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Quantification of long-term wastewater fluxes at the surface water/groundwater-interface: An integrative model perspective using stable isotopes and acesulfame

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HIGHLIGHTS

- Acesulfame missed surface water volumes that still remained in the hyporheic zone under stream-gaining conditions.
- Under stream-losing conditions acesulfame based predictions lead to an overestimation of the surface water volume in the riparian zone.
- Acesulfame is a less-ideal tracer as a portion of acesulfame might be stored in smaller pores and is released again under high water events.

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ABSTRACT

The suitability of acesulfame to trace wastewater-related surface water fluxes from streams into the hyporheic and riparian zones over long-term periods was investigated. The transport behavior of acesulfame was compared with the transport of water stable isotopes ($\delta^{18}O$ or $\delta^{2}H$). A calibrated model based on a joint inversion of temperature, acesulfame, and piezometric pressure heads was employed in a model validation using data sets of acesulfame and water stable isotopes collected over 5 months in a stream and groundwater. The spatial distribution of fresh water within the groundwater resulting from surface water infiltration was estimated by computing groundwater ages and compared with the predicted acesulfame plume obtained after 153 day simulation time. Both, surface water ratios calculated with a mixing equation from water stable isotopes and simulated acesulfame mass fluxes, were investigated for their ability to estimate the contribution of wastewater-related surface water inflow within groundwater. The results of this study point to limitations for the application of acesulfame to trace surface water–groundwater interactions properly. Acesulfame completely missed the wastewater-related surface water volumes that still remained in the hyporheic zone under stream-gaining conditions. In contrast, under stream-losing conditions, which developed after periods of stagnating hydraulic exchange, acesulfame based predictions lead to an overestimation of the surface water volume of up to 25% in the riparian zone. If slow seepage velocities prevail a proportion of acesulfame might be stored in smaller pores, while when released under fast flowing water conditions it will travel further downstream with the groundwater flow direction. Therefore, under such conditions acesulfame can be a less-ideal tracer in the hyporheic and riparian zones and additional monitoring with other environmental tracers such as water stable isotopes is highly recommended.

1. Introduction

Surface waters like streams often receive micro-pollutants such as pharmaceuticals or personal care products that predominantly originate from discharges of sewage water treatment plants (e.g., Ternes, 1998; Reddersen et al., 2002). The critical areas where potentially polluted surface water can exchange with groundwater are the hyporheic and riparian zones along rivers. The area of saturated sediments around the stream bed that contains at least 10% stream water and less than 90% groundwater is defined as hyporheic zone (Triska et al., 1989). The area that surrounds the stream in the watershed is the riparian zone (Gregory et al., 1991) and thus forms an important link between terrestrial and aquatic ecosystems (Martínez-Santos et al., 2012). Research over the past two decades has established that both, the hyporheic and riparian zones, enhance the mass transfer of dissolved solutes

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between streams, the stream bed and groundwater (e.g., Puckett and Hughes, 2005; Edwards, 1998). The interaction between streams and the hyporheic or riparian zones takes place in three principle ways (Winter et al., 1998):

- streams gain water from inflow of groundwater through the streambed (gaining stream),
- they lose water to groundwater by outflow through the streambed (losing stream),
- they gain groundwater in some sections and lose surface water in others.

In the riparian and hyporheic zones, transport of wastewater-related micro-pollutants can only be assessed properly by environmental tracers that truly mirror the migration of surface waters and the hydrodynamic patterns during losing and gaining stream conditions. Well-established environmental tracers to quantify surface water fluxes into groundwater are temperature (e.g., Brookfield et al., 2009; Anderson, 2006; Stonestrom and Constantz, 2003), water stable isotopes (e.g., Adomako et al., 2010; Kalbus et al., 2006), and also wastewater-related tracers such as the artificial sweetener acesulfame-K ($C_8H_8KN_2O_8S_2$) (Buerge et al., 2009) or rare earth elements such as gadolinium (Gd) (Verplanck et al., 2005). Surface water temperature signals are often quickly reduced in groundwater due to retardation and therefore reach only the first few meters beneath the river bed (e.g., Engelhardt et al., 2011; Therrien et al., 2010). Thermal retardation accounts for the fact that energy travels through both fluid-filled pores and the sediment matrix and is therefore "retarded" by the sediment matrix relative to the heat transport by fluid flow (Shook, 2001).

Over the last years, sewage water-related tracers such as acesulfame or gadolinium are often characterized by rising background concentrations in groundwater. This in turn will i) introduce more bias and uncertainty into numerical modeling investigations analyzing sewage water-related tracers, especially for assigning initial conditions, and ii) limit the difference between the tracer concentrations in the surface water and groundwater (Engelhardt et al., 2013; Wolf et al., 2012). Rising and spatial variable background concentrations will make sewage water-related tracer therefore less useful in the hyporheic and riparian zones. High uncertainties prevail also in the wastewater mass fluxes that are released from sewage water treatment plants and drive highly variable fluctuations of the environmental tracers within the surface water (Engelhardt et al., 2013; Wolf et al., 2012; Lewandowski et al., 2011).

