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C. Schmidt, E. Kalbus, M. Martienssen, M. Schirmer. The influence of heterogeneous groundwater discharge on the timescales of contaminant mass flux from streambed sediments? field evidence and long-term predictions. *Hydrology and Earth System Sciences Discussions*, 2008, 5 (2), pp.971-1001. hal-00298942

HAL Id: hal-00298942

<https://hal.science/hal-00298942>

Submitted on 18 Jun 2008

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Papers published in *Hydrology and Earth System Sciences Discussions* are under open-access review for the journal *Hydrology and Earth System Sciences*

The influence of heterogeneous groundwater discharge on the timescales of contaminant mass flux from streambed sediments – field evidence and long-term predictions*

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Received: 11 March 2008 – Accepted: 17 March 2008 – Published: 9 April 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

*Invited contribution by C. Schmidt, one of the Union Young Scientist Award winners 2007.

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Abstract

Streambed sediments can act as long-term storage zones for organic contaminants originating from the stream water. Until the early 1990s, the small man-made stream, subject of our study, in the industrial area of Bitterfeld (Germany), was used for waste water discharge from the chemical industry nearby. The occurrence of contaminants in the streambed is resulting from aqueous-phase transport and particle facilitated deposition. Groundwater discharge through the streambed can otherwise induce a remobilization and an advective contaminant flux so that contaminants are released back from the streambed to the stream water. We investigated the long-term mass flow rates of chlorinated benzenes (MCB, DCBs) from the streambed to the overlying stream water driven by advection of groundwater. The spatial patterns and magnitudes of groundwater discharge were examined along a reach of 220 m length. At 140 locations groundwater discharge was quantified using streambed temperatures and ranged from 11.0 to $455.0 \text{ Lm}^{-2}\text{d}^{-1}$. According to locations with high and low groundwater discharge, time-integrating passive samplers were used to monitor current contaminant concentrations in the streambed. Streambed contaminant concentrations at high groundwater discharge locations were found to be lower than at low discharge locations. Based on data from batch experiments and field observations we parameterized and run multiple one-dimensional advective transport models for the observed range of groundwater discharge magnitudes to simulate the timescales of contaminant release and their dependence on the magnitude of groundwater discharge. The results of the long-term predictive modeling revealed that the time required to reduce the concentrations and the resulting mass fluxes to the water to 10% of the initial values will be in the scale of decades for high-discharge locations and centuries for low-discharge locations, respectively.

HESSD

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1 Introduction

Streambed sediments often act as long-term storage zones for organic contaminants and metals. The occurrence of contaminants in the streambed is a result of aqueous-phase transport, particle facilitated deposition and sorption to sediments. Contaminants may enter the streambed either by infiltration of stream water into the sediments (e.g., Zaramella, 2006; Wörmann, 1998) or by discharging groundwater (e.g., Conant et al., 2004). When the streambed sediments are permeable, hyporheic exchange and groundwater discharge drive advective transport with the streambed. Advection controls or is coupled to biogeochemical processes (Cardenas and Wilson, 2007; Jones and Mullholland, 2000).

In temperate climates, groundwater typically discharges into surface water bodies such as streams and rivers. When contaminated groundwater discharges to a stream, the contaminant plume might get substantially modified in its concentration distribution and composition during the passage through the streambed and the near-stream zone (Conant et al., 2004). However, the discharge of contaminated groundwater to a stream, either as a diffuse contamination or as a distinct contaminant plume, may be associated with significant mass fluxes of contaminants to the surface water system (Kalbus et al., 2007; Chapman et al., 2007). On the other hand, the discharge of uncontaminated groundwater may induce the release and transport of contaminants from streambed sediments to the surface water. In this case, the advection of groundwater and the apparent mass transfer from the sediment may be the governing processes that control mass fluxes (Lick, 2006; Schmidt et al., 2008).

In the literature, a few field studies can be found addressing contaminant fluxes to surface waters associated with groundwater discharge. The majority of the studies focused on characterizing the spatial distribution of contaminants in the streambed and the adjacent aquifer when a plume discharges to the surface water (Conant et al., 2004; Lorah and Olsen, 1999; Westbrook et al., 2005) or on mapped plan-view distributions of contaminants in the streambed (Vroblesky, 1991). Site assessment

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and remediation design may benefit from determining contaminant mass flow rates as alternative criterion instead of maximum concentration levels. Recently, approaches were published to quantify contaminant mass fluxes and contaminant mass flow rates to streams (Chapman et al., 2007; Kalbus et al., 2007; Schmidt et al., 2008). Schmidt et al. (2008) showed that contaminated streambed sediments can substantially contribute to contaminant mass flow into the stream water.

Even after the source areas at contaminated sites have been cleaned up, the contaminants stored in the streambed sediments, originating either from the surface water or from groundwater plumes, may be released from the sediments back to the stream and may represent a dominant, long-term contamination source for downstream areas. Processes that contribute to the sediment-water transfer of contaminants include molecular diffusion, bioturbation, and pore-water advection due to groundwater discharge (Erickson et al., 2005). These processes are usually lumped together and modelled as diffusive flux by means of a mass transfer approximation (Lick, 2006). In this study, however, we highlight the potential influence of groundwater discharge on the mass flow rates from the streambed to the overlying stream water. In particular, the study focuses on the influence of spatial patterns of groundwater discharge on contaminant mass flow rates along a 220 m long reach. We hypothesize that spatial heterogeneities of groundwater discharge influence the timescales of contaminant release from the streambed to the stream. The contaminant mass flux entering a stream with the discharging groundwater depends on the concentration of contaminants in the groundwater and the water flux across the streambed. The total contaminant mass flux entering the stream will decay with time because contaminants will be successively removed, controlled by the desorption behaviour of the specific compound.

