Dynamics of the nitrogen transformation in a shallow stream and possible interventions

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Abstract This paper presents the assessment of the efficiency of the main biological nitrogen transformation processes in a shallow well-oxygenated river and conditions under which they are active and stabilise. The process dynamics was studied with the help of mathematical modelling of 2 years on-line data series measured in a reach of the Toess River, Switzerland. The algal nitrogen uptake was very stable and unaffected by most but frequent flood events. Daylight photosynthetic nitrogen uptake stabilised at 6 mgN m$^{-2}$ streambed h$^{-1}$ (15°C), dark uptake on storage products at rates of 0.5–2.5 mgN m$^{-2}$ streambed h$^{-1}$. Nitrogen uptake by heterotrophic bacteria in the hyporheic zone was relatively constant at a level of 1.5–3.5 mgN m$^{-2}$ streambed h$^{-1}$. Streambed nitrification could establish only during periods with average daily concentration of at least 0.3 gNH$_4$-N m$^{-3}$ in river water for several weeks. The maximum nitrification rate was 35 mgN m$^{-2}$ streambed h$^{-1}$ for 3 gNH$_4$-N m$^{-3}$. The effects of reduced nitrification in the WWTP and of river banks shading on a sudden ammonium peak were simulated. A river reach endangered by ammonium spills should be kept open to sun to favour ammonium uptake by algae. In-stream nitrification reduces ammonium peaks efficiently but leads to toxic nitrite concentrations.

Keywords Ammonium; biofilm; flood events; nitrification; nitrogen uptake; river

Introduction
Basic tasks of the integrated approach to the urban wastewater management can be the expressed by the following three points: 1) minimising the integral mass flux of pollutants passed into the river, 2) minimising the peak pollutants concentration, and 3) minimising duration of pollutants concentration above an acceptable threshold. To achieve these goals, different measures at different parts of the system can be applied. These measures range from measures at the pollutant source being the most efficient to real time control of the flow in the sewer system, storm water tanks and sophisticated wastewater treatment technologies. However, the following questions arise: Are these investments always justified or can a part of their function under suitable conditions be transferred to the receiving water without unduly degrading its quality? Can or should we influence self-purification processes in rivers and make use of them in the framework of the urban water management to reduce the overall pollution impacts?

If predictions are to be made of the effect of introducing pollutants into the streams or utilising the self-purification capacity of the stream, we must understand the processes acting upon those pollutants and know something about the probable rates at which those processes occur and about their variability.

One of the key pollutants released from the urban drainage system to the receiving waters is ammonium, whose unionised form has pronounced toxic effects on aquatic organisms (Whitelaw and de Solbè, 1989). In rivers, ammonium is assimilated by algae and bacteria and oxidised by nitrifying bacteria. In shallow streams, algae and bacteria are attached to the streambed in the form of a multispecies biofilm (Lock, 1993).
The structure and metabolic activity of the biofilm is an outcome of complex interactions between hydrological, water quality and biotic factors (Allan, 1995). The accumulation of the biofilm biomass is affected by the resources substrate, nutrients and light and, with them, interacting temperature. The biomass loss is first of all caused by scouring during flood events (Stevenson et al., 1996). Due to the number of controlling factors, the development of river biofilms shows a large temporal and spatial variablity. Thus, also the dynamics of the nitrogen transformation potential is considerable and the process rates of individual nitrogen transformations may differ substantially depending on historic and present environmental conditions.

Some of the environmental conditions affecting nitrogen transformations can be intentionally changed as a consequence of the urban drainage system operation and river habitat restoration to inhibit or favour the development of the streambed biofilm or of a certain species in the biofilm. In this way the transformation rates can be influenced and the peak ammonium concentrations and duration of ammonia concentrations above an acceptable threshold can be reduced.

This paper deals with two items: (1) the dynamics of individual nitrogen transformation processes in a shallow well-oxygenated river, and (2) possible changes of environmental conditions leading to ammonium peak reduction.

In the first part, an analysis of measured data over a river reach will be performed to discuss the following questions:

- What is the variability and efficiency of the individual nitrogen transformation processes in shallow well-oxygenated rivers?
- Under which conditions are they active and when do they stabilise?

