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Application of integral pumping tests to investigate the influence of a losing stream on groundwater quality

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Abstract

Losing streams that are influenced by wastewater treatment plant effluents and combined sewer overflows (CSO's) can be a source of groundwater contamination. Released micropollutants such as pharmaceuticals, endocrine disrupters and other ecotoxicologically relevant substances as well as inorganic wastewater constituents can reach the groundwater, where they may deteriorate groundwater quality. This paper presents a method to quantify exfiltration mass flow rates M_{ex} of wastewater constituents from losing streams by the operation of integral pumping tests (IPT's) up- and downstream of a target section. Due to the large sampled water volume during IPT's the results are more reliable than those from conventional point sampling. We applied the method at a test site in Leipzig (Germany). Wastewater constituents K^+ and NO_3^- showed M_{ex} values of 1241 to 4315 and 749 to 924 $\text{mg m}_{\text{stream}}^{-1} \text{d}^{-1}$, respectively, while Cl^- (16.8 to 47.3 $\text{g m}_{\text{stream}}^{-1} \text{d}^{-1}$) and SO_4^{2-} (20.3 to 32.2 $\text{g m}_{\text{stream}}^{-1} \text{d}^{-1}$) revealed the highest observed M_{ex} values at the test site. The micropollutants caffeine and technical-nonylphenol were dominated by elimination processes in the groundwater between upstream and downstream wells. Additional concentration measurements in the stream and a connected sewer at the test site were performed to identify relevant processes that influence the concentrations at the IPT wells.

1 Introduction

Contamination of streams and groundwater by substances that originate from wastewater have been reported in many studies (Eiswirth et al., 2004; Vazquez-Sune et al., 2005; Ellis, 2006). Streams can become contaminated, for example, from wastewater treatment plant discharge containing contaminants that are not completely eliminated during the treatment process. Untreated wastewater is discharged to streams during combined sewer overflows (CSO's) where it leads to increased loadings of wastewater constituents (Mulliss et al., 1996). Mendoza et al. (2008) demonstrated that con-

taminated streams with alternating conditions between losing and gaining may pose a threat to groundwater quality. Micropollutants such as persistent pharmaceuticals, originating primarily from wastewater, have become emerging contaminants in surface water and groundwater (Fenz et al., 2005; Schwarzenbach et al., 2006; Schirmer et al., 2007; Schirmer and Schirmer, 2008). Various groundwater studies have focused on the occurrence of these substances during bank filtration (e.g. Heberer, 2002), but few studies exist on the transport of wastewater constituents from losing streams to the groundwater under natural conditions.

This paper aims to improve the knowledge on the influence of temporally losing streams on groundwater quality by presenting a method to estimate exfiltration mass flow rates M_{ex} of wastewater constituents from a stream during losing conditions. The approach of Kalbus et al. (2007) that uses integral pumping tests (IPT's; Bayer-Raich et al., 2004) for the estimation of mass fluxes J at the stream-aquifer interface of gaining streams was extended to the application to losing streams. The study was performed in 2008 at a test site in Leipzig, Germany (Strauch et al., 2008). The analysis was derived for four inorganic substances (K^+ , Cl^- , NO_3^- and SO_4^{2-}) as well as for the micropollutants caffeine (CAF) and technical-nonylphenol (NON). We operated IPT's up- and downstream of the investigated target section to account for heterogeneous concentration patterns in the vicinity of the stream. On the one hand, we faced varying concentrations resulting from heterogeneities in the aquifer and the fluctuating household-related input of wastewater to the stream during dry- and wet-weather conditions. Under these conditions, sampling during long-time pumping with IPT's yields more reliable average concentrations c_{av} than conventional point sampling in space and time. On the other hand, natural hydraulic gradients between stream and groundwater are disturbed by pumping. The dimensioning of the IPT needs to account for this by increasing the distance between the pumping well and the stream so that the capture zone of the pumping well does not reach the groundwater that is influenced by the intensified exfiltration from the stream. The mass flow increase ΔM downstream of the investigated stream yields M_{ex} .

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In order to interpret the concentrations and mass flow rate data from IPT's, processes that influence the concentration pattern in the groundwater need to be defined. We assume that the following processes (a) to (h) may occur at the test site. Exfiltration water concentrations from the stream are influenced by (a) temporally high concentrations in the stream as a result of variable wastewater treatment plant effluents and CSO's in the upper catchment of the stream, (b) retardation in the streambed, (c) degradation in the streambed and (d) exchange with storage pools in the pore water of the streambed and the stream banks that are fed during times of high water levels in the stream. Concentrations of target substances in the groundwater increase or decrease along the flow path from the upstream to the downstream wells due to (e) mixing of groundwater with exfiltration water from the stream, (f) hydrodynamic dispersion and mixing with groundwater recharge, (g) retardation in groundwater and (h) degradation in groundwater. Additional concentration measurements in the stream and in a connected sewer at the test site were performed to identify these processes.

2 Materials and methods

2.1 Test site

The investigated stream *Bauerngraben* (Fig. 1) is located in the urban area of the city of Leipzig (Germany). The small, artificial watercourse is constructed of cobbled pavement, whose joints are filled with sand. It has an average width of 1 m in the study area. The inflow to the *Bauerngraben* originates from a flood protection reservoir and is controlled by a weir. Under dry-weather conditions the *Bauerngraben* has a discharge of 0.01 to $0.03 \text{ m}^3 \text{ s}^{-1}$. The *Bauerngraben* is strongly influenced by three outlet pipes for CSO's that are located in the east of the test site (only one is shown in Fig. 1). Due to the controlled inflow to the *Bauerngraben*, water level fluctuations in the stream are mainly an effect of CSO's. In the period from April 2006 to April 2007 43 CSO's were detected by water level logging in the *Bauerngraben* with water level

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fluctuations between 10 and 105 cm. Observation wells near the *Bauerngraben* show variable groundwater levels that are above the streambed in winter and below it in summer. The IPT's were performed during losing conditions of the *Bauerngraben*.