At a small stream in Germany, we selected different locations with respect to the magnitude of groundwater flux through the streambed. At these locations we installed passive samplers in the streambed to characterize the current contaminant distribution. Batch experiments were conducted to elucidate the desorption behaviour of the target compounds monochlorobenzene (MCB) and the isomers of dichlorobenzene (1,2-

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DCB, 1,3-DCB, 1,4-DCB) as input data for a streambed transport model. We applied a numerical one-dimensional advective transport model to predict the timescales of contaminant release and their dependence on the magnitude and spatial patterns of groundwater discharge.

2 Study site

The study was carried out in the industrial area of Bitterfeld/Wolfen, about 130 km south of Berlin, Germany (Fig. 1). The region is one of the oldest centres of chemical industry in Germany (Heidrich et al., 2004a, b). One century of chemical production has resulted in a regional groundwater contamination with an estimated extent of 25 km² (Weiß et al., 2001). The main contaminants are volatile halogenated hydrocarbons, monoaromatic hydrocarbons such as BTEX or chlorinated benzenes and phenols, hexachlorocyclohexanes (HCH), polychlorinated biphenyls, dioxins, and a variety of other substances. Soils and floodplain sediments downstream of the site show increased levels of persistent organic contaminants such as β -HCH, a waste product of former lindane (γ -HCH) production (Barth et al., 2007).

The investigations were conducted along a 220 m long reach of the Schachtgraben. The stream is part of the Mulde River system which is a tributary to the Elbe River. The Schachtgraben was man-made and had originally been constructed for mine water discharge from open-cast lignite mines. Later, it was also used for waste water discharge from the chemical industry for a period of three decades until 1990. In the early 1990s, monitoring programmes revealed a rapid decline of organic contaminants between 1990 and 1992 in the streams and rivers downstream of the study site, in particular in the Mulde River (LSA, 1993). In 1993, chlorinated benzenes were the substances with highest individual concentrations observed in the Mulde River with, for example, MCB concentrations up to 31 $\mu\text{g L}^{-1}$ (LSA, 1993). This value is quite impressive when considering the mass flow rate since the average stream flow rate in the Mulde River is approximately 60 m³ s⁻¹ (Schachtgraben: 0.2 m³ s⁻¹, Kalbus et al.,

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2007). Unfortunately, no monitoring data from the Schachtgraben itself is available for this time. A recent report of a monthly monitoring programme in the Mulde River revealed a maximum concentration of MCB of $0.06 \mu\text{g L}^{-1}$ (LSA, 2005). In comparison, during a five-day pumping test in October 2005 of Kalbus et al. (2007), the average concentration of MCB in the Schachtgraben was $24.7 \mu\text{g L}^{-1}$.

The streambed of the Schachtgraben consists of a 0.6 m thick layer of crushed rock. The pore space of the crushed rock layer is filled with autochtone, sandy, fluvial material. The stream is about 3 m wide and has an average water depth of 0.6 m. It partially penetrates a Quaternary alluvial Aquifer. The water table in the aquifer is generally higher than the water level in the stream. Hence, the Schachtgraben can be classified as a gaining stream. To characterize the interaction between the groundwater and the stream, Schmidt et al. (2006) recorded 140 streambed temperature profiles in the summer of 2005. The water fluxes through the streambed can be estimated based on observed streambed temperatures (Conant, 2004; Schmidt et al., 2007). At the study site, the water fluxes ranged from $455 \text{Lm}^{-2} \text{d}^{-1}$ of groundwater discharge to $10 \text{Lm}^{-2} \text{d}^{-1}$ of stream water entering the streambed (Schmidt et al., 2006). The dominant contaminants in the Quaternary aquifer are chlorinated benzenes. The main contamination source is believed to be about 3.5 km south of the study site. Preliminary investigations showed that the contamination level of pore water in the streambed sediments is significantly higher than in the alluvial aquifer (Schmidt et al., 2008; Kalbus et al., 2007). After the close-down of main parts of the chemical industry and the implementation of new environmental regulations and waste water treatment facilities, the contaminant release from streambed sediments and the discharge of contaminated groundwater became the dominant contamination source for the streams and rivers at the site, which is persisting until today.

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3 Methods

3.1 Passive sampling

Snapshot sampling of contaminant concentrations in the streambed and contaminant mass flux calculations already identified the streambed as a current source of contaminants (Schmidt et al., 2008). However, to gain further insight into the transport processes to the streambed, it is expedient to obtain depth-orientated profiles of contaminant concentrations within the upper streambed layer. Because the streambed of the Schachtgraben is constructed of crushed rock, it turned out to be difficult to take sediment cores or to install streambed piezometers to conduct depth-oriented snapshot sampling of the pore water. Hence, to achieve robust estimates of contaminant concentrations with fine vertical spatial resolution, time-integrating passive samplers were deployed in the streambed. These devices can be placed directly in the streambed sediments at well-defined depths and presumed to be capable to capture representative aqueous concentrations. Additionally, possible short-term variations in aqueous concentrations are averaged by time-integrating samplers. However, if frequent changes in the flow direction occur the averaging might be problematic for the calculation of mass fluxes (Kalbus et al., 2006). But hydraulic head observations suggest that the Schachtgraben is constantly a gaining stream.

