, mostly in the cases of strong rain event and peaks of discharge, when streamflow concentration achieves the most significant drops. MAP are $k_{Q,min} = 0.3$, $k_{Q,max} = 0.51$, u = 0.27, $S_0 = 508 \text{ mm}$, $k = 0.278 \text{ d}^{-1}$, $c = 0.134 l/(mm \cdot ha)$. The problem related to the inversion of the extremes of the variation interval of affinity k_Q is solved. Nevertheless, the value returned for the initial storage S_0 seems to be fairly lower than a reasonable one.

4.3.3 Other solutes

Besides magnesium and nitrate, a calibration was performed for chloride, silicon and sodium, in order to widely test the reliability of the model formulation.

Chloride is a fairly conservative solute, classified as micronutrient for crops and applied on fields under the form of animal manures or chemicals. In absence of a dedicated



Figure 4.15. Best output of posterior simulations of nitrate streamflow concentration, resulting from the calibration run with respect to the sole periods characterized by high flow rate.



Figure 4.16. Detail of figure 4.15.



Figure 4.17. Best output of posterior simulation of chloride streamflow concentration.

formulation to model streamflow concentration, the simple mass-transfer equation formulation is chosen, as for geogenic solute, since there is no natural process by which chloride is degraded into the environment. Input through fertilization and plant uptake are not taken into account, although rather relevant.

Figure 4.17 reports the obtained posterior simulations. MAP are $k_{Q,min} = 0.31$, $k_{Q,max} = 0.69$, u = 0.05, $S_0 = 2982 mm$, $k = 0.5 d^{-1}$, $C_{lim} = 35.6 mg/l$. It is remarkable how chloride streamflow concentration follows the same trend of magnesium, accurately reproduced by geogenic solutes' equations set, except for two peaks observed in autumn 2000 and winter 2001-2002. Both those deviations coincide with a period of low flow rate, the same one during which nitrate presents a decrease.

As regards silicon and sodium, being geogenic solutes by definition, the formulation applied for magnesium and chloride was used. Sodium is an alkali metal, found in groundwater due to erosion of salt deposits and sodium bearing rock minerals. Both are main constituent of earth's crust and commonly detected in surface water. Silicon is released to groundwater through weathering of silicate and quartz. Inputs from atmospheric deposition are also remarkable.

The outcome of the calibration run with respect to sodium is displayed in figure 4.18. MAP are: $k_{Q,min} = 0.32$, $k_{Q,max} = 0.74$, u = 0.015, $S_0 = 2998 \text{ mm}$, $k = 0.5 \text{ } d^{-1}$, $C_{lim} = 18.65 \text{ } mg/l$. Sodium modeled C_Q resembles the one of magnesium. Measured data reports the same peaks observed for the other solutes.

Figure 4.19 reports the best output of posterior simulations of silicon streamflow concentration resulting from the calibration. By comparing the evolution of geogenic solutes



Figure 4.18. Best output of posterior simulations of sodium streamflow concentration.

streamwater concentration along the analyzed period, it appears that silicon presents a peculiar behaviour, with wider fluctuations. Although during the majority of the periods the measured trend is well reproduced, peaks located around October 2000 and the end of year 2001 are not reflected by the modeled concentration timeseries. Reported MAP are: $k_{Q,min} = 0.39$, $k_{Q,max} = 0.43$, u = 0.034, $S_0 = 2426 \text{ mm}$, $k = 0.014 \text{ } d^{-1} \text{ } C_{lim} = 5.26 \text{ } mg/l$. NSE is equal to 0.22.

As for chloride, silicon C_Q rises in autumn 2000 and winter 2001, when the flow is particularly scarce, those spikes are not fully captured by the model.

