**DOCTORAL SCHOOL IN ENVIRONMENTAL ENGINEERING**

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# Modeling biogeochemical and hydrodynamic processes into the hyporheic zone

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## Abstract

The hyporheic zone is the saturated volume of sediment surrounding the stream and providing the linkage between rivers and  aquifers. It is a rich ecotone where most of the uptake and transformation of solutes occurs with kinetics chiefly controlled by the solute residence time (Alexander et. al., 2000). As a consequence, modeling transport of nutrients and contaminants along riverine systems calls for including the effect of the hyporheic zone.

Stream waters continually exchange into and out of the hyporheic zone primarily through a mechanism note as pumping (Elliott and Brooks, 1997a 1997b). The pumping processes is generated by near-bed pressure variations, which induce intra-gravel flows. In particular, zones of high and low near-bed pressures characterize  the upstream and downstream end of the bed forms. This causes complex flow patterns within the hyporheic zone, which interacts with the streamflow through an alternate sequence of downwelling and upwelling zones reflecting bed morphology. As a consequence, solutes are temporary stored within the hyporheic zone, thus creating long tailing in the solute breakthrough curves in stream waters.  Additionally, this exchange effects water temperature both in the riverine and hyporheic environments. Water temperature is a key variable responsible for shaping the aquatic habitats (Constantz and Stonestorm, 2003). It influences chemical processes, oxygen, nutrient, and contaminant concentrations besides the development of aquatic organisms and the rate of photosynthesis of aquatic pants (Allan, 1995). Furthermore, temperature variations may influence the timing, speed, and direction of fish migration (Jonsson ,1991).

The activity, growth, and reproduction of aquatic organisms become teeming with life as temperature stream is within an optimal range, while the activity slows and growth and reproduction cease if temperature conditions are too low or too warm. However, plants and animals are adapted to survive in specific temperature conditions that change with species. Optimal conditions might be wide for some organisms, yet for others, quite narrow. Most studies relate river temperatures with the ambient atmospheric conditions (Ward, 1985; Gu and Li, 2002) and underline that the water temperatures chiefly fluctuate on two different time scales: the daily and the seasonal scales (Hohen and Cirpka, 2006). Moreover, discharge may influence in-stream water temperatures. In this context the role of the hyporheic zone becomes very important because it acts as buffer between the downwelling and the upwelling zones. Spatially and temporally the thermal regime of the hyporheic zone may be highly dynamic due

to variations of flows, groundwater levels, bed forms, and sediment composition (White et al., 1987; Evans and Petts, 1997). Therefore, we developed a set of analytical solutions of the hyporheic flows in gravel bed rivers with pool-riffle morphology. Then we coupled them with a heat transport and bio-chemical reaction models to study temperature and solute exchanges between surface and subsurface waters. We modeled heat transport within sediments accounting for conduction, dispersion, and advection (Anderson, 2005; Hohen and Cirpka, 2006; Cardenas and Wilson, 2007, Arrigoni et al. 2008) and we predicted temperature daily patterns in rivers.

The heat transport equation is solved with a Lagrangian approach (Dagan, 1989; Rubin, 2003; Bellin and Rubin, 2004), assuming that the transverse dispersivity is negligible and considering that the thermal boundary conditions of the sediment is the daily temperature fluctuation of the in-stream water. Our goal was to identify the dominant processes that affect the hyporheic zone heat transport and the thermal gradients, which influence the rates of microbial and biogeochemical processes. We observed different patterns of hot and cold spots passing from day to night with an arrangement, which is strongly related to the residence time into the hyporheic zone and consequently to the bed morphology. Furthermore, we compared the hyporheic role of large low-gradient streams and of small steep-gradient streams. We showed that the averaged upwelling-hyporheic waters temperature have smaller daily variations in the formers than in the latter case because of long residence times. Moreover, we quantified the importance of the hyporheic zone flux in respect to the heat flux that travels along the stream and we showed that in small steep streams, the hyporheic zone plays a more important role in affecting in-stream water temperatures.

On the solute transport, we investigated the fate of nitrogen (N), whose transformations take primarily place within the streambed sediments rather than within the in-stream water, (Seitzinger, 1990; Master et al., 2005). Several studies showed the importance of microbial processes in removing nitrogen from rivers and in reducing the total load. Although molecular nitrogen (N2) has generally been considered the main product of denitrification in aquatic systems (Master et al., 2005), recent studies provide evidence that the production of nitrous oxide (N2O) cannot be discounted, especially in heavily polluted water bodies (Garcia-Ruiz et al., 1998; McMahon and Dennehy, 1999). Most of the streams flowing in agricultural and urban areas suffer from the impact of excessive nitrogen inputs under the form of ammonium (NH+4) and nitrate (NO−3). Under oxidized conditions, aerobic bacteria (Nitrosomonas) use oxygen as a terminal acceptor during the transformation of ammonium to nitrate (nitrification) which in turn is reduced to nitrous oxide (N2O) or molecular nitrogen (N2) by "Nitrobacter" bacteria (denitrification). However, as the environment becomes increasingly reduced, nitrification is inhibited while denitrification continues to reduce nitrate to nitrogen gases (N2O or N2).

Along the flow paths from downwelling to upwelling zones the environment becomes increasingly reduced as oxygen is consumed by aerobic bacteria. We focused on the export of ammonium (NH+4), nitrate (NO−3), nitrogen gases (N2O or N2) and their fates within the streambed. Moreover, along hyporheic streamline nitrification is limited by oxygen concentration whereas denitrification is limited by the concentration of nitrate. Several methods have been proposed to quantify the hydrological exchange between streams and shallow ground waters in the hyporheic zone.

In this work, we sought for and answered to the following questions:

- what are the important factors controlling the export of ammonium, nitrate and nitrogen gases by the hyporheic zone?
- And moreover, under which conditions the hyporheic zone acts as a source rather than a sink of this inorganic nitrogen species for the stream water?

- Finally, what is the role of the land use on the production of nitrous oxide?

To answer these questions we modelled the hyporheic exchange with analytical solutions of the intra-gravel flows induced by alternate bars in gravel bed rivers and the inorganic compound of the nitrogen cycle with a set of transport equations coupled with first order kinetics.

We solved transport with a Lagrangian approach (Dagan, 1989; Cvetkovic and Dagan, 994; Rubin, 003), assuming that local dispersion is negligible and considering that temperature affects the reaction rate coefficients. We studied the interplay between streambed morphology and nitrogen fate within the hyporheic zone of gravel bed rivers with pool-riffle morphology.

We observed that while the hyporheic zone acts as a sink of ammonium to an extent that depends on the nitrification rate, it may act as a source or a sink of nitrate. Additionally, it can influence the emission of nitrogen gases (N2 and N2O), depending on the ratio between ammonium and nitrate concentrations in the stream and on the role of biomass uptake.

We also compared the hyporheic role in small steep and large low-gradient streams showing that in the formers because of short residence times nitrification processes dominate, whereas in the latter case denitrification also plays a major role. We observed that the emission of nitrogen gases increases with temperature in small steep streams, but not with the alluvium depth because hyporheic flows mostly develop near the surface. Whereas, the emission of nitrogen gases increases with both temperature and alluvium depth in low-gradient streams.

At last we showed the role of the land use (agriculture or forest) on the production of nitrous oxide, one of the most important greenhouse gases. We concluded that nitrogen fate within the hyporheic zone depends on the interplay among the parameters controlling nitrification and denitrification reactions, the streambed morphology, and the land use in a complex manner.

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