The stratigraphy below the study area consists of Tertiary fine sands overlain by a Quaternary sand and gravel layer. The Quaternary sediments form a highly permeable aquifer with a hydraulic conductivity K of 3×10^{-4} to $4 \times 10^{-3} \text{ ms}^{-1}$. Heterogeneous floodplain loams with an average thickness of 1.5 m cover the aquifer. Ram sounding in the streambed of the *Bauerngraben* indicated no floodplain loam below the investigated reach.

2.2 Observed wastewater constituents

The four inorganic substances (K^+ , Cl^- , NO_3^- and SO_4^{2-}) and two micropollutants (CAF and NON) were chosen according to preliminary studies (Musolff et al., 2007; Reinstorf et al., 2008) in which these substances had already been used as wastewater indicators. Regarding possible sources of the chosen wastewater constituents, K^+ originates from laundry discharge (Wolf et al., 2007). Large amounts of Cl^- are washed from roads during the winter period when road salting occurs (Mayer et al., 1999), but other sources are also known (e.g. dishwashers). Nitrification of NH_4^+ , which can originate from urine, is a common source of NO_3^- . Industrial wastewater represents a source of SO_4^{2-} (Barrett et al., 1999). CAF is a constituent of different beverages such as coffee or tea and of numerous food products (Buerge et al., 2003). Technical-nonylphenol (NON) is used for the production of non-ionic tensides, thus it originates mainly from industrial wastewater and laundry (Bradley et al., 2008).

2.3 IPT method background

Average concentrations c_{av} and mass flow rates M_{CP} along control planes (CP) in an aquifer can be reliably estimated by the IPT method (Bayer-Raich et al., 2004). The CP's are oriented perpendicular to the natural groundwater flow direction and con-

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tain one or more pumping wells. Long-time pumping (several days) of the wells and simultaneous sampling gives more reliable information about c_{av} and M_{CP} at the pre-defined CP than conventional point sampling, because the sampled volume is larger and small-scale plumes cannot be missed. The code CSTREAM (Bayer-Raich, 2004) can be used to estimate c_{av} and M_{CP} from the obtained concentration-time series by using the data from a one-layer Modflow groundwater model. The resulting isochrones define the boundary of the capture zone for the respective sample at this time. Successful operations of IPT's are reported in Bockelmann et al. (2003), Bayer-Raich et al. (2006) and Kalbus et al. (2007).

2.4 IPT design at the study area

Four IPT wells (11, 12, 13 and 14), two upstream and two downstream of the *Bauerngraben*, were drilled in the study area (Fig. 1) and screened along the Quaternary aquifer with HDPE-tubes. Over a period of five days (28 May to 2 June 2008), wells 11, 12 and 13 were operated with a pumping rate of 1 L s^{-1} . Due to operational problems at well 14, pumping was reduced to 0.5 L s^{-1} and stopped already after 32 h. The standard parameters of pH, electrical conductivity, oxygen content and temperature were measured in the pumping wells during the entire pumping period. The drawdown in 12 observation wells was measured at least every 2 h (with shorter intervals directly after the beginning of pumping) using a water level logging device in the pumping wells.

2.5 IPT evaluation

A groundwater model of the Quaternary aquifer was built with the software model Processing Modflow. The homogeneous, semi-confined model covers an extent of $200 \times 300 \text{ m}$ with an average aquifer thickness of 5.8 m at the wells. In the model grid cell sizes vary from 1 m at model boundaries to 0.25 m in the pumping area. Fixed head cells were implemented at the north and south boundaries of the model domain. The parameters of hydraulic conductivity $K = 4.5 \times 10^{-4} \text{ ms}^{-1}$, gradient $i = 4.1 \times 10^{-3}$ and

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effective porosity $n_e=0.2$ were estimated from various field measurements and set for water flow calculations. Water levels in groundwater on 25 May before the start of pumping were measured to be 20 cm below the streambed of the *Bauerngraben*, indicating that water was flowing from the *Bauerngraben* to the groundwater. Due to the disconnection between the stream and groundwater, pumping-induced drawdown would not increase the leakage from the *Bauerngraben*. Therefore, the leakage was implemented as a constant discharge rate Q_{ex} . Best fitting of observed to simulated water levels at the observation wells was obtained for a Q_{ex} of 85 L m_{stream}⁻¹ d. The average deviation between the simulated and observed water levels was 3 cm. Isochrones for the respective sampling schedule and streamlines (Fig. 1) were obtained by the particle tracking code Modpath. In order to get a complete overlapping of the upstream CP's (13, 14) by the downstream CP's (11, 12), the considered volume was reduced by neglecting samples of wells 12 and 13 at the end of the pumping period (Fig. 1). The CP lengths of wells 13 and 14 define the width b of the streamtubes 1 and 2. These streamtubes were used for mass balance calculations between the up- and downstream wells of the *Bauerngraben*. The estimation of c_{av} for the different CP's was derived with the code CSTREAM in combination with the groundwater model. Corresponding M_{CP} values were obtained by multiplying c_{av} with the respective water flow Q_{CP} . Thus M_{CP} specifies only the part of the CP at wells 11 and 12 that is located in the respective streamtube. Values of Q_{CP} were derived from the groundwater model. Differences of M_{CP} values between upstream and downstream wells depend on concentrations differences Δc and on different water flows Q_{CP} . For the comparison of the two streamtubes the mass fluxes J_{CP} at each CP are given. Values of M_{ex} were calculated by

$$M_{ex} = \frac{M_{CPY} - M_{CPX}}{L_{BG}}, \quad (1)$$

where M_{CPX} and M_{CPY} are the mass flow rates up- and downstream of the *Bauerngraben* and L_{BG} is the affected stream length, which is marked in Fig. 1. The estimation of M_{ex} was only possible for substances that show a downstream concentration

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increase (positive ΔM_{CP}).