4.3.4 Nash-Sutcliffe efficiencies

Figure 4.20 reports the Nash-Suctliffe efficiencies calculated for the posterior simulations following the calibration process. As regards geogenic solutes, the model reported values around 0.4 and 0.5 for magnesium, chlorine and sodium. Silicon showed a lower NSE, indeed, posterior simulation depicted in figure 4.19 showed a poor fitting to measured data. The two graph at the bottom of figure 4.20 reports the NSE obtained when simulating nitrate streamflow concentration. It appears that NSE is significantly higher when the model is run with respect to the sole periods characterized by high flow (~ 0.55), rather than over the whole interval of time (~ 0.26).



Figure 4.19. Best output of posterior simulations of silicon streamflow concentration.



Figure 4.20. NSE of the posterior simulations of different solutes.

5 Discussion

In the first section of this chapter the validity of the model is assessed, in the second one the main processes explaining peculiar solutes dynamics highlighted by the the calibration phase are investigated. Finally, some example of future applications are presented.

5.1 Robustness of the model

5.1.1 Relevance of TTDs

TTDs have proved to be a useful tool to describe water transport within catchments. This has been pointed out when comparing model outputs with observed data of streamflow concentration and discharge: despite a certain level of uncertainty derived by parameters related to solutes properties, the model was able to reproduce the main dynamics observed in the data.

Additionally, it was possible to assess the proper functioning of the time-varying SAS functions formulation, addressing two days belonging to the simulation interval and observing the related age distributions. As depicted in figure 4.9, the 14 December 2000 was chosen as an example of a day with a high discharge ("wet" day, blue dot) and the 16 May 2000 was identified as an example of a "dry" day (yellow dot). For both days the probability density function of the streamflow water age and its cumulative form were analyzed (figure 5.1). The CDFs, plotted on a logarithmic scale, show how during the wetter day, the streamflow contains a higher fraction of younger water. In fact, in the drier day, there is no contribution of water younger than two days in the discharge, because no precipitation fell on the catchment during those days. Accordingly, the pdf of the wetter days presents a pronounced spike at the beginning located ahead of the one related to the drier day. This is reflected in the streamflow concentration: in the drier day, a large amount of older water, which had more time within the catchment's soil to be charged with solute, entails a higher concentration. During the wet day, instead, stream outflow was mainly composed by young water brought by precipitation, carrying a lower solute contribution and diluting the concentration. In the plot on the right, the computation stops when the age overcomes a certain



Figure 5.1. pdf and CDF of the water age of the streamflow in the selected days. In blue the wet day and in orange the dry one. The plots are enlargements, to focus on the youngest part of the distributions.

value of time. Over 20% of the water in the wet day and 50% in the dry day have an age older than that threshold.

5.1.2 Applicability of mass-transfer equation

The robustness of the mass-transfer equation approach can be further appreciated by means of the test presented in the following. The outcome of a simulation, run to compute stream-flow concentration of a generic geogenic solute by means of the MAP obtained for magnesium, was superimposed to the concentration time series of several solutes recorded at Naizin catchment outlet, following proper normalization (figure 5.2). It becomes clear how, despite some spikes and drops distinctive of each one, the model proved to be suitable to describe the general trends of every solute investigated. Except for nitrate, which undergoes different dynamics, detailed in the following paragraphs, the formulation could be applied to geogenic solutes varying on case-by-case basis the kinetic constant and the limit concentration. This is enabled by the fact that parameters defining solute transport (k_Q) and geochemical parameters (C_{lim} and k) are not coupled.

Figure 5.3 shows a comparison between the posterior distributions of the main parameters for the different solutes investigated. Parameters $k_{Q,min}$ and $k_{Q,max}$ present, in general, well defined distributions for all the solutes. In particular, geogenic solute reported



Figure 5.2. Streamflow concentration of solutes recorded in Naizin catchment, in black is reported the output of the model when using the equation set defined for geogenic solutes ($k = 0.37d^{-1}$). Solutes concentration timeseries are normalized, subtracting the mean and dividing by the standard deviation, in order to allow the comparison among them.



