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Coupling catchment hydrology and transient storage to model the fate of solutes during low-flow conditions of an upland river

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SUMMARY

The residence time of solutes in catchments is longer during low-flow conditions, due to the lengthening of transport routes and the decrease in transfer velocities. In rivers, transient storage depends largely on exchanges with channel storage and the hyporheic zone and reflects the capacity of the river to buffer pollutant loads before they enter the aquatic environment of final receptors. Our objective was to evaluate the fate of solutes along a typical confined river of upland catchments. First, we calculate lateral inflows using a variable-source hydrology approach. Then, water motion and quality in the river channel are predicted by combining hydrodynamics and exchanges with channel storage and the hyporheic zone. The model is mainly parametrized from literature data during baseflow conditions to mimic the fate of adsorptive and non-persistent pollutants. Residence time in surface water, channel storage and the hyporheic zone were found to be sensitive to lateral inflows from groundwater seepage. Channel storage is the main process controlling residence time in upstream conditions, where the riverbed is mainly composed of stones and bedrock. Downstream, along with the formation of sediment deposits and riffle-pool units, hyporheic exchanges also control the lag time in the transfer of solutes. By integrating physicallybased processes, the number of parameters is small, but the model still requires a detailed description of stream geometry and morphology. It can be used to evaluate stream restoration or catchment-river management when detailed data of stream geometry and morphology are available.

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1. Introduction

Many compounds, such as xenobiotics, heavy metals or nutrients, can be transported in solution, affecting the ecological state, quality and use of rivers and other surface waters (Tlili et al., 2008). For ecological and economic issues, evaluating the environmental fate of solutes in river ecosystems remains a challenge to the preservation and management of natural resources (Martin and McCutcheon, 1998). The behaviour of river ecosystems depends on sequential inflows of water from groundwater seepage or surface run-off (USAEWES, 1995; Trévisan et al., 2012). Lowflow conditions, corresponding to events during which water and solute flows depend only on groundwater seepage, are of particular importance, as residence time increased. For forested or grassland upland catchments, where soils are relatively shallow and overlie impervious substrata, groundwater seepage occurs in contributing areas located at the bottom of slopes or in the centre of thalwegs (Obled and Zin, 2004; Trévisan et al., 2010). These processes are

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described by the "variable-source hydrology" concept and are modelled by semi-distributed models, such as TOPMODEL (Beven and Kirkby, 1979), or fully distributed models, such as SMDR (Hively et al., 2006). Once chemicals have entered a hydrological network, their fate depends on their chemical properties, biochemical and biological interactions, and also transient storage. Transient storage of chemicals within a river channel is related to channel storage (CS), corresponding to transfer delays occurring in the surface water (SW) column due to eddies or dead water zones, and to exchanges with the hyporheic zone (HZ), a compartment such as sediments or bank material within which SW can infiltrate and move (Gooseff et al., 2005; Uijttewaal et al., 2001). In headwaters, major representative river features, such as colluvial, step-pool and riffle-pool channel types, have been identified by Hassan et al. (2005) and Chin and Wohl (2005). They have been associated with specific transient exchange patterns (Buffington and Tonina, 2009).

Considering the role transient storage plays in the river buffering effect, more information about transient storage is necessary to quantify, control and manage pollution, and to better recognise where transient storage occurs in stream. Transient storage has







been the subject of many modelling studies. Water exchanges within gravel beds have been simulated in laboratory conditions (Tonina and Buffington, 2007; Cardenas and Wilson, 2007), coupling the St. Venant equation and Darcy's law to predict hyporheic residence time. Under field conditions, given the inherent variability of hydraulic properties and exchange rates along rivers and their alluvial deposits, models consider advection-diffusion in the SW and a source-sink term -a kernel- to account for transient storage. The kernel estimates a density of mass-transfer rate within transient stores, often with an exponential or power-law distribution (Haggerty et al., 2002; Gooseff et al., 2005, 2006). Transientstorage equations with exponential laws represent a typical case modelled by the One-Dimensional Transport with Inflow and Storage model (OTIS), which was developed to analyse feedback between SW and groundwater (Bencala and Walters, 1983; Herrman et al., 2010), the effect of flow obstruction on transient storage (Stofleth et al., 2008) or the fate of nitrogen along a river network (Stewart et al., 2011). Neilson et al. (2010) and Briggs et al. (2009) improved OTIS equations, separating transient storage into surface (dead zones) and HZ components. Whilst there is a consistent body of studies concerning processes occurring within rivers, sediments and aquifers, models of transient storage mainly have site-specific parameters or concern short river reaches. They do not help for regional scale analysis – notably several-km-long rivers - of relations between catchment and river morphology and their consequences on water flows and transient storage of solutes (Environment Agency, 2009).

To contribute to this topic, we applied a one-dimensional transport model that considers morphological and hydrodynamic descriptors, to couple water inputs from groundwater seepage, and the transport of solutes in a river system during low-flow conditions. Model predictions were compared to breakthrough curves (BTC) recorded at two locations downstream of the injection point of a non-persistent-reactive dye (Rhodamine WT, or RWT). Sensitivity analysis was performed to study relations between catchment and river features and the residence time of solutes in SW, CS and HZ.