The passive sampling system used in this study (ceramic dosimeter, Bopp et al., 2005) consists of 4.5 cm long ceramic tubes filled with an adsorbent material. To prevent the dosimeter from damages, a steel casing was used (see Fig. 1 in Bopp et al., 2005), which increased the entire length of the passive sampling system to 5.0 cm. In order to obtain depth-orientated estimates of contaminant concentrations, we deployed the dosimeters at four different depths at each sampling location (0.10–0.15, 0.20–0.25, 0.30–0.35 and 0.40–0.45 m below the streambed surface) in the streambed sediments. The sampling locations were chosen with respect to the groundwater discharge regime as identified by Schmidt et al. (2006) in a previous study. One array of dosimeters (array 1) was deployed at a low-discharge zone with a groundwater flux

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of $10 \text{ Lm}^{-2} \text{ d}^{-1}$, arrays 2 and 3 were placed at high-discharge zones with fluxes of $300\text{--}400 \text{ Lm}^{-2} \text{ d}^{-1}$. Additionally, two dosimeters were placed in groundwater monitoring wells and two were deployed in the surface water (Fig. 1). The ceramic dosimeters stayed in the streambed, surface water and groundwater from June–September 2006.

Contaminants are diffusing across the ceramic membrane and are adsorbed over the entire sampling period at the adsorbent material. The average contaminant concentration in the water can be obtained from the adsorbed contaminant mass and the duration of exposure (Martin et al., 2003; Bopp et al., 2005). The parameters required to derive the average concentration from the adsorbed mass are given in Table 1. For sample extraction from the adsorbent material within the ceramic dosimeters a modification of the method described by Bopp et al. (2005) was used. Prior to extraction, the metal cage of the ceramic dosimeter was opened and the caps were removed. In the first step, the adsorbent material was extracted two times with 5 mL of acetone and 5 min contact time. To obtain a duplicate sample, the procedure was repeated.

3.2 Batch experiments

Batch experiments were conducted with the streambed sediments to study the desorption behaviour of the target compounds and obtain input parameters for the streambed transport model. Since the crushed rock in the streambed precluded successful sediment coring, pooled sediment samples were taken that integrated the upper 0.5 m of the streambed.

For the determination of the sediment-water partitioning coefficient a volume of 50 mL of water was added to different masses of sediments (4.2, 7.5, 14.6, 29.4, 60.9, 118.0, 218.9, 369.9 g (dry)) in 250 mL glass bottles. The bottles were placed on a mechanical tumbler and were incubated for 48 h. After that incubation period, the supernatants were removed and analyzed for contaminant concentrations by Headspace-GC/MS (Varian GC/MS, Type CP 3800 MS1200, Column 60 m Zebron ZB1, Injection 1 ml). To determine the initial sediment contaminant concentrations were 10.1 g of fresh

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sediment were extracted with 20 ml Acetone and analysed in the GC.

The sediment-water partitioning coefficient (K_d) was calculated for each sediment-water ratio. For the subsequent calculations the average K_d value was applied. The contaminant release and K_d were determined based on the liquid phase concentrations by assuming that changes in the liquid-phase concentrations are equal to changes in sediment contaminant concentrations.

Additionally, two batch desorption experiments were carried out parallel in 10 bottles. In the first experiment, 100 g sediment and 20 mL of water were filled into each bottle. The concentration of the target compound was measured in the water using the same analytic procedure as for the determination of the partition coefficient. The compound concentrations were determined after 2, 4, 8, 16, 24, 48, 72, 96, and 168 h. In a second experiment, 100 g sediment and 30 mL of water were filled into each bottle and the compound concentrations were measured after 0.5, 1, 2, 3, 4, 5, 6, and 24 h to experimentally underpin the quasi-instantaneous equilibrium assumption.

3.3 Modelling approach

The underlying idea of this study is to show that spatially heterogeneous groundwater discharge affects the release and the resulting mass flow rates of contaminants from the streambed to the stream along a reach. For this purpose, we selected a very simple modelling approach that accounts for groundwater advection but simplifies the desorptive mass transfer to a linear equilibrium process. Moreover, it is assumed that flow and transport through the streambed are vertical and steady. We further assume that advection is the governing process along the short flow domain of 1 m in length and hence, we do not consider dispersion. The governing equation for one-dimensional advective transport is given with:

$$\frac{\partial C_w}{\partial t} = -\frac{q_z/n_e}{R} \frac{\partial C_w}{\partial z} \quad (1)$$

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where C_w is the concentration of the contaminant in the pore water, q_z is the vertical Darcy flux (positive upward), R is the retardation factor, z is the vertical spatial coordinate, t is the time, and n_e is the effective porosity. Batch experiments indicated that it is reasonable to apply a simple linear isotherm. The retardation factor R is then given with:

$$R = 1 + \frac{\rho}{n_e} K_d \quad (2)$$

where ρ is the bulk density of the sediment and K_d is the sediment-water partitioning coefficient.

The sediment properties are assumed to be homogeneous at all locations with a homogeneous initial contaminant load of the sediment. The only parameter variable in space is q_z .

Simulations were run until the contaminant load of the sediment (C_s) has decreased by 90% from its initial value at the outflow (the sediment water interface) of the domain. To predict the timescales of contaminant release it is not required to know the absolute concentrations since the timescales are only depending on q_z and K_d .

We used an explicit finite difference approximation to calculate the removal of each target compound from the sediment layer with equation 1. The model domain was set to a thickness of 1 m with a space increment of 0.04 m. The time step was set to 0.5 days to comply with the Courant criteria for numerical stability. The water fluxes (q_z) for each observation point were taken from the results of Schmidt et al. (2006).

The contaminant mass flux can be calculated for each observation point (x, y) for time t from $q_z(x, y) \times C_{\text{out}}(t)$. The total contaminant mass flow rate through a given area of the streambed S as a function of time can be calculated using:

$$M_S(t) = \int_S q_z(x, y) C_{\text{out}}(t) dS \quad (3)$$

For the evaluation of timescales and the influence of the heterogeneity of groundwater discharge, contaminant mass flow rates were normalized by $M_S(t)/M_{S_i}$ where M_{S_i} is

the calculated total mass flow rate at t_0 .