Figure 5.3. Posterior distributions of some model parameters, for the different solutes investigated. The unit on the y-axes are relative number per x-axis unit.

very similar distributions of the parameter $k_{Q,max}$. The parameters distributions obtained for nitrate when calibrating the model excluding the very driest periods (light blue line), are closer to the ones of geogenic solutes than the ones obtained when calibrating over the whole dataset extent (purple line). On the contrary, the value of parameter k is not determined, especially in the case of geogenic solutes. This may be related to a correlation between k value and the water age scale, regulated by the storage S_0 . Indeed, at the calibration stage, the model probably modulated the value of k in order to induce the adequate dilution to compensate S_0 impact on the final output. In other words, to obtain the same value of streamflow concentration, to a small S_0 , which implies generally younger water ages, the model associated an higher k, denoting a faster mass-transfer of solute. It would be possible to address this issue by defining a priori the value of the initial storage S_0 , subjecting to calibration only the constant k.

5.2 Solutes dynamics during dry periods

The model showed the best performances, in terms of fit to the measured data, when applied to the periods characterized by an abundant or regular flow. As regards the drier periods, other dynamics of solute transport came into play, questioning the comprehensive nature of the model, based on a catchment-scale approach.

5.2.1 Geogenic solutes

Geogenic solutes streamflow concentration revealed a considerable increase during periods characterized by a low flow rate. As resulting from the calibration process, model output is not able to fully reproduce that trend, since the value of C_Q reached during those spikes is higher than the value identified for limit concentration C_{lim} . This behaviour could be explained accounting for the input brought by smaller volumes of water which infiltrates flowing through particular pathways, referred to as seep flow. In such a case, solute concentration is no longer representative of the whole water stored in the catchment, since it could be particularly enriched by one or more geogenic solutes through the contact with rocks and minerals. The contribution of seep flow to river hydrochemistry is merged when flow rate is high and arises when the latter decreases, up to be the only constituent of the flow when it is extremely low. Seep flow solute concentration is no longer related to water age, high values of concentration is, indeed, not necessarily indicative of older water, but it could be result of an interaction with a more weatherable region of the subsoil [5].

As mentioned in chapter 4, the comparison between streamflow concentration of different solutes recorded in Naizin catchment drew attention to some peculiarity of nitrate behaviour. Over dry periods, in fact, nitrate streamflow concentration drops, contrary to what happens for geogenic solutes. This phenomenon disclosed interesting discussions about catchment's solutes transport dynamics, further investigated in the following paragraphs.

5.2.2 Seasonal water table dynamics

Molenat et al., 2008, as a result of a study involving Naizin area, links seasonal variations of nitrate concentration in stream with water table dynamics along the catchment's hillslopes. In wet conditions, the water table is fairly shallow and the main contribution to the base flow is due to upland groundwater. Uplands, where fields are located, are exposed to fertilizer load, whose components accumulate and slowly infiltrate within the soil. Shallow groundwater is, thus, richer in nutrients and contributes significantly to nitrate export to the stream. In late spring and summer, instead, drier condition lead to a lower discharge and to the lowering of the water table. Therefore, stream flow is mainly regulated by bottom lands groundwater. Moreover, degradation processes such as denitrification, occurring in riparian fully-saturated zones, although being of minor relevance in winter, assume more importance due to the very low flow. Similarly, plant uptake rates are low during winter, because vegetation is in the dormant state, and increases in spring and summer, contributing to nitrate removal [17]. This study suggest thus that nitrate streamflow concentration drops during periods of low flow are due to the fact that the contribution of uplands groundwater, richer in nitrate, is substantially reduced, in favor of lower lands groundwater, with a lower concentration. In bottom land groundwater is in fact shallower and "nitrate leached by upslope field may flow through highly biologically reactive zones, where it can be denitrified or taken up by the vegetation" [14].