2. Site and methods

2.1. Site

The Gordes River catchment (10 km²) is representative of upland rivers of the southern shore and foothills of the Lake Léman basin in France (Fig. 1). The head of the catchment is located in calcareous sedimentary formations. On the upper part of the catchment (upstream of point A, Fig. 1), where the substratum consists of shales and sandstones, slopes are steep (mean 25-30%) and dominated by forests. Calcareous moraines are well represented in the foothills in the centre of the catchment (from A to C, Fig. 1), associated with a gently rolling landscape, where slopes range from 10% to 15%. Here grasslands and annual crops dominate, with scattered spots of urban development. The flat lower and morainic part (0.5-5%) of the basin is mainly covered by forests, whereas urban areas increase near the lake shore. The soils developed on the upper part are mainly Haplic Cambisols (brownish discolouration and structure formation in the soil profile, with no particular soil features). Those on moraine areas are Eutric Cambisols (base saturation of 50-70% from 20 to 100 cm) (World Reference Base for Soil Resources, 2006).

The river studied (7 km long) drains the entire sequence of forest – agricultural land – forest (Fig. 1). From points A to C, the depth and width of the riverbed were recorded every 10–20 m. We used a GPS (MobileMapper-Magellan) to reference the geographic coordinates of recorded data. The high of river banks, river width and depth were evaluated from direct or trigonometric measurements by means of a clinometer, a decameter and a tape fixed on a stick. Field data were interpolated using a geographic information system (Quantum GIS) to map the river bottom and define a 1D computational domain consisting of a succession of cells 1 m long, each associated with a rectangular section of defined width and surface area. Mean diameter of gravels, stones, and boulders and mean texture of bed sediments were also recorded, as was the presence of woody debris and the overall configuration of riverbed morphology (width, depth, presence of riffle, pools, etc.). Approximately 500 m downstream of point B (Fig. 1), a firstorder tributary reaches the studied river, causing a net increase in river flow. According to Buffington and Tonina (2009), reach A–B (mean slope: 3.6%) belongs to the "bedrock" type, in which mainly pebbles (5-20 cm diameter) and sometimes boulders (>40 cm) cover the riverbed. This reach also has short passages of riffle and step-pool channel types, in which fine sediments can be observed in flow paths with lower velocity. These features were systematically described, their length, width and geographical location where measured and recorded. Reach B-C (mean slope 1.9%) meanders somewhat and mainly corresponds to a succession of confined riffles from alluvial deposits and step-pool features. Along this lower part of the river, depth and width increase. Sediments mainly consist of gravels in riffles preceding step-pools and of fine sandy material in pools. The mean distance between pools is about 5-10 m. The studied river has about 85% of its morphological features associated with colluvial and alluvial fill. Each cell of the computational domain was assigned to bedrock, riffle or pool, which meant that its HZ was assigned to stone, gravel or fine sediment, respectively.

2.2. Dye injection

To mimic in-stream effects (degradation, retention-release) that commonly affect the fate of solutes, RWT was injected during lowflow conditions. Given its adsorptive and extinction behaviour, 46.76 g of RWT was injected in a single dose at point A (Fig. 1). Fluorescence was recorded at point B (1022 m down-slope of the injection point) for 5.5 h using a CGUN-FL fluorimeter. The probe was then moved to point C (4198 m down-slope of point B), and data recording continued for 24 h until noise was detected in the probe signal. Steady-state conditions for discharge were verified throughout the monitoring. Sodium chloride was also injected to measure local water discharges at points B and C, using a CS547A Campbell conductivity probe.

2.3. Model

2.3.1. River and transient storage

We considered both CS and HZ exchanges (Fig. 2). The river is composed of a succession of one-dimensional cells of length Δx (1 m), where exchanges of water and solutes take place between SW, CS and the HZ (underlain by an impervious layer).

Longitudinal water velocity u in the SW (m s⁻¹) is:

$$\frac{\partial u}{\partial t} = -u\frac{\partial u}{\partial x} - g\left(\frac{\partial \eta}{\partial x} + \frac{u|u|}{C^2h}\right) \tag{1}$$

where *t* is time (s), $g = 9.81 \text{ m s}^{-2}$ is acceleration due to gravity, η is the height of the water surface-measured above a reference level (m), *h* is the depth of SW (m) and *C* is Chezy's friction coefficient $(m^{-1/2} \text{ s}^{-1})$. This is obtained from $C = \frac{1}{n} W_p^{1/6}$, where *n* is Manning's roughness coefficient $(m^{-1/3} \text{ s})$ and W_p is the hydraulic radius (m). Following Cardenas and Wilson (2007) and Tonina and Buffington (2007), longitudinal velocity u_z (m s⁻¹) in the HZ is obtained from Darcy's law:

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