In the second part, interventions intentionally changing environmental conditions affecting nitrogen transformations will be simulated to answer questions such as:

- Is it better to aim at perfect nitrification in the WWTP or is a continuous release of ammonium to the river to maintain a certain ammonia oxidisers density ready to transform sudden ammonium loads more beneficial (considering also savings in aeration energy for nitrification or reduction of tank volumes)?
- Is renewal of the river banks’ shading often accompanying river restoration advantageous in a reach endangered by ammonium spills or should the reach be kept open to sun?
- What is the effect of the dry weather flow duration in both scenarios?

Methods

Study stream and measurements

The investigations were carried out at a Swiss pre-alpine gravel-bed river the Toess, downstream of a small partly nitrifying municipal WWTP (5000 IE). Ammonium, nitrite and environmental parameters (oxygen, pH, temperature, water level/discharge) were measured continuously with a 2 min resolution in two on-line monitoring stations over a 1.2 km long river reach for 2 years. Short-term monitoring campaigns provided additional information on nitrate concentrations. Pulse tracer experiments with coinjection of sodium bromide and ammonium chloride imitated a sudden spill. The extent of biofilm scouring was inspected in the field for floods of different magnitude. The presence of nitrifying bacteria in the biofilm on the streambed substrata was followed in aerated batch reactors filled with river water enriched with ammonium (8 gNH4-N m−3) as potential nitrification activity. Meteorological data on global radiation were obtained from the Swiss Meteorological Institute for station Tänikon.
Mathematical model and simulation tool

The examination of processes stabilisation and analysis of measured data were performed with a mathematical model developed, calibrated and verified by Jancarkova (1999). This model enables the simulation of both the short- and long-term dynamics of nitrogen uptake during ecosystem assimilation and of nitrification in a shallow river in dependence on growth, decay and scouring of algae and bacteria in the biofilm. Diurnal variation of algal nitrogen uptake is described as a result of its coupling to CO₂ assimilation and considers light stimulated assimilation as well as biosynthesis on storage products at dark (Morris, 1980). Further nitrogen uptake is ascribed to the oxidation of dissolved and particulate organic matter by heterotrophic bacteria in the hyporheic zone (Naegeli and Uehlinger, 1997). The nitrification model views the nitrifying bacteria as covering algal filaments and surrounded by a stagnant liquid layer. Ammonium must diffuse through the boundary layer before it is utilised by ammonia oxidisers at the filament surface. Nitrite produced at the filament surface is consumed by nitrite oxidisers. When nitrite production rate is higher than its utilisation, nitritediffuses through the boundary layer to river water. Simulations were performed with the computer program AQUASIM (Reichert, 1994).

A hypothetical situation and scenarios

A hypothetical 5 km long river reach below a wastewater treatment plant experiences a major flood event leaving a residual biofilm density. A certain period of low flow (10, 20 and 50 d, respectively) follows when a sudden ammonium peak of \(4 \text{ gNH}_4\text{-N m}^{-3}\) occurs (a sudden spill or a combined sewer overflow). The river reach is either exposed to sun or shaded and it either receives no continuous ammonium input or a certain low input because of imperfect nitrification in the WWTP.

The evaluation criterion is the peak concentration at the end of the river reach. The reference is the peak concentration considering transport processes only.

Results and discussion

Variability and stabilisation of the algal and bacterial nitrogen uptake

Algal nitrogen uptake exhibited a strong diurnal variation due to its tight coupling to the light stimulated CO₂ assimilation. The photosynthetic nitrogen uptake rate showed a strong density limitation with increasing biofilm thickness (only the upper 3 mm of the biofilm was photosynthetically active). For the highest global radiation values (900 W m⁻²) and highest values of algal densities identified for the field data \(X_{\text{alg}} = 350 \text{ gCOD m}^{-2}\text{ streambed}\), it can theoretically approach \(8 \text{ mgN m}^{-2}\text{ streambed h}^{-1}\) (Figure 1). The examination of the field data revealed that the reach-averaged photosynthetic nitrogen uptake stabilised under optimal conditions at approximately \(6 \text{ mgN m}^{-2}\text{ streambed h}^{-1}\) during day light hours. It was temperature independent.