2.6 Sampling in groundwater, surface water and wastewater

Groundwater samples were taken during the pumping period 28 May to 2 June 2008 from a tap at the IPT wells following a predefined schedule: inorganic samples every 4 h and organic samples every 8 h. After 56 h the sampling frequency for organic substances was reduced to 16 h. Surface water sampling was completed with an automatic sampling device that pumped surface water from the *Bauerngraben* (location in Fig. 1) to storage bottles every 5 min during the period 17 May to 2 June 2008. A reduction of the sample number from the surface water was achieved by mixing all 5 minutes samples from one day in one bottle. The obtained 17 mix-samples were analyzed for the target substances. In a former study (Leschik et al., 2009), grab samples of wastewater were taken from a sewer that was connected to the overflow pipe which discharges into the *Bauerngraben* (Fig. 1). These samples were picked during a 24 h period in February 2008 at an interval of 2 h for inorganic analysis and 8 h for organic analysis to quantify daily concentration variations of target substances.

2.7 Sample preparation and chemical analysis

Samples were stored cooled in 60 mL HDPE bottles for inorganic analysis and 1 L amber glass bottles for organic analysis. Ion chromatography was applied to analyze K^+ , Cl^- and SO_4^{2-} with limits of detection (LOD) of 1, 0.1 and 1 mg L⁻¹, respectively. NO_3^- was analyzed by the photometric salicylic acid method (LOD of 0.5 mg L⁻¹).

The sample preparation for micropollutant analysis was derived by solid phase extraction to enrich the target compounds from the water samples. Before they were concentrated, samples (1 L, pH at about 7) were filtered through a glass fiber filter and spiked with the internal standards (100 ng 4-n-nonylphenol). The filtrates were adjusted to pH2 and concentrated by SPE using a sorbent mixture (C18 and Lichrolut[®] EN) preconditioned with methanol and water. After application of the water sample, the

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sorbent was dried under inert gas and finally eluted with methanol and acetone. After evaporation of the solvent to a final volume of 300 μL a cleanup with silica gel was accomplished using a mixture of acetone and hexane. Evaporation of the solvent to a volume of 200 μL gives the sample for GC-MS analysis.

5 The GC-MS analyses of the micropollutants were performed using a Varian GC/MS (CP 3800, MS 1200) equipped with a temperature-programmable injection port. The gas chromatographic separation was carried out on a 60 m long Zebron ZB1 capillary column of 0.25 mm internal diameter and 0.25 μm film thickness (Phenomenex). The samples (5 to 10 μL each) were injected at 50°C by large volume injection. The GC
10 oven program started at an initial temperature of 50°C. Helium was used as the carrier gas in a constant flow mode at 1 mL min^{-1} . The mass spectrometer operated at positive electron impact ionization mode with 70 eV. The GC-MS interface temperature was set at 270°C and the source temperature at 200°C. A solvent delay of 8 min was used to fade out the solvent signal. The investigations utilized selected ion monitoring
15 (SIM) for sensitive detection of the target analytes (target ions caffeine –194, 149, 109; nonylphenols –220, 149, 107). All sample extracts were twice analyzed and after every fourth analysis blank analysis was carried out to check carryover and memories of previous analyses. The standard mixture was measured repeatedly within every sample series.

20 3 Results and discussion

3.1 Concentrations of wastewater constituents in groundwater

Concentration-time series and standard parameters of the IPT wells were evaluated in order to derive concentration differences Δc between the wells, especially downstream of the *Bauerngraben*. These Δc 's identify how the inflow from the *Bauerngraben* influ-
25 ences the groundwater quality at the test site.

The measured pH of 6.2 to 6.4, an oxygen content of 0 to 1 mg L^{-1} and temperatures

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of 9 to 10°C obtained from the wells during the pumping period did not indicate a large difference between the pumped water from different locations, whereas the electrical conductivity in well 12 of 1360 to 1450 $\mu\text{S cm}^{-1}$ in comparison to the other wells (1260 to 1370 $\mu\text{S cm}^{-1}$) points to a difference in the ion composition of the groundwater.

5 The influence of the *Bauerngraben* can be identified by higher concentrations of K^+ , Cl^- and lower concentrations of SO_4^{2-} at the downstream wells 11 and 12 (Fig. 2). NO_3^- shows a similar concentration gradient between upstream and downstream wells with increased concentrations downstream of the *Bauerngraben* in both streamtubes, but concentrations in streamtube 2 are generally higher than in streamtube 1. This
10 is caused by heterogeneous inflows of wastewater constituents upstream of the test site where parts of the urban area of Leipzig are located. The comparison of the obtained ion concentrations at the test site with other studies of urban groundwater (e.g. Choi et al., 2005) reveals high ion concentrations in the urban aquifer of Leipzig. This indicates a strong influence of the urban area of Leipzig on the groundwater com-
15 position, but also shows that additional sources of the investigated ions (unassociated with wastewater) exist upstream of the test site. Examples of these additional sources are abandoned metalworking and chemical industries that act as point sources of the investigated substances.

A higher variability in the concentration-time series for micropollutants in comparison to inorganic substances points to a more heterogeneous concentration pattern of micropollutants in the groundwater. Due to these high variations, the identification of micropollutant Δc values between IPT wells from concentration-time series alone is not feasible. A more reliable comparison of the average concentration c_{av} at the IPT wells was conducted using M_{CP} and J_{CP} values from the CSTREAM code calculations.

25 3.2 Mass flow rates of wastewater constituents

Values of M_{CP} from IPT's depend on the estimated water flow through the CP. Since the CP length L_{CP} is defined by the isochrone shape, in this section we will briefly discuss these isochrones. The isochrone shape in Fig. 1 is influenced by pumping-induced

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interaction between wells and natural groundwater flow, which shifts the isochrones upstream. At the end of the pumping period, the capture zones of wells 11 and 12 reach areas of the aquifer that are upstream of the *Bauerngraben*, thus measured concentrations at this time are mixed between up- and downstream groundwater. As the concentration-time series did not show a significant change in the water composition at this time, and the pumped upstream volume is small compared to the pumped downstream volume, this was neglected for the evaluation of the IPT's.