4 Results and discussion

4.1 Current contaminant concentrations

Aqueous concentrations from the ceramic dosimeters versus aqueous concentrations from a snap-shot sampling programme parallel to the passive sampling are displayed in Fig. 3. In addition, the aqueous concentrations in the groundwater and surface water obtained during an integral pumping test (IPT) at the study site by Kalbus et al. (2007) are plotted versus the dosimeter-derived concentrations. Overall, the concentrations derived from the ceramic dosimeters matched well the averaged concentrations from the snap-shot sampling. A slight tendency to underestimate the snap-shot sampling results can be seen in Fig. 3. It seems that the dosimeters underestimate in particular the concentrations in the groundwater, when compared with both the snap-shot sampling results and the IPT results. The scatter between dosimeter-derived aqueous concentrations and snap-shot sampling-derived aqueous concentrations does not follow a substance-specific or sampling location-specific pattern. One significant deviation is that no 1,2-DCB was detected in the snap-shot samples of the streambed but was found in the dosimeters. This is supposedly a random error because the results from groundwater and surface water matched reasonably. For the further discussion we consider the concentrations obtained from the dosimeters as representative.

The results show that concentrations in the interstitial pore water in the streambed sediments were approximately one order of magnitude higher than in the groundwater and the surface water. Significant differences occur between zones of high and low groundwater discharge.

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4.1.1 Contaminant concentrations in surface water and groundwater

Passive samplers deployed in the stream upstream and downstream of the investigated reach revealed comparable concentrations, which were generally (except for 1,4-DCB) slightly higher though at the upstream position closer to the chemical plant, where the source zone of the contaminants is located. At the upstream sampling location the concentrations in the stream water were $14.1 \mu\text{g L}^{-1}$ (MCB) and 0.8, 5.0, $2.6 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB) and at the downstream location $13.8 \mu\text{g L}^{-1}$ (MCB) and 0.9, 4.5, $2.8 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB). Obviously, the inputs from the streambed did not result in an increasing concentration in the surface water along the study reach of 220 m in length.

In two groundwater monitoring wells adjacent to the stream (Fig. 1) the monitored concentrations were characteristic for the diffuse background contamination present at the site with average values of $5.1 \mu\text{g L}^{-1}$ (MCB) and 0.1, 0.2, $0.3 \mu\text{g L}^{-1}$ (1,2-DCB, 1,3-DCB, 1,4-DCB). In one of the monitoring wells no DCB was observed (Fig. 4). A five-day IPT at four groundwater monitoring wells (in two of which dosimeters were deployed) revealed average concentrations of $12.6 \mu\text{g L}^{-1}$ MCB and $3.2 \mu\text{g L}^{-1}$ DCB (sum of isomers) (Kalbus et al., 2007). Average concentrations in the single wells ranged from 9.6 to $18.2 \mu\text{g L}^{-1}$ MCB and from 2.6 to $4.0 \mu\text{g L}^{-1}$ DCB (sum of isomers). Hence, the background contamination of the groundwater can be assumed to be in the range of 5– $20 \mu\text{g L}^{-1}$ MCB and 2.5– $4 \mu\text{g L}^{-1}$ for the sum of isomers of DCB, respectively. The inputs originating from the streambed are not necessarily reflected in the contaminant concentrations of the surface water because dilution and volatilization might significantly reduce the concentrations (Conant et al., 2004).

4.1.2 Aqueous concentrations in the streambed

In the streambed, the aqueous concentrations differed between zones of high and low groundwater discharge as well as vertically at each passive sampler array. The highest concentrations were observed at the low-discharge zone (array 1), the lowest at one of

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the high-discharge zones (array 3). Average concentrations at the low-discharge zone were $65.5 \mu\text{g L}^{-1}$ MCB, $6.5 \mu\text{g L}^{-1}$ 1,2-DCB, $22.4 \mu\text{g L}^{-1}$ 1,3-DCB and $32.9 \mu\text{g L}^{-1}$ 1,4-DCB. The two high-discharge zones, although spatially separated only by two metres, differed significantly in their average concentrations. At one zone (array 2) the average concentration of MCB ($65.6 \mu\text{g L}^{-1}$) was similar to that at the low-discharge zone (array 1). Conversely, the average concentrations of the DCB isomers ($1.3 \mu\text{g L}^{-1}$ 1,2-DCB, $8.5 \mu\text{g L}^{-1}$ 1,3-DCB and $8.3 \mu\text{g L}^{-1}$ 1,4-DCB) at array 2 were within the order of magnitude of the DCB concentrations at array 3 ($0.7 \mu\text{g L}^{-1}$ 1,2-DCB, $4.4 \mu\text{g L}^{-1}$ 1,3-DCB and $4.1 \mu\text{g L}^{-1}$ 1,4-DCB). Overall, the aqueous contaminant concentrations in the streambed were lower at zones of high groundwater discharge than at zones of low groundwater discharge.

Focusing on the vertical distribution of contaminants in the streambed, Fig. 4 illustrates that the lowest aqueous concentrations of all substances in the streambed were observed in the shallow dosimeters (no. 8, 12, 16) installed between 0.10–0.15 m below the streambed surface. In the arrays 1 and 2, the highest concentrations were present at the subsequent depth of 0.20–0.25 m. Then, with increasing depth the concentrations decreased in the two arrays. Array 3 did not show this vertical pattern. Here, the concentrations of MCB increased from 33.6 to $24.6 \mu\text{g L}^{-1}$ from the top to the bottom of the streambed, while concentrations of DCB were virtually independent from the sampling depth (Fig. 4). The low aqueous concentrations at the top of the streambed are likely a result of non-vertical hyporheic exchange between the streambed and the stream water. For greater depths, water flow and contaminant transport in the streambed is assumed to be essentially vertical towards the surface water. Schmidt et al. (2006) provide evidence to this assumption because their one-dimensional vertical water flow and heat advection model matches well the observed temperature profiles.