Nitrogen uptake accompanying biosynthesis on storage products contributed to the ecosystem nitrogen consumption at dark until the internally stored carbon was exhausted early in the morning. Rates of \(0.5−2.5 \text{ mgN m}^{-2}\text{ streambed h}^{-1}\) (15°C) were observed.

The algal nitrogen uptake was very stable and unaffected by most of the flood events. Isolated major floods with biofilm scouring had little consequence for the primary productivity of the ecosystem with a high pre-flood algal biomass due to the strong biomass density limitation of photosynthesis and due to rapid ecosystem recovery (1–2 weeks), also observed by Uehlinger and Naegeli (1998). Only frequent major floods (approximately once a week) over a longer period (witnessed for 2 months) disabled development of a thick algal mat and reduced the photosynthetic nitrogen uptake significantly (1 \text{ mgN m}^{-2}\text{ streambed h}^{-1}).
The nitrogen uptake ascribed to the heterotrophic bacteria in the hyporheic zone was the most constant process at a level of 1.5–3.5 mg N m$^{-2}$ streambed h$^{-1}$ (15°C) and was nearly unaffected by floods. It gained significance at night and during periods with low algal biomass.

Ammonium was assimilated utterly preferentially over nitrate. The imitation of a sudden ammonium spill showed that the ecosystem switched over from nitrate uptake to ammonium uptake immediately, even after a prolonged period without ammonium in river water.

Variability and stabilisation of nitrification

Two aspects of stabilisation of nitrification are important:

1. development of a steady-state bacterial density for certain ambient ammonium concentrations,
2. stabilisation of the ammonium flux into the biofilm, i.e. conditions when the transformation rate is controlled primarily by mass transport into the biofilm.

The growth and loss processes are balanced when a minimum ammonium concentration of 0.004 g NH$_4$-N m$^{-3}$ is available for bacterial growth at the filament surface. This concentration is maintained when the rates of ammonium diffusion through the boundary layer and its utilisation at the filament surface are equal. Figure 2 determines a steady-state ammonia oxidiser density that develops at a certain bulk ammonium concentration.

Streambed nitrification could establish in the Toess River only in times of reduced nitrification in the WWTP (minimum averaged concentration in river water 0.3 g NH$_4$-N m$^{-3}$ for several weeks). During a 6 month period with frequent rain, driven ammonium spills from the WWTP (approximately once a week) but otherwise no ammonium in the WWTP discharge, the short intervals of growth were not sufficient for the development of a significant ammonia oxidisers population and practically no nitrification occurred. Potential nitrification activity in the streambed biofilm was approximately 15 times lower than in other periods (Figure 3).

Flood events acted on nitrifying bacteria in two ways: their biomass was decreased because of both biofilm erosion and bacteria decay, due to absence of sufficient ammonium concentrations in the diluted water. Thus, floods events exhibited often a prolonged effect.

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**Figure 1** Nitrogen flux into the streambed during photosynthesis (15°C) for various algal densities $X_{alg}$ and intensities of global radiation (GLR).
Model calculations show that well-established nitrification is strongly mass transport limited and independent of bacterial concentration (Figure 4). It can be approximated as a 1st order reaction as to the ammonium concentrations. The maximum nitrification rate in the Toess River was approximately $35 \, \text{mgN} \, \text{m}^{-2} \, \text{streambed} \, \text{h}^{-1} (15^\circ\text{C})$ for the ambient peak concentration of $3 \, \text{gNH}_4\text{-N} \, \text{m}^{-3}$, and thus stabilised.

**Efficiency of the individual nitrogen transformation processes**

Nitrification rates of a well-developed nitrifier population exceeded the rates of algal and bacterial ammonium uptake several times (Figure 5).

