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Inferences from catchment-scale tracer circulation experiments

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SUMMARY

In this paper the mechanisms determining the mobilization and transport of solutes driven by rainfall through runoff pathways at catchment scales are investigated through the analysis of tracer experiments. The hydro-chemical response of a small catchment in Northern Italy has been monitored in continuous during 4 weeks by properly measuring rainfall rates, streamflows and stream flux concentrations. The chemical response has been analyzed by employing two different tracers: nitrates from diffuse agricultural sources (NO_3^-) and lithium from a point injection (Li^+). A modelling exercise simulating the observed hydro-chemical response of the test catchment has also been carried out. Inferences from the comparative analyses prove instructive, in particular concerning the scaling of mobilization processes and the age of runoff water. Indeed, the interactions between old and new water were found to be central to understand the mechanisms driving the transfer of solutes and pollutants from soil to stream water. The modeling exercises also evidenced the noteworthy potential of the formulation of transport by residence time distributions to describe large scale solute transport processes.

Introduction

To date, the behavior of pollutants in soils and their interactions with hydrologic processes at catchment or regional scales has been only partially understood. This gap of knowledge is likely to be progressively filled by the recent outbreak of theoretical, observational and modellistic studies about loading, mobility and turnover of pollutants in complex and heterogeneous systems (see, e.g., Gerzabek et al., 2007; Barth et al., 2007 and references therein). One of the major difficulties arising when interpreting and describing the hydro-chemical response of natural systems (i.e., river basins) relies in the spatial and temporal heterogeneities stemming both from soil moisture dynamics and from transport processes. In this context, natural or applied tracer studies are fundamental to assess observationally water and solute pathways and behaviors. They are commonly employed to probe hillslope, aquifer or entire catchment transport processes. In particular, large-scale tracer studies have been employed to address issues such as the aging of soil water, the role of macropores and preferential transport in streamflow formation, and the proper estimation of residence time distribution (see, e.g., Maloszewski and Zuber, 1982; McDonnell et al., 1991; Wilson et al., 1991a,b; Leaney et al., 1993; Bazemore et al., 1993; Rodhe et al., 1996; Burns et al., 1998; Evans and Davies, 1998; Peters and Ratcliffe, 1998; Nyberg et al., 1999; Jones and Swanson, 2001; Weiler and Flühler, 2004; Botter et al., 2008a,b).

Here we report on novel field experiments and analyses where point and nonpoint source tracers are used: nitrates (NO_3^-) from diffuse agricultural sources and lithium (Li^+) from a point injection. Owing to their chemical and physical properties, nitrates constitute a relatively conservative tracer which travels mostly dissolved in soil moisture and mobile soil water. Nitrate transport may build up remarkably high concentrations of nitrogen in soils and in streamflows, especially in catchments where agricultural practices are significant (e.g., Vanclooster et al., 1995; Baresel and Destouni, 2005, 2006; Botter et al., 2006; Darracq et al., 2005; Darracq and Destouni, 2007). Nitrate concentrations in runoff (i.e., streamflow) are generally considered a relevant indicator of water quality in riverine systems for the number of impacts that may be generated (e.g., Darracq and Destouni, 2007) and consequently nitrate leaching through runoff has received growing attention from hydrologists and ecologists, leading to a number of coupled experimental and modeling studies (e.g., Creed et al., 1996; Creed and Band, 1998a,b; Evans and Davies, 1998; Hill et al., 1999; Worral and Burt, 1999; Gupta and Cvetkovic, 2000, 2002; Porporato et al., 2003; Lindgren et al., 2004, 2007; Darracq et al., 2005; Rinaldo et al., 2006b; Weiler and McDonnell, 2006; Botter et al., 2006, 2008a,b; Darracq and Destouni, 2007; Bosch, 2008). Nitrate dynamics at the watershed scale is a complex issue, however, and a satisfactory closure is still lacking for several questions like, e.g., the hysteretic

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nature of discharge–concentration relationships; the impact of point or nonpoint source distributions in space and time; the role of catchment topography and geomorphology; the effect of large-scale in-stream denitrification processes (e.g., Brusseau and Rao, 1990; Alexander et al., 2000; Mulholland et al., 2008); and the upscaling of the main biogeochemical and hydrological processes that control the storage and transport of nutrients, to name a few.

Lithium is a weakly sorbing solute widely employed in tracer studies for its chemical features (e.g., Wrenn et al., 1996; Packman et al., 2000; Fernandez-Garcia et al., 2005; Botter et al., 2008a). Its high measurability and the negligible impact on the environment suggest its use in many contexts, particularly in fragile ecosystems. Moreover, transport through heterogeneous soils characterized by relatively small clay contents is only weakly affected by sorption phenomena onto mineral soil components (Anghel et al., 2002). As the percentage of clay in the experimental catchment does not exceed a few percents ('Test catchment and experimental setting'), lithium may be safely considered a conservative tracer. One may thus reasonably assume that dispersion is largely controlled by hydrological processes (Botter et al., 2008a).

The merits of jointly studying the behavior of different tracers characterized by point and nonpoint sources have been discussed elsewhere (Botter et al., 2008a,b). Here we integrate a previous study (Botter et al., 2008a) with new data including sequence of events, with new modelling exercises aimed at distinguishing the role of event and pre-event waters during solute mobilization through rainfall.