The relative contribution to streamflow concentration of shallow and deep groundwater provides, in addition, insight into the state of uplands and bottom lands and the nature of the agricultural practices carried out on the catchment. Indeed, if shallow groundwater are richer in nitrate, it could be indication that the catchment is still enriching in nutrients, on the contrary, higher concentrations in the deep groundwater would mean that the fertilizer load has been reduced and concurrently the catchment is under cleaning. However, these considerations are subordinated to an estimation of the propagation speed of the nutrients plume.

According to what has been described above, given that shallow groundwater plays a major role in wetter periods, the use of TTDs to evaluate the contact time of water and soil, and estimate its nitrate concentration, becomes more significant during those periods. This

thus justifies the choice of running a calibration over the sole periods characterized by an high flow rate.

Despite this theory is reliable and this processes are proved to be occurring in the case study catchment, the observed nitrate dynamics should not be exclusively ascribed to them. Indeed, drawing a comparison between nitrate and chloride streamflow concentration (figure 5.2) it appears that, during periods of low flow, chloride concentration does not experience a decrease like nitrate does. Since chloride can be considered as an inert and non-decaying solute which, as nitrate, enters the natural environment as a result of agricultural practices and chemical fertilization, its different behaviour suggests that the reasons behind nitrate concentration drops are also attributable to bio-chemical processes involving specifically nitrate such as denitrification [23].

5.2.3 Influence of denitrification

Model performances on reproducing nitrate streamflow concentration may be affected by the uncertainties linked to the definition of the denitrification flux. In the model developed in this thesis, for the sake of simplicity, denitrification is set as proportional to nitrate concentration in water. Actually, denitrification is a phenomenon strongly dependent on temperature and available oxygen and it does not occur at the same rate over the whole catchment. A study carried out by van der Velde, 2010, estimated the nitrate removed by denitrification to be around 20 and 60% of the yearly input, suggesting a more careful modeling of the process [23].

As stated in paragraph 5.2.2, denitrification becomes a significant flux in periods of low flow, where bottom lands assume a crucial role, being nitrate supply from uplands reduced. TTDs approach, however, considers the storage as a single system and does not allow to account for the contribution of different section of the basin. To address while keeping the integrated nature of the formulation, since it constitutes the main strength of the model, denitrification could be modeled as proposed by van der Velde, 2010. The paper describes a model to simulate catchment-scale nitrate transport in lowland watersheds characterized by intensive agriculture. The pursued approach presents several analogies with the one carried on in this thesis: both modeling are based on a mass-transfer function containing a variable expressing the equilibrium (or limit) concentration, both confine exchange processes to a fraction of the system volume ("root zone water volume" or S_{NO_3}) and both exploit TTDs. However, the study accounts for denitrification both directly in the mass-exchange equation and in the computation of C_{lim} , whose proposed form is

$$\frac{\partial C(T,t)}{\partial t} = -r_n C(T,t) + r_d (C_{lim}(t) - C(T,t))$$
(5.1)



Figure 5.4. Evolution of stored water concentration of nitrate and chloride, from van Der Velde, 2010 [23].

where C can be considered as nitrate concentration of stored water parcels, r_d the diffusion rate, comparable to k, and r_n coincides with the denitrification rate. $C_{lim}(t)$ is calculated as $C_{lim}(t) = C_{lim_0}(t) \cdot e^{-r_n T}$, being C_{lim_0} the equilibrium concentration for particles with zero travel time.

Denitrification processes becomes significant as nitrate concentration rises, reducing the nitrate dissolved in water and preventing the reaching of equilibrium concentration as it would instead happen for chloride (figure 5.4). Such an approach would be in agreement with the requirement of a different modeling for nitrate and chloride, in view of the opposite concentration trends shown in periods with a low flow rate.

5.3 Examples of future applications

Once the calibration phase identified the best parameters combination, the model is able to run different simulations

On the basis of the results of the calibration phase, by means of the best combination of parameters the model can be used to predict scenarios related to the effects of fertilization. These projections can be useful, not only to concretely visualize the link between anthropogenic nutrients release into the environment, but also to estimate catchment retention time. Indeed, modeling a constant nitrate input and sharply stopping the supply after a certain period of time, it is possible, on the basis of the decrease of streamflow concentration, to unravel the time needed for the watershed to export the excess nitrate.