The obtained M'_{CP} s and J_{CP} 's (Table 1) mainly confirm the differences in the groundwater composition between the IPT wells from the concentration-time series. K^+ , Cl^- and NO_3^- show higher M_{CP} 's downstream of the *Bauerngraben*. Due to increased Q_{CP} at the downstream CP's M_{CP} 's of SO_4^{2-} are higher downstream even if the concentrations are higher at the upstream CP's. Micropollutant M_{CP} 's are mostly lower at the downstream wells with the exception of CAF in streamtube 2. The major ions Cl^- and SO_4^{2-} show the highest J_{CP} 's at the test site. Differences of one order of magnitude in J_{CP} between both streamtubes for NO_3^- indicate a more heterogeneous concentration pattern of NO_3^- in the groundwater upstream of the test site in comparison to the other wastewater constituents. Higher values of ΔM_{CP} in streamtube 2 for the majority of substances can be explained by higher Q_{ex} from the affected stream section L_{BG2} . The reasonably conservative ion SO_4^{2-} (reasons for the conservative behavior at the test site are given in the next section) can be used for the estimation of Q_{ex} by

$$Q_{ex} = \frac{Q_{CP \text{ upstream}}}{L_{BG}} \times \frac{C_{\text{downstream}} - C_{\text{upstream}}}{C_{\text{surface water}} - C_{\text{downstream}}}, \quad (2)$$

with the average concentration in the *Bauerngraben* $c_{\text{surface water}}$, at the upstream CP C_{upstream} and at the downstream CP $C_{\text{downstream}}$. The affected stream length L_{BG} and the water flow Q_{CP} are given in Table 1. The application of Eq. (2) with the measured data yields Q_{ex} values of 52 and 104 $L \cdot m_{\text{stream}}^{-1} \cdot d^{-1}$ for streamtube 1 and 2, respectively.

Therefore less dissolved wastewater constituents infiltrate the groundwater from the *Bauerngraben* in streamtube 1. Due to the increased Q_{ex} to streamtube 2, the M_{ex}

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values of K^+ , Cl^- and CAF (Table 1) are higher in this streamtube than in streamtube 1. NO_3^- shows an inverse pattern with a higher M_{ex} in streamtube 1. The calculated Q_{ex} 's from SO_4^{2-} are in the same magnitude of the Q_{ex} value ($85 L \cdot m_{\text{stream}}^{-1} \cdot d^{-1}$) that was implemented in the groundwater model. A spatially variable Q_{ex} as a boundary condition for the groundwater model was not assigned because the influence of the stream on the groundwater flow is limited. Streamlines in Fig. 1 were only marginally deflected by the stream.

3.3 Identification of processes that influence concentrations in the groundwater

The sampled concentrations in the wastewater in February 2008, those in the *Bauerngraben* from 17 May to 2 June 2008 and from the IPT wells from 28 May to 2 June 2008 are summarized in the boxplot in Fig. 3. The wastewater concentrations were included to show how CSO's from the connected sewer can affect the water composition in the *Bauerngraben*. The resulting concentrations of wastewater constituents in the *Bauerngraben* during CSO's may be lower than in the wastewater due to dilution from precipitation and mixing with water from the *Bauerngraben*, but can still be higher than in the groundwater. Gasperi et al. (2008) compared wastewater concentrations during wet-weather and dry-weather conditions and found out that concentrations during wet-weather conditions are not strictly reduced. The erosion of in-sewer deposits formed within sewer during dry periods was identified as a potential reason for this. However, measurements in the wastewater during precipitation events were not undertaken to prove this. Thus the shown wastewater concentrations can be helpful to identify CSO's as a cause of temporally high concentrations of the investigated substances in the *Bauerngraben*. Temporally high concentrations during CSO's are accompanied by high water levels in the *Bauerngraben* that induce bank storage (Li et al., 2008). The outflow from the stream banks can also influence the groundwater composition following the CSO event. Concentrations of the three water compartments in Fig. 3 are used

to identify processes (a) to (h) that influence the observed M_{CP} 's depending on the components' transport properties. In the following section we thus discuss M_{CP} , J_{CP} and M_{ex} substance by substance. Process (f) hydrodynamic dispersion and mixing with groundwater recharge was not included in the detailed discussion because the short flow path of approximately 32 m between the up- and downstream wells and the floodplain loam cover of the observed aquifer reduce the influence of this process.

3.3.1 K^+

Higher M_{CP} 's downstream of the *Bauerngraben* point to an exfiltration of K^+ from the *Bauerngraben*. Measured concentrations of K^+ in the *Bauerngraben* are below concentrations in groundwater. In order to explain the positive M_{CP} 's process (a) temporally high concentrations in the stream must play an important role. Reversible sorption of K^+ on streambed materials ((b) retardation in the streambed) and (d) exchange with storage pools in the streambed may lead to an accumulation of K^+ in the streambed. High K^+ concentrations in the wastewater indicate that this temporal storage may be supplied by (a). Leaching of the streambed and the stream banks can lead to the observed M_{ex} . A reduction of K^+ via (g) retardation in groundwater is possible, but is likely less important because ΔM_{CP} is still positive.

3.3.2 Cl^-

Cl^- behaves conservatively in the groundwater (Barrett et al., 1999), thus processes (b) retardation in the streambed, (c) degradation in the streambed, (g) retardation in groundwater and (h) degradation in groundwater do not occur. Concentrations in the groundwater lie above those in the *Bauerngraben*, therefore exfiltration from the *Bauerngraben* must reduce concentrations of Cl^- downstream of the *Bauerngraben*, but the opposite was observed. The calculated ΔM_{CP} 's were positive in both streamtubes. Mayer et al. (1999) reported an accumulation of Cl^- in the pore water of benthic sediments of surface waters. Process (d) exchange with storage pools in the

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streambed can thus be an explanation of the increased Cl^- concentrations downstream of the *Bauerngraben*. Temporally high concentrations of Cl^- in the *Bauerngraben* (a) can originate from CSO's, because concentrations in the wastewater are higher than in the groundwater. Because a high ΔM_{CP} (especially in streamtube 2) cannot be explained by exfiltration from the *Bauerngraben* alone, we thus assume an additional Cl^- source in the groundwater or in the streambed that could not be identified with the observed concentrations.