Water stable isotope ratios ($^2H/^1H$ and $^{18}O/^{16}O$) are environmental tracers that are not affected by retardation as they are transported with the water molecule itself (Granger et al., 2010). Their signal can be retrieved not only beneath the river bed, but also further away from the river bank, especially after flood event waves (Barth et al., 2006; Yehdegho et al., 1997; Stichler et al., 1986). However, the extent of the traceability of flood events requires a pronounced different isotope composition between the flood wave in the surface water and the groundwater.

Groundwater water stable isotope ratios often are constant with values close to the annual mean isotope composition of the local precipitation. In contrast to the isotopic composition of the groundwater, stable isotopes of surface waters usually follow and record seasonal changes of local precipitation and evaporation effects, provided that the elevation of catchment area and river-water sampling stations are comparable (Henderson and Shuman, 2010; Dutton et al., 2005; Kendall and Coplen, 2001). The isotopic seasonal cycle of precipitation is generally characterized by a sinusoidal function with lower isotope values during the cold season, whereas the warm season is characterized by higher values. However, the amplitudes of such seasonal patterns in river water isotopes are often less pronounced when compared to those found in local precipitation. This results from mixing (i) of water from different sources, and (ii) between the surface water and the groundwater within the stream (Dutton et al., 2005).

Several studies demonstrated the value of stable isotopes to trace surface water fluxes in groundwater (e.g., Adomako et al., 2010; Henderson and Shuman, 2010; Barth et al., 2006; Barth and Veizer, 2004). However, only few studies monitored water stable isotopes in the riparian zone over time scales longer than 100 days (Lamontagne et al., 2005). In addition, these studies did not compare wastewater-related mass fluxes of micro-pollutants with results obtained from stable isotope analysis.

The aims of our study were therefore to compare and assess the suitability of acesulfame concentrations and water stable isotope ratios ($\delta^{18}O$ or δ^2H) to trace wastewater-related surface water fluxes from the stream into the riparian zone over an observation period of several months. For this purpose, we employed a calibrated model that relied on a joint inversion of temperature, acesulfame and piezometric pressure heads (Engelhardt et al., 2013). In a model validation new data sets of acesulfame and water stable isotopes that were collected over a period of 5 months from May to October 2011 were analyzed.

The results of this long-term study point to limitations for the application of acesulfame to trace wastewater-related stream discharge into the riparian zone that might be missed when data are considered for time periods of days to weeks only.

2. Materials and methods

2.1. Study site

The Schwarzbach stream is located in the federal state of Hesse near Frankfurt, Germany. The region is intensely used for industry and agriculture, while – with conflicting interests – it also serves as source for the freshwater supply.

Precipitation and air temperature were recorded 3 km east from the field site (49°56.420′N and 8°30.090′E) on a daily basis at the meteorological station in the town Groß-Gerau. The field experiment lasted over a period of five months from spring to autumn (May, 1st to October, 1st, 2011). During this period some intense rain events occurred with a maximum rainfall intensity of 30 mm d^{-1} in June and 42 mm d^{-1} in September. The majority of days remained dry or received smaller amounts of precipitation below 10 mm d^{-1} and the mean rain fall intensity was 3.8 mm d^{-1} during the investigated period. The mean discharge of the Schwarzbach was at the study site ~0.6 m^3 s^{-1} (averaged between 2008 and 2011). Short-term discharge could increase up to 4 m^3 s^{-1} after intense rain events. Accordingly, the depth of the stream varied from 0.2 m in dry summer periods to 0.8 m within a few hours after the intense rain in September 2011.

The aquifer beneath the stream consists of quaternary sediments with successively increasing grain sizes from silt at the top towards sand and fine gravel at the bottom. The hydraulic conductivity, thickness, and porosity of the aquifer and river bed sediments were defined with pumping tests in a previous study and are described in detail in Engelhardt et al. (2011). The aquifer is structured into layers with thicknesses varying between 1 m at the top (layer 1) and more than 10 m at the bottom (layer 5, Fig. 1). The hydraulic conductivity increases from values between 4×10^{-7} and 4×10^{-5} m s^{-1} (silt layer) at the top to 3×10^{-4} (fine sand layer) and reaches 1×10^{-3} m s^{-1} at the fine-gravel-bottom layer. No pronounced clogging layer with a reduced permeability could be identified and the hydraulic conductivity of the stream bed sediments varies between 5×10^{-5} and 4×10^{-4} m s^{-1}.

Under these hydrogeological conditions a semi-confined groundwater system was developed with a general flow direction from east to west towards the river Rhine. The mean horizontal hydraulic gradient is 5‰ with a regional mean flow velocity of about 1 m d^{-1}. The depth to the groundwater table ranged between 0.9 m and 1.4 m close to the Schwarzbach and increases to >2 m at 220 m distance from the stream thus follows the regional horizontal hydraulic gradient. During summer periods with a low stream level infiltration is reduced due to a small vertical hydraulic gradient between the stream and the groundwater. However, in autumn when higher water levels prevail in combination with a