Figure 5.5. Nitrate streamflow concentration simulated over 12 years, supposing a constant application of fertilizer for about one year and no supply for the period thereafter. In the background it is reported the actual nitrate streamflow concentration measured in the stream.

Figure 5.5 displays nitrate streamflow concentration in the case of a fertilizer load of 150 kg_{NO_3}/ha applied for the duration of about one year and suddenly interrupted. Although during the period around 2005 and 2006, a temporary increase occurs, the general trend is decreasing. Predicted values are considerably lower than the one measured with the fertilization under way, indicating that the observed in-stream nitrate concentration is extremely affected by the anthropogenic load of nutrients.

Furthermore, the model could be used to predict the impact of climate changes on nitrate transport. Recent studies agree about an increase of the mean temperature and an amplification of climate extremes (wetter winter and drier summers) in the next decades. Nitrogen cycle, being strongly controlled by temperature and hydrology, would be inevitably altered [10]. This model would be able to outline future scenarios under different conditions, to foresee the evolution and hence retain nitrate pollution of surface water. Indeed, it would be sufficient to generate new timeseries of hydrological fluxes, simulated solving the hydrological water balance accounting for climate modifications, and run the model using this new dataset.

6 Conclusions

This thesis outlines the development process of a model implemented on Matlab, able to trace non-conservative solutes concentration in the stream draining a catchment, on the basis of hydrological fluxes and anthropogenic inputs of solute at stake in upstream lands. The model is based on the interaction between hydrology and water quality sciences and relies on the previously formulated theories of travel time distributions. Water age, or the time spent by the water within the catchment's ground, rules solutes mass-exchange dynamics between flowing water and soil determining water parcels' chemical composition. Defining an adequate SAS-function to describe the composition of the outflow in terms of water ages, it is possible to estimate the overall solutes concentration in the streamwater.

Data made available from Naizin research catchment allowed to evaluate model performances over long periods and various solutes. As evidenced by testing the model on magnesium, it reported a significant fit when dealing with geogenic solutes, whose presence in the subsurface is regulated by relatively simple processes. The simulation run using calibrated parameters, besides showing a good fitting, confirmed time-variant SAS functions as a powerful tool which successfully links catchment wetness conditions and streamflow solute concentration. The modeling of nitrate involves a larger number of bio-chemical reactions, nevertheless, the results of the run simulations are equally impressive. Preliminary testing phase underlined the fact that nitrate concentration dynamics are not in line with the general trend of the monitored solutes, from which diverge especially during periods characterized by a low flow. Results obtained when testing the model on periods sorted on the basis of the flow rate support the idea that the model is particularly suitable to predict nitrate streamflow concentration in conditions of high flow. Whereas when the flow rate is scarce and the catchment is rather dry, different processes must be taken into account and other formulations are preferable.

The most remarkable strength of this model is the versatility. On the one hand, given the spatially implicit catchment-scale approach, it could be applied to watersheds with different characteristics with just a calibration phase. Furthermore, the modeling of solute migration between soil and water by means of a single mass-transfer equation makes it suited to describe the transport of several solutes. The uncertainties on the fertilization inputs are definitely a limitation for this study. Being human activities often the main cause of nitrate pollution, detailed information about the applied fertilizer load on field are fundamental to obtain accurate results from the model. A case study catchment where agricultural practices are continuously monitored and recorded would be advisable to pursue in this direction.

In conclusion, this model has the potential to represent an important instrument in the framework of the protection of surface water resources against nitrate pollution. Although requiring further refinements, it allows to understand the processes regulating nitrate presence in streams and to evaluate the impacts of the possible countermeasures to be implemented. From a forward-looking perspective, the model could be applied to wider control volumes and used to predict how climate changes could affect solutes transport in water-sheds under cultivation.

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