3.3.3 NO_3^-

Figure 3 shows higher NO_3^- concentrations in the *Bauerngraben* than in groundwater. Positive ΔM_{CP} 's as a result of (e) mixing of groundwater with exfiltration water seem to be reasonable due to the high mobility of NO_3^- in groundwater that is not affected by sorption processes (b) retardation in the streambed and (g) retardation in groundwater (Freeze and Cherry, 1979). Measured low oxygen concentrations at the test site indicate that denitrification may cause (c) degradation in the streambed and (h) degradation in groundwater. NO_3^- concentrations in wastewater are considerably low, but will be increased if enough oxygen is available to nitrify dissolved NH_4^+ to NO_3^- , thus (a) temporally high concentrations in the stream may increase NO_3^- concentrations in the *Bauerngraben*. During the wastewater sampling program NH_4^+ concentrations of 41 to 64 mg L⁻¹ were observed, whereas concentrations in the *Bauerngraben* and groundwater were mostly below 1 mg L⁻¹.

3.3.4 SO_4^{2-}

We identify (e) mixing of groundwater with exfiltration water as the most important process at the field site which is affecting SO_4^{2-} concentrations. Similar SO_4^{2-} concentrations in wastewater and the *Bauerngraben* indicate that CSO's will not increase concentrations of SO_4^{2-} in the *Bauerngraben*. Concentration gradients between the

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Bauerngraben and groundwater point to a dilution of groundwater with exfiltrating water from the *Bauerngraben* (e). Anions such as SO_4^{2-} are not affected by sorption thus (b) retardation in the streambed and (g) retardation in groundwater can be excluded for SO_4^{2-} . Sulfate reduction ((c) degradation in the streambed and (h) degradation in groundwater) is not relevant because alternative electron donors (O_2 or NO_3^-) are available at the test site.

3.3.5 CAF

A gradient between surface water and groundwater concentrations points to a possible input of CAF into the groundwater via (e) mixing of groundwater with exfiltration water. Higher concentrations in the wastewater than in the *Bauerngraben* indicate that (a) temporally high concentrations in the stream may occur. Lower limits of CAF concentrations that are below the LOD in surface water and groundwater can be explained by natural elimination processes. Buerge et al. (2003) reported biodegradation as an important elimination process of CAF in surface water. In contrast, sorption was identified to be negligible by the same authors, due to a low octanol-water partition-coefficient $p_{\text{OW}} \approx 0$. Attenuation of organic contaminants in streambeds was reported by Hoehn et al. (2007). Thus we assume that CAF loadings are reduced by (c) degradation in the streambed and (h) degradation in groundwater, but not by (b) retardation in the streambed and (g) retardation in groundwater. The reduction processes lead to a negative ΔM_{CP} in streamtube 1. Parts of the CAF input from the *Bauerngraben* must be degraded in the streambed because the input does not increase $M_{\text{CP}11}$ above the level of $M_{\text{CP}13}$. In contrast, streamtube 2 revealed a positive ΔM_{CP} . Assuming similar degradation conditions in the groundwater of both streamtubes, the additional mass flow of CAF in streamtube 2 must originate from the *Bauerngraben*. Whether this is an effect of reduced degradation in the streambed of streamtube 2 or of the increased Q_{ex} in streamtube 2 cannot be distinguished with the applied method. An influence of process (d) exchange with storage pools in the streambed may increase or decrease concentrations in the groundwater depending on the degradation rate in the pore water

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of the streambed.

3.3.6 NON

Groundwater concentrations of NON are below concentrations in the *Bauerngraben*. Thus (e) mixing of groundwater with exfiltration water may lead to positive ΔM_{CP} 's, but observed negative ΔM_{CP} 's in both streamtubes reveal that ΔM_{CP} is dominated by (g) retardation in groundwater and (h) degradation in groundwater. Due to the hydrophobic character of NON (Ying et al., 2008), its concentration may be affected by sorption onto streambed sediments. Degradation in streambeds was reported in Bradley et al. (2008). Considering these studies, the outflow concentrations from the *Bauerngraben* are strongly reduced by (b) retardation in the streambed and (c) degradation in the streambed. Therefore (a) temporally high concentrations in the stream and (d) exchange with storage pools in the streambed show only a small influence on the observed M_{CP} 's. A reliable quantification of degradation and sorption processes in the groundwater and in the streambed using the NON data is not possible. However, the calculated M_{CP} 's indicate that NON has only a low mobility in the groundwater at the test site.

4 Conclusions

This study shows that the application of integral pumping tests (IPT's) can provide detailed information about the influence of losing streams on the groundwater composition. The operation of IPT's up- and downstream of a wastewater affected target section yields reliable mass flow rates M_{CP} in groundwater that are not based on conventional point measurements. Exfiltration mass flow rates M_{ex} from the investigated stream can be estimated for substances that show increased M_{CP} 's downstream of the stream. The evaluation of the M_{CP} 's was derived for two streamtubes that are defined by two IPT wells per streamtube. The observed four inorganic and two organic wastew-