The contamination of the streambed originates from the stream water which was highly contaminated during a period of approximately 25 years of intense waste water discharge from the chemical industry. The upper 0.6 m of the streambed consist of

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crushed rock. Deposition of fine, fluviually transported sediments in the pores of the crushed rock layer was probably one main transport pathway of organic contaminants into the streambed, besides diffusion and hyporheic exchange. We therefore conclude that initially the upper 0.6 m of the streambed were nearly homogeneously contaminated without any vertical gradients.

When the contamination level in the stream rapidly decreased after the close-down of main parts of the chemical industry in the early 1990s, the contaminant input to the streambed has presumably ceased. The relatively clean groundwater flowing into the contaminated sediment layer could then have induced the removal of contaminants starting at the bottom of the streambed. We interpret the observed decrease of the aqueous concentrations with increasing depth as a result of this desorptive process. With time, the desorption front moves successively towards the top of the streambed. More than 15 years after the close-down of the chemical industry, the current vertical distribution of aqueous contaminant concentrations in the streambed indicates that the contaminant removal is still in progress.

4.2 Results of batch desorption experiments

The results of the desorption kinetic experiments for the target compounds are shown in Fig. 5. Each data point represents the remaining solid-phase fraction after a given time. The batch desorption experiment lasted 7 days. In general, only a very small fraction of the initial solid-phase contaminant load desorbed. The highest extent of desorption was found for MCB. All isomers of DCB were characterized by a similar desorption behaviour showing no increase of the desorbed fraction with time (Fig. 5). In the first experiment, aqueous-phase concentrations were sampled after two hours (Fig. 5). In order to observe temporal desorption patterns, a second experiment was conducted where the first sample was taken after 30 min (Fig. 5).

The desorptive sediment-water partition coefficient (K_d) is given by the proportionality of the concentration in the solid and in the liquid phase. The resulting average K_d values for the different compounds were as follows: 61 (MCB), 229 (1,2-DCB), 311

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(1,3-DCB), 369 (1,4-DCB). However, we are aware that the observed K_d values are empirical values that do not necessarily reflect the mechanisms of desorption from sediments. Volatile organic compounds sorbed to soils have been observed to resist desorption into water for several days and longer (Pavlostathis and Mathavan, 1992).

5 Typically, desorption from sediments is characterized by a biphasic behaviour, meaning that the desorption process consists of a fast release phase followed by a slower stage. In this light, the observed K_d values should be regarded as apparent values which are strictly site-specific and which may also depend on the experimental set up.

Nevertheless, our results indicate that:

- 10 – only a very small fraction of the solid phase desorbs;
- the apparent desorption does not show a biphasic behaviour for the duration of the experiment,
- all isomers of DCB do not show a trend in the desorbed fraction with time,
- only for MCB the desorbed fraction tends to increase with the duration of the experiment.

In our study the duration of the desorption experiment was set to 7 days (168 h) in order to cover the residence time of water in the streambed. Taking a streambed thickness of 0.6 m, the residence time at average groundwater discharge is approximately 5 days.

20 The K_d values appear to be relatively high compared to other studies (Ball and Roberts, 1991; Chiou et al., 1983; Sharer et al., 2003a). The streambed sediments have presumably been exposed to contamination for decades. Ageing effects on desorption behaviour of VOC were examined in several studies (Pignatello, 1990a, b; Pavlostathis and Mathavan, 1992; Sharer et al., 2003b). There is consensus that ageing increases the fraction of irreversibly sorbed contaminants. Laboratory adsorption and desorption experiments also revealed that adsorption is not always reversible. Several researches observed a desorption resistant fraction remaining in the solid-phase

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(e.g., Fu et al., 1994; Kan et al., 1998). The experimental results lead to the conclusion that a small fraction of the contaminants desorbs nearly instantaneously. Hence, an apparent equilibrium mass transfer between the sediments and the water can be assumed at least for the observed residence times of groundwater in the streambed.

5 To date there is no common theory or fundamental understanding of the processes to predict contaminant release a priori (Birdwell et al., 2007). The experimental evidence justifies the application of a simple equilibrium mass transfer to simulate the contaminant mass fluxes from the streambed.

4.3 Model results

10 4.3.1 Concentrations

The numerical modelling was conducted to predict the timescales of a natural streambed clean-up by discharging groundwater. The clean-up time (t_{90}) is defined as the time required to reduce the contaminant concentrations in the water entering the stream to 10% of the initial value. The concentrations in the pore water are proportional to the contaminant concentration of the sediment with the K_d value as a factor of proportionality. Hence, the clean-up time can also be described as the time required to reduce the initial contaminant concentrations in the sediment in the top cell of the model domain by 90%. The simulations were run for groundwater fluxes ranging between 11 and 455 $\text{Lm}^{-2} \text{d}^{-1}$, which corresponds to the fluxes determined from streambed temperature measurements by Schmidt et al. (2006). From the data set
15
20 of Schmidt et al. (2006) 22 locations were excluded from the simulations because the groundwater flux was insignificantly small ($<10 \text{Lm}^{-2} \text{d}^{-1}$) or recharge occurred (up to $10 \text{Lm}^{-2} \text{d}^{-1}$).