The modeling approach employed is based on mass-response functions that integrate the description of the hydrologic response based on the formulation of transport by residence time distributions (Rinaldo and Marani, 1987; Rinaldo et al., 1989; Cvetkovic and Dagan, 1994; Botter et al., 2005; Rinaldo et al., 2006a,b). The approach synthetizes Lagrangian dispersion of solutes by characterizing arrival time distributions at suitable compliance surfaces thought of as trapping states for solutes and water, and specifically aims at modeling basin-scale, nonpoint transport processes. Despite other definitions could be found in the literature (e.g., McGuire and McDonnell, 2006) in this paper we will term "residence time" the time elapsed between the injection of a water particle into the soil as rainfall and the time at which the same particle exits the control volume as runoff. In this observational context, to better highlight the role of the mixing processes taking place into soils and the related modeling implications, we shall focus on a simplified setting composed by only two serially coupled geomorphic states (i.e., a transition from a hillslope to a channel).

The paper describes a broad comparative observational and modelling study of the hydro-chemical response of the test catchment. The comparative analysis of observations and their models proves particularly useful to infer the degree of mixing of old/new water and their immobile and mobile phase concentrations, which bears profound modeling implications. Our main finding deals with the crucial role of modeling the mixing processes involving soil saturation and the age of runoff (meant as the time elapsed between the infiltration through rainfall and the passage through the compliance outlet – the absorbing barrier – confining the control volume). Such processes directly affect the solute flux concentration and overall the hydrochemical response even at catchment scales, and must be suitably reproduced. As we shall see, the above issue is particularly relevant to determine solute concentration of streamflows and the related breakthrough curves when considering the transport of native or injected tracers under various field conditions. Notice that our long-term goal concerns generalized real-time solute load release predictions at timescales comparable with the lead time of the hydrologic response from the 2000 km^2 catchment draining into the Venice Lagoon, a receiving water body whose ecological dynamics are much affected by them (Fig. 1) (Rinaldo et al., 2006a,b).

The paper is organized as follows: 'Test catchment and experimental setting' provides a detailed description of the tracer experiment set up and of the test catchment. The modeling tools employed are summarized in 'Modelling solute mobilization through the hydrologic response and the age of runoff'. The comparison between experimental evidence and modelling results is presented and discussed in 'Results and discussion'. A set of conclusions closes then the paper. All the details pertaining the model employed, which do not represent the core of this paper, are confined to an Appendix for completeness.

Test catchment and experimental setting

The Piovega Tre Comuni is a small tributary of the Dese catchment, a complex River/drainage system discharging into the Venice Lagoon, north-east Italy (Fig. 1a). The site selected has been already described in several recent hydrologic studies (Zuliani et al., 2005; Collavini et al., 2005; Rinaldo et al., 2006a,b; Botter et al., 2006, 2007, 2008a), where a detailed characterization of the site is provided (see in particular Botter et al., 2008a).

The Piovega Tre Comuni watershed is mainly devoted to agricultural uses (e.g., wheat, maize and alfalfa), and is characterized by a moderate (10%) presence of urban, impermeable areas (chiefly houses, roads and farms) (Fig. 1b). The drainage network is composed of a main straight channel and several smaller channels, partially dry during the dry season (Fig. 1b). The control section selected corresponds to a drop in bottom elevation located along the main channel, 300 m upstream of the confluence of the Piovega Tre Comuni with the Rio S. Ambrogio stream (Section A in Fig. 1b). The drainage area at the selected outlet is 0.7 km^2.

An important flow component is represented by the flow component resulting from the interception of deep groundwater operated by the farmers (thus poorly related to the soil–water dynamics occurring in the upper soil layer). This flow component, Q_b, will be denoted in what follows as base-flow, even though in the literature the latter term usually refers to the slow components of the hydrologic response. Q_b shows a moderate seasonal and inter-annual variability (at least at the temporal scales investigated) with values weakly fluctuating around 85 l/s.

Due to extensive agricultural and farming activities, high levels of dissolved nutrients (e.g., nitrates, ammonia and phosphates) have been detected in the drainage waters since the seventies. As a consequence, enhanced eutrophication and algal blooms are frequently observed, especially during spring and late summer (e.g., Collavini et al., 2005; Botter et al., 2006).

The point injection of lithium chloride was conducted within a small hillslope (about 1 ha) directly drained by the main channel of the Piovega Tre Comuni (area B in Fig. 1b). The site is a private crop field where, e.g., alfalfa and radicchio (*Chicorium intybus*) is grown, and is characterized by a gentle slope (3°) toward the main drainage channel (see Fig. 2b). The channel banks are vegetated and quite steep, with average slope of 45°.

A rough geo-pedological characterization of the site was achieved by means of several soil cores, which were sampled and analyzed. The stratigraphy was found to be weakly variable in space (i.e., from drill to drill), with a superficial horizon of unconsolidated loam (0—70 cm), and a deep horizon of consolidated silty loam (70—200 cm). Negligible fractions of clay were detected in all the soil samples examined.

The free surface of the water table in hydraulic contact with the main drainage channel was found at an average depth of about 200 cm. Hence, the upper water table is mostly comprised within the deeper soil horizon.