ater constituents reveal different influences on groundwater quality. Concentrations of major ions K^+ , Cl^- and NO_3^- increased, whereas the concentration of SO_4^{2-} was diluted by exfiltration from the stream at the test site. The application of IPT was reasonable, especially for micropollutants, because high variability of concentration-time series during pumping points to a high spatial heterogeneity in groundwater. Lower M_{CP} 's of technical-nonylphenol (NON) downstream of the target section were primarily caused by elimination processes in groundwater. Similar M_{CP} patterns were observed for caffeine (CAF) in one streamtube. Higher downstream values of M_{CP} for CAF in the other streamtube can be a result of stronger exfiltration Q_{ex} from the stream section in this streamtube or can be due to degradation processes in the streambed. Consequently, M_{ex} was only given for CAF in one streamtube as well as for K^+ , Cl^- , NO_3^- and SO_4^{2-} . The comparison of the concentrations in the groundwater with additional concentration measurements in wastewater and surface water at the test site were used to identify processes that influence the concentrations at the IPT wells downstream. Accordingly, the streambed was recognized as an important storage area, but also as an important area where degradation processes of the wastewater constituents occurs. Wastewater concentrations indicate that combined sewer overflows (CSO's) can induce temporally high concentrations of wastewater constituents in the target stream and thus can influence the groundwater composition at the test site. The results show that losing streams can be a relevant source of inorganic wastewater constituents. For the micropollutants, investigated here, losing streams seem a less important source due to the degradation potential of the streambed. The proposed IPT method can be operated at other field sites to investigate the influence of small streams on groundwater quality. Due to the significant effort required to carry out an IPT, a complete survey of a stream is impossible. Another limitation is that the method gives only integral ΔM values, therefore the distinction between different sources (groundwater or surface water) or processes (retardation or degradation) is difficult. Despite these limitations, this study shows that IPT's can be a powerful tool to quantify the influence of losing streams on groundwater quality.

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5 References

- Barrett, M. H., Hiscock, K. M., Pedley, S., Lerner, D. N., Tellam, J. H., and French, M. J.: Marker species for identifying urban groundwater recharge sources: A review and case study in Nottingham, UK, *Water Res.*, 33, 3083–3097, 1999.
- Bayer-Raich, M.: Integral pumping tests for the characterization of groundwater contamination, Geowissenschaftliche Fakultät, Eberhard-Karls-Universität, Tübingen, Germany, 2004.
- Bayer-Raich, M., Jarsjoe, J., Liedl, R., Ptak, T., and Teutsch, G.: Average contaminant concentration and mass flow in aquifers from time-dependent pumping well data: Analytical framework, *Water Resour. Res.*, 40, W08303, doi:10.1029/2004WR003095, 2004.
- Bayer-Raich, M., Jarsjoe, J., Liedl, R., Ptak, T., and Teutsch, G.: Integral pumping test analyses of linearly sorbed groundwater contaminants using multiple wells: Inferring mass flows and natural attenuation rates, *Water Resour. Res.*, 42, W08411, doi:10.1029/2005WR004244, 2006.
- Bockelmann, A., Zamfirescu, D., Ptak, T., Grathwohl, P., and Teutsch, G.: Quantification of mass fluxes and natural attenuation rates at an industrial site with a limited monitoring network: a case study, *J. Contam. Hydrol.*, 60, 97–121, 2003.
- Bradley, P. M., Barber, L. B., Kolpin, D. W., McMahon, P. B., and Chapelle, F. H.: Potential for 4-n-nonylphenol biodegradation in stream sediments, *Environ. Toxicol. Chem.*, 27, 260–265, 2008.
- Buerge, I. J., Poiger, T., Mueller, M. D., and Buser, H. R.: Caffeine, an anthropogenic marker for wastewater contamination of surface waters, *Environ. Sci. Technol.*, 37, 691–700, 2003.
- Choi, B. Y., Yun, S. T., Yu, S. Y., Lee, P. K., Park, S. S., Chae, G. T., and Mayer, B.: Hydrochemistry of urban groundwater in Seoul, South Korea: effects of land-use and pollutant recharge, *Environ. Geol.*, 48, 979–990, 2005.
- Eiswirth, M., Wolf, L., and Hoetzel, H.: Balancing the contaminant input into urban water resources, *Environ. Geol.*, 46, 246–256, 2004.

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- Ellis, J. B.: Pharmaceutical and personal care products (PPCPs) in urban receiving waters, *Environ. Pollut.*, 144, 184–189, 2006.
- Fenz, R., Blaschke, A. P., Clara, M., Kroiss, H., Mascher, D., and Zessner, M.: Quantification of sewer exfiltration using the anti-epileptic drug carbamazepine as marker species for wastewater, *Water Sci. Technol.*, 52, 209–217, 2005.
- Freeze, R. A. and Cherry, J. A.: *Groundwater*, Prentice-Hall, Englewood Cliffs, New Jersey, 604 pp., 1979.
- Gasperi, J., Garnaud, S., Rocher, V., and Moilleron, R.: Priority pollutants in wastewater and combined sewer overflow, *Sci. Total Environ.*, 407, 263–272, 2008.
- Heberer, T.: Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.*, 131, 5–17, 2002.
- Hoehn, E., Plumlee, M. H., and Reinhard, M.: Natural attenuation potential of downwelling streams for perfluorochemicals and other emerging contaminants, *Water Sci. Technol.*, 56, 59–64, 2007.
- Kalbus, E., Schmidt, C., Bayer-Raich, M., Leschik, S., Reinstorf, F., Balcke, G. U., and Schirmer, M.: New methodology to investigate potential contaminant mass fluxes at the stream-aquifer interface by combining integral pumping tests and streambed temperatures, *Environ. Pollut.*, 148, 808–816, 2007.
- Leschik, S., Musloff, A., Martienssen, M., Krieg, R., Bayer-Raich, M., Reinstorf, F., Strauch, G., and Schirmer, M.: Investigation of sewer exfiltration using integral pumping tests and wastewater indicators, *J. Contam. Hydrol.*, submitted, 2009.
- Li, H. L., Boufadel, M. C., and Weaver, J. W.: Quantifying Bank Storage of Variably Saturated Aquifers, *Ground Water*, 46, 841–850, 2008.
- Mayer, T., Snodgrass, W. J., and Morin, D.: Spatial characterization of the occurrence of road salts and their environmental concentrations as chlorides in Canadian surface waters and benthic sediments, *Water Qual. Res. J. Can.*, 34, 545–574, 1999.
- Mendoza, J. A., Ulriksen, P., Picado, F., and Dahlin, T.: Aquifer interactions with a polluted mountain river of Nicaragua, *Hydrol. Process.*, 22, 2264–2273, 2008.
- Mulliss, R. M., Revitt, D. M., and Shutes, R. B.: The impacts of urban discharges on the hydrology and water quality of an urban watercourse, *Sci. Total Environ.*, 190, 385–390, 1996.
- Musloff, A., Leschik, S., Reinstorf, F., Strauch, G., Moeder, M., and Schirmer, M.: Xenobiotics in groundwater and surface water of the city of Leipzig, *Grundwasser*, 12, 217–231, 2007.