25 Figure 6 shows the timescales of clean-up and their dependence on the magnitude of groundwater discharge for MCB and the DCB isomers. In our modelling approach the clean-up timescales depend on the water velocity and the K_d value. A higher K_d value results in a higher retardation and therefore in a slower concentration decay.

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At the location with the highest observed groundwater flux of $455 \text{ Lm}^{-2} \text{ d}^{-1}$ it takes 14 years to reach t_{90} for MCB and 63, 86 and 102 years for 1,2-DCB, 1,3-DCB, 1,4-DCB, respectively. The values for t_{90} increase to 559 (MCB), 2607 (1,2-DCB), 3537 (1,3-DCB) and 4198 (1,4-DCB) years at the location with the lowest groundwater flux of $11 \text{ Lm}^{-2} \text{ d}^{-1}$. Groundwater fluxes as low as $11 \text{ Lm}^{-2} \text{ d}^{-1}$, which equals a groundwater flow velocity of 0.036 md^{-1} (for $n_e=0.3$), are comparable to molecular diffusion which is approximately between 0.01 and 0.1 md^{-1} (Lick, 2006). Since molecular diffusion can be assumed to be the slowest transport mechanism, t_{90} calculated from these low fluxes can be regarded as the upper bound of the release timescale. For the reach-average groundwater flux of $58.2 \text{ Lm}^{-2} \text{ d}^{-1}$, t_{90} is 106 (MCB), 495(1,2-DCB), 671 (1,3-DCB), 796 (1,4-DCB) years.

4.3.2 Mass fluxes and mass flow rates

Assuming that the groundwater discharge rates are constant with time, the mass fluxes for each discharge value would evolve with the concentrations. Mass fluxes will reduce to 10% of the initial value within the same time as the concentrations since the mass fluxes for each observation point (x, y) for time t can be calculated with $q_z(x, y) \times C_{\text{out}}(t)$. However, the total mass flow rate along the entire reach of 220 m in length or 660 m^2 of streambed area depends on the spatial distribution of the magnitudes of groundwater discharge. If groundwater discharge was spatially homogeneous the total mass flow rates would develop proportionally to the concentrations. However, along the investigated reach the groundwater discharge is characterized by spatially distinct high-discharge zones. Approximately 50% of the total water fluxes occur on 20% of the total length of the reach (Schmidt et al., 2006). Heterogeneous patterns of groundwater discharge have essential implications on the evolution of the total mass flow rates. Initially, a significant proportion of the total mass flow rate originates from the high-discharge zones. However, the mass fluxes at the high-discharge zones will decay faster than at zones with lower discharge. As apparent in Fig. 7 for the het-

erogeneous case the mass flow rate declines much faster at the beginning than for the theoretical homogeneous case. The concentrations and the related mass flow rates start to decrease when the desorption front reaches the top of the model domain. For heterogeneous groundwater discharge the slow, long-term release from the low-discharge zones results in a pronounced tailing compared to the homogeneous conditions. Assuming a homogeneous groundwater flux at the reach-average value of $58.2 \text{ Lm}^{-2} \text{ d}^{-1}$, the resulting t_{90} of the total mass fluxes will be equal to the t_{90} of the concentrations (106 (MCB), 495(1,2-DCB), 671 (1,3-DCB), 796 (1,4-DCB) years). In the heterogeneous case, t_{90} for the total mass fluxes increases to 145 years for MCB and to 685 (1,2-DCB), 928 (1,3-DCB), 1100 (1,4-DCB) years, respectively (Fig. 7).

The effects of spatially heterogeneous groundwater discharge on mass fluxes are analogue to the effects of heterogeneous hydraulic conductivity (K) fields on tracer breakthrough curves. The transport of solute through low K regions can contribute significantly to tailing as descriptively visualized by Zinn et al. (2004). In the same way the slow release of contaminants from zones of low groundwater discharge contributes to tailing of the total mass flow rate along the stream reach.

In our simple, somewhat unsophisticated modelling approach, a variety of processes has not been considered but they potentially affect the timescales of contaminant removal. Rate-limited mass transfer would mask the influence of groundwater discharge on the contaminant release because it would result in tailing also at high-discharge zones. Biodegradation processes in the streambed would reduce the time required to remove the contaminants. Small-scale heterogeneities of the streambed sediments, which are the conceptual base for the physical mobile-immobile zone approach, would result in increased tailing compared to the homogeneous streambed assumed in this study. Also diffusive mass fluxes were not included in our approach. However, despite the significant simplifications and the limited scope of our study we could elucidate the potential effects of heterogeneous patterns of groundwater discharge on the timescales of contaminant release from streambed sediments.

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The Schachtgraben is gaining groundwater from the shallow, adjacent aquifer. The discharge of groundwater to the stream is characterized by spatial heterogeneities with distinct zones of high groundwater discharge. The streambed sediments at the study site have been contaminated with a variety of substances but mainly with MCB and DCBs because untreated industrial waste water has been discharged for decades from chemical production sites close by. Today the streambed is a contaminant source for the overlying stream water.

The streambed of the investigated artificial stream is constructed of crushed rock. The pores of the crushed rock layer are filled with sandy, allochthonous, organic carbon-rich material. Time-integrating passive samplers were deployed in the streambed to gain insight into the spatial contaminant distribution. The sampling locations were chosen with respect to the groundwater discharge regime. The results of the passive sampling in the streambed revealed that aqueous concentrations of MCB and the DCBs depend on the magnitude of groundwater discharge. Highest concentrations were observed at zones of low groundwater discharge and vice versa. Assuming that the initial contaminant distribution in the streambed was homogeneous, this is presumably a result of higher contaminant advection rates at zones of high groundwater discharge. Although concentrations are low at the high-discharge zones, the contaminant mass fluxes to the stream water are higher here because of the higher water flux.