The relative importance of the nitrification increased at night, in late autumn and in winter. However, the establishment of a nitrifier population depends on a continuous presence of ammonium. Algal growth and nitrogen uptake, on the contrary, were much more stable because algae can also utilise nitrate as a supplementary nitrogen source.
Scenario simulations

The continuous release of ammonium was adjusted to keep 0.3 \( \text{gNH}_4\text{-N m}^{-3} \) in river water at the beginning of the river reach. This concentration sustains ammonia oxidisers density of 0.5 \( \text{gCOD m}^{-2} \text{streambed} \) (Figure 2), sufficient to reduce higher ammonium concentrations efficiently (Figure 4). The ammonia concentration is 0.03 \( \text{gNH}_3\text{-N m}^{-3} \) (\( 20^\circ\text{C}, \text{pH} = 8.5 \)) which equals long-term LC10 (Whitelaw and de Solbé, 1989).

The light exposed reach received global radiation of 800 \( \text{W m}^{-2} \), the shaded one 20 times less. The initial algal and bacterial densities were selected 10 times lower for the shaded reach because of the absence of filamentous algae and thus diminished surface area for bacterial growth (Hepinstall and Fuller, 1994).

Figure 4 Ammonium flux into the streambed during nitrification (15°C) for various ammonia oxidisers densities \( X_A \) and ammonium concentrations

Figure 5 Ammonium concentrations and rates of the ammonium transformation processes at the first measurement station. The gap is due to the measurement fallout during a flood event
Results are summarised in Table 1. Considering transport processes only, the simulated reference peak concentration at the end of the river reach was 2.09 gNH₄-N m⁻³. As a result of the transformation processes, the peak decreased to 0.83 gNH₄-N m⁻³ under light conditions and to 1.19 or 0.86 gNH₄-N m⁻³ under shaded conditions (after 10 or 50 d of dry weather flow, respectively). Due to the induced nitrification, the peaks were 1.93 times lower than due to solely algal and bacterial nitrogen uptake for the light exposed reach. For the shaded reach, the reduction factor was 1.55 and 2.15 after 10 and 50 d, respectively.

Shading favours nitrification through decreased algal competition for ammonium. Thus, the ammonium peak at the end of the enriched shaded reach was only 1.4 times higher compared to full light conditions after 10 d and nearly equal after 50 d. Nitrification under shaded conditions was the only process not yet stabilised after 10 d.

The induced nitrification leads to a significant decrease of sudden ammonium peaks; however, it might be accompanied by toxic nitrite concentrations (Müller, 1990) depending on conditions for nitrite oxidisers growth. When there was no nitrite in river water, concentrations up to 0.10 gNO₂-N m⁻³ were simulated at the end of the river reach during dry weather ammonium enrichment, with maxima of approximately 0.80 gNO₂-N m⁻³ during ammonium peaks, whereas for an established nitrite oxidisers population (on nitrite concentration of 0.10 gNO₂-N m⁻³ at the beginning of the reach), concentrations at the downstream end decreased to 0.06 and 0.30 gNO₂-N m⁻³, respectively. The nitrite concentrations were slightly higher under shaded conditions than for a light exposed reach because of the more rapid nitrite production rate.

### Conclusions

The investigations performed gave some answers on the variability and stabilisation of the nitrogen transformation processes in a shallow well-oxygenated stream. The process rates simulated can be used as estimates that can be expected in similar streams.

Practical recommendations concerning river water quality modelling, operation of the urban drainage system and river health protection can be summarised in the following points:

- Process rates of stabilised nitrogen transformations are only marginally dependent on algal and bacterial densities due to strong density limitation of photosynthetic nitrogen uptake and mass transport limitation of nitrification. However, high frequency of major flood events accompanied by streambed biofilm scouring and ammonium concentrations decrease might reduce the rates significantly. This must be considered when assessing the effect of introducing wastewater into the stream.
- No nitrification occurs (and thus has to be modelled) below a CSO unless there is a continuous ammonium concentration in river water of approximately 0.3 gNH₄-N m⁻³.
- Although a continuous release of ammonium from a WWTP leads to a significant decrease of sudden ammonium peaks and thus reduction of ammonia toxicity, it might...
be accompanied by toxic nitrite concentrations. This makes the idea of intentionally reduced nitrification in the WWTP to sustain in-stream nitrifiers highly questionable.

- A river reach endangered by ammonium spills should be kept open to the sun to favour ammonium uptake by algae.

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References