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- Reinstorf, F., Strauch, G., Schirmer, K., Glaeser, H. R., Moeder, M., Wennrich, R., Osenbrueck, K., and Schirmer, M.: Mass fluxes and spatial trends of xenobiotics in the waters of the city of Halle, Germany, *Environ. Pollut.*, 152, 452–460, 2008.
- Schirmer, K. and Schirmer, M.: Who is chasing whom? A call for a more integrated approach to reduce the load of micro-pollutants in the environment, *Water Sci. Technol.*, 57, 145–150, 2008.
- Schirmer, M., Strauch, G., Schirmer, K., and Reinstorf, F.: Urban hydrogeology – Challenges in research and practice, *Grundwasser*, 12, 178–188, 2007.
- Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., Gunten, U., and Wehrli, B.: The Challenge of Micropollutants in Aquatic Systems, *Science*, 313, 1005–1184, 2006.
- Strauch, G., Moeder, M., Wennrich, R., Osenbrueck, K., Glaeser, H. R., Schladitz, T., Mueller, C., Schirmer, K., Reinstorf, F., and Schirmer, M.: Indicators for assessing anthropogenic impact on urban surface and groundwater, *J. Soil. Sediment.*, 8, 23–33, 2008.
- Vazquez-Sune, E., Sanchez-Vila, X., and Carrera, J.: Introductory review of specific factors influencing urban groundwater, an emerging branch of hydrogeology, with reference to Barcelona, Spain, *Hydrogeol. J.*, 13, 522–533, 2005.
- Wolf, L., Klinger, J., Hoetzel, H., and Mohrlok, U.: Quantifying mass fluxes from urban drainage systems to the urban soil-aquifer system, *J. Soil. Sediment.*, 7, 85–95, 2007.
- Ying, G. G., Toze, S., Hanna, J., Yu, X. Y., Dillon, P., and Kookan, R. S.: Decay of endocrine-disrupting chemicals in aerobic and anoxic groundwater, *Water Res.*, 42, 1133–1141, 2008.

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Table 1. Mass flow rates M_{CP} , mass fluxes J_{CP} of the different control planes and exfiltration mass flow rates M_{ex} for two streamtubes. The water flow Q_{CP} through the respective control planes, the width of the streamtubes b_1 and b_2 as well as the affected stream length L_{BG1} and L_{BG2} of the two streamtubes are given.

Streamtube 1						Streamtube 2							
$b_1 = 14.25 \text{ m}$ $L_{BG1} = 18.55 \text{ m}$						$b_2 = 5.84 \text{ m}$ $L_{BG2} = 7.23 \text{ m}$							
Upstream			Downstream			Upstream			Downstream				
well			Well			Well			Well				
$Q_{CP\ 13} =$			$Q_{CP\ 11} =$			$Q_{CP\ 14} =$			$Q_{CP\ 12} =$				
$13.72 \text{ m}^3\text{d}^{-1}$			$15.30 \text{ m}^3\text{d}^{-1}$			$5.00 \text{ m}^3\text{d}^{-1}$			$5.61 \text{ m}^3\text{d}^{-1}$				
$M_{CP\ 13}$	$J_{CP\ 13}$		$M_{CP\ 11}$	$J_{CP\ 11}$	ΔM_{CP1}	M_{ex1}	$M_{CP\ 14}$	$J_{CP\ 14}$		$M_{CP\ 12}$	$J_{CP\ 12}$	ΔM_{CP2}	M_{ex2}
$\left[\frac{\text{mg}}{s} \right]$	$\left[\frac{\text{mg}}{m^2 s} \right]$		$\left[\frac{\text{mg}}{s} \right]$	$\left[\frac{\text{mg}}{m^2 s} \right]$	$[\%]$	$\left[\frac{\text{mg}}{md} \right]$	$\left[\frac{\text{mg}}{s} \right]$	$\left[\frac{\text{mg}}{m^2 s} \right]$		$\left[\frac{\text{mg}}{s} \right]$	$\left[\frac{\text{mg}}{m^2 s} \right]$	$[\%]$	$\left[\frac{\text{mg}}{md} \right]$
K ⁺	2.24	0.026	2.50	0.029	11.9	1241	0.73	0.023	1.10	0.034	49.2	4315	
Cl ⁻	17.90	0.206	21.50	0.248	20.1	16750	5.85	0.184	9.81	0.308	67.6	47261	
NO ₃ ⁻	0.37	0.004	0.57	0.007	53.3	924	0.42	0.013	0.48	0.015	14.9	749	
SO ₄ ²⁻	85.70	0.987	92.62	1.066	8.1	32204	31.03	0.975	32.73	1.029	5.5	20321	
$\left[\frac{\text{ng}}{s} \right]$	$\left[\frac{\text{ng}}{m^2 s} \right]$		$\left[\frac{\text{ng}}{s} \right]$	$\left[\frac{\text{ng}}{m^2 s} \right]$	$[\%]$	$\left[\frac{\text{ng}}{md} \right]$	$\left[\frac{\text{ng}}{s} \right]$	$\left[\frac{\text{ng}}{m^2 s} \right]$		$\left[\frac{\text{ng}}{s} \right]$	$\left[\frac{\text{ng}}{m^2 s} \right]$	$[\%]$	$\left[\frac{\text{ng}}{md} \right]$
CAF	3.17	0.036	3.15	0.036	-0.5	-	0.86	0.027	1.40	0.044	63.8	6528	
NON	17.01	0.196	8.58	0.099	-49.6	-	5.30	0.167	2.83	0.089	-46.7		