With a numerical advective transport model the timescales of contaminant releases induced by groundwater discharge were estimated. The simulations of aqueous concentrations and total mass flow rates indicated that the time required to reduce the mass flow rates to 10% of the initial value would be in the scale of hundreds of years. Although the results are subject to uncertainty because diffusion and biodegradation were not considered in the present approach, they demonstrate the persistence of the streambed as contaminant source. The simulations further elucidated the influence of

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spatial patterns of groundwater discharge on the mass flow rates. The observed heterogeneous groundwater discharge leads to a tailing of mass flow rates compared to the theoretical homogeneous case.

The long timescales of contaminant release are a direct result of the high observed sediment-water-distribution coefficients of MCB and DCB. The streambed sediments of the studied reach were exposed to the contaminated water for years, probably for decades. Long contact times can cause strong sorption and yield to a slow but reversible mass transfer from sediment to the pore water.

Summarizing, the results demonstrate that heterogeneous patterns of groundwater discharge may result in significant tailings of contaminant mass flow rates from streambed sediments which may act as long-term, secondary contaminant source for streams even though the primary sources have been remediated.

Acknowledgements. The authors thank R. Krieg for his technical support. This work was supported by the European Union FP6 Integrated Project AquaTerra (Project no. 505428) under the thematic priority “Sustainable Development, Global Change and Ecosystems”.

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Table 1. Parameters required for time-weighted average contaminant concentration determinations using the ceramic dosimeter (adapted from Bopp et al., 2005).

	Symbol	Value	Comment
Parameters defined by the membrane			
Thickness	Δx	0.15 [cm]	Flux-controlling barrier; diffusion distance
Surface area (tube length: 5 cm; tube diameter: 1 cm)	A	8.5 [cm ²]	Taking reduction of total surface area due to PTFE caps into account (from Martin et al., 2003)
Porosity	ε	0.305 [–]	from Martin et al., 2003
Archie's law exponent	m	2.0 [–]	from Martin et al., 2003
Analyte-specific parameters			
Diffusion coefficient in water	D_w	6.505 × 10 ⁻¹⁰ (MCB) [m ² s ⁻¹] 5.646 × 10 ⁻¹⁰ (DCB) [m ² s ⁻¹]	Calculated for each substance according to Worch, 1993
Accumulated mass	M	[g]	Measured during sampling; a determinant of water viscosity thus influencing diffusivity D_w
Equations			
$C_w = \frac{M \cdot \Delta x}{A \cdot t \cdot D_e}$		$D_e = D_w \cdot \varepsilon^m$	

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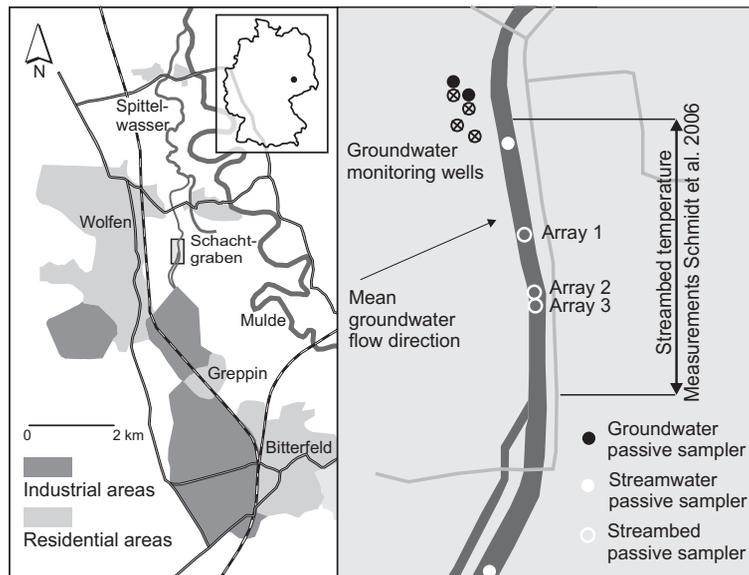


Fig. 1. Location of the study site, position of streambed temperature measurements and the passive sampling arrays.

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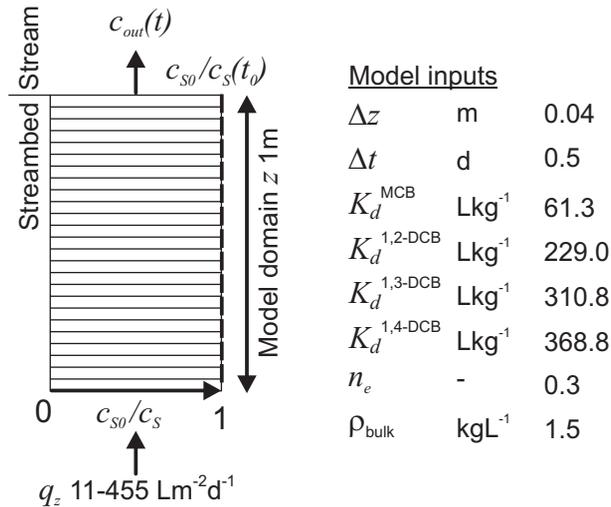


Fig. 2. Concept and input parameters of the multi one-dimensional transport model where the release of contaminants is modeled for q_z ranging between 11 and 455 Lm⁻² d⁻¹.