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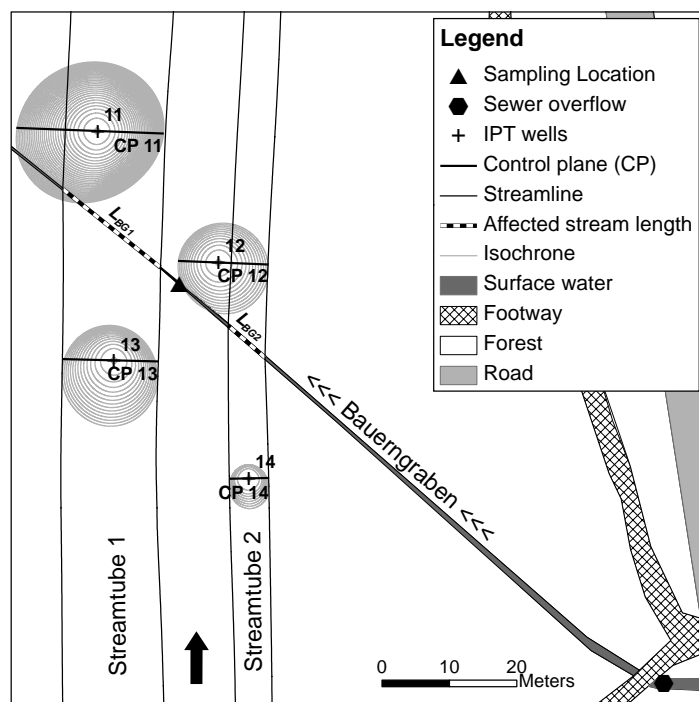


Fig. 1. Test site showing the temporally losing stream *Bauerngraben*, IPT wells and isochrones at sampling times. Streamlines define streamtube 1 (wells 11 and 13) and streamtube 2 (wells 12 and 14). The mean groundwater flow direction is indicated by the black arrow. Isochrones are for the 4 h sampling interval.

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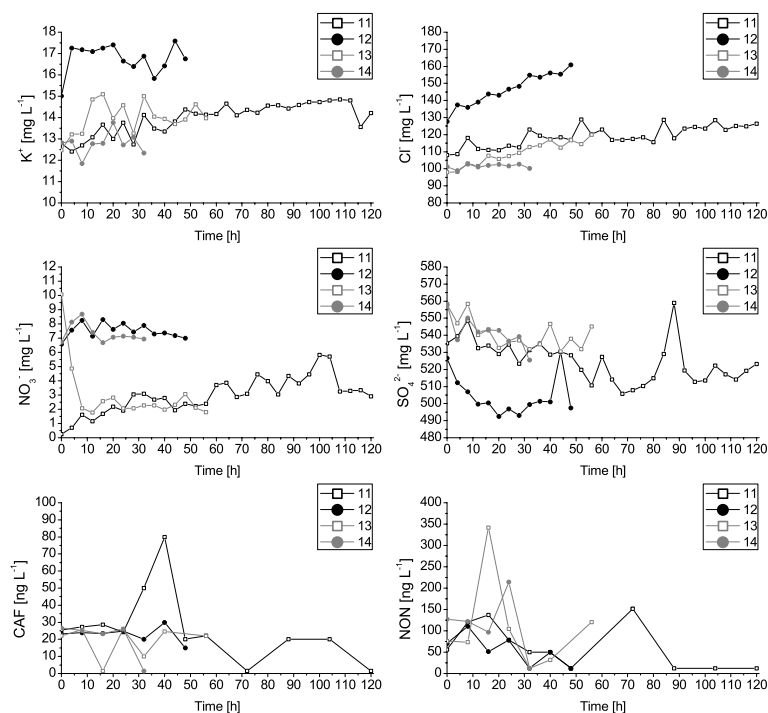


Fig. 2. Concentration-time series for the estimation of M_{CP} with the CSTREAM code. Concentrations are given for inorganic wastewater constituents as well as for caffeine (CAF) and technical-nonylphenol (NON) at the four IPT wells 11, 12, 13 and 14. Concentrations below the LOD were set to half of the LOD.

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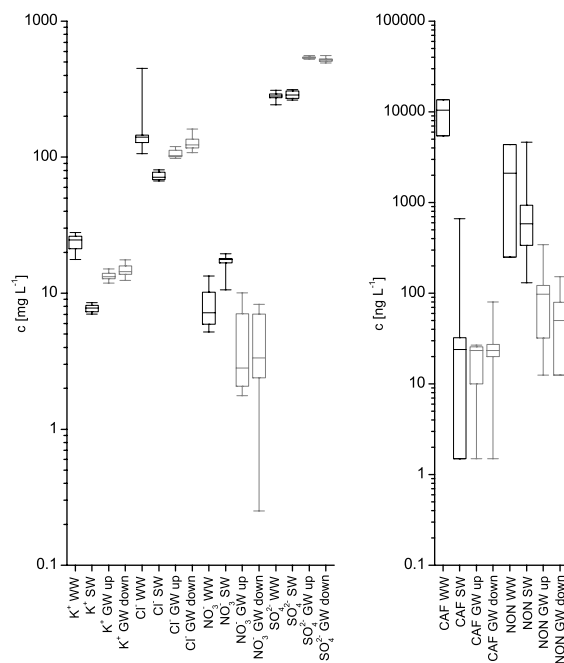


Fig. 3. Boxplot of measured concentrations in the wastewater (WW), surface water (SW) *Bauerngraben* and groundwater (GW). Black boxplots mark WW and SW. Grey boxplots mark GW. The boxes show the 25th and 75th percentile and the median. The whiskers mark the lowest and the highest concentrations. Boxplots of CAF WW and NON WW include no whiskers, because only three values were considered. The lowermost concentration limit for all samples was half of LOD.

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