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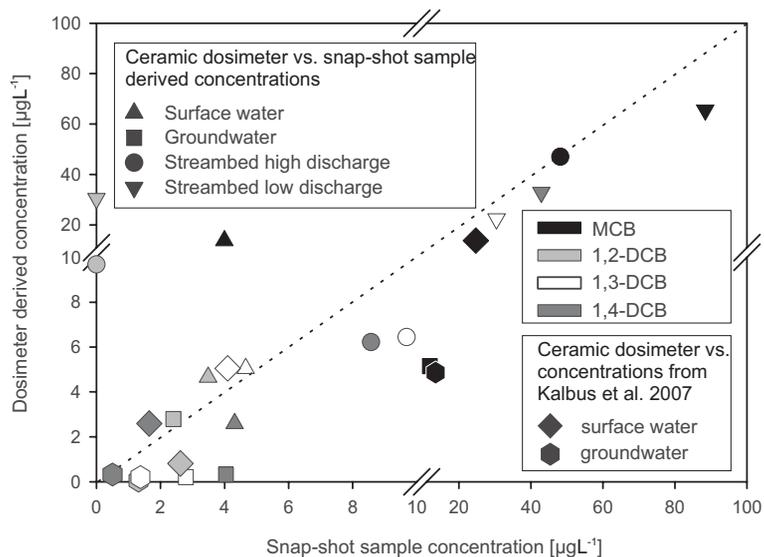


Fig. 3. Comparison of snap-shot sampling and ceramic dosimeter derived aqueous concentrations of MCB and DCBs in different compartments (surface water, groundwater, streambed).

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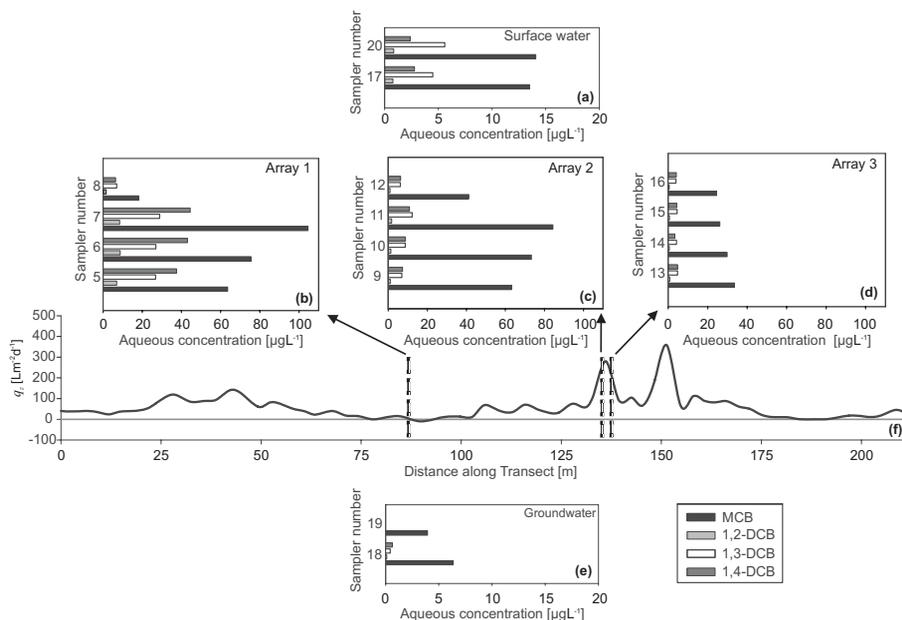


Fig. 4. Average aqueous concentrations of MCB and DCBs derived from the ceramic dosimeters in the surface water (a), the groundwater (e). Aqueous concentrations in the streambed are plotted for different depths at a low groundwater discharge location (b) and two high groundwater discharge locations (c), (d); along the studied reach with heterogeneous groundwater discharge patterns (f).

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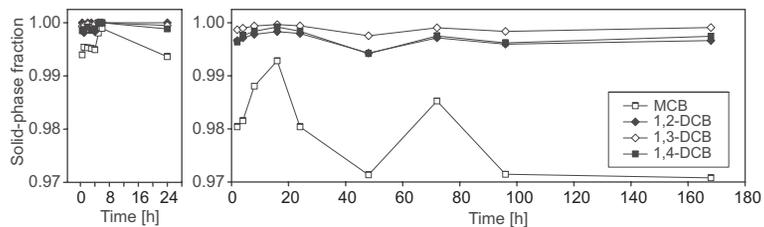


Fig. 5. Remaining solid phase fraction of MCB and DCBs in the streambed sediments after two desorption experiments of different duration.

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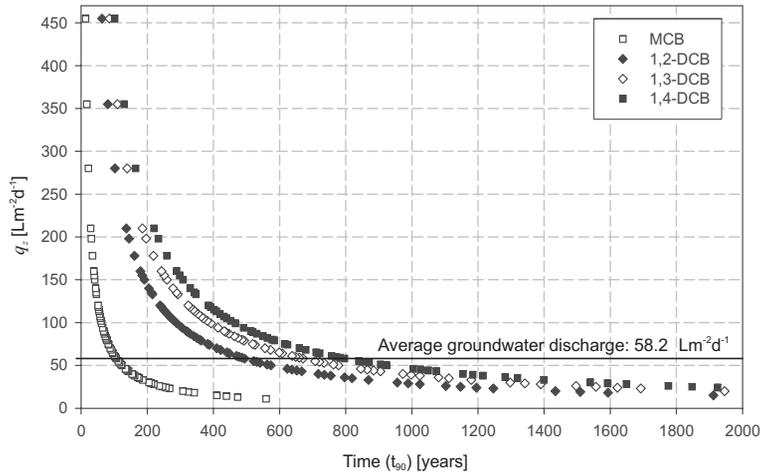


Fig. 6. Dependence of the timescales to reduce the concentrations of MCB and DCBs in the discharging groundwater (C_{out}) by 90% from the initial value on the magnitude of groundwater discharge (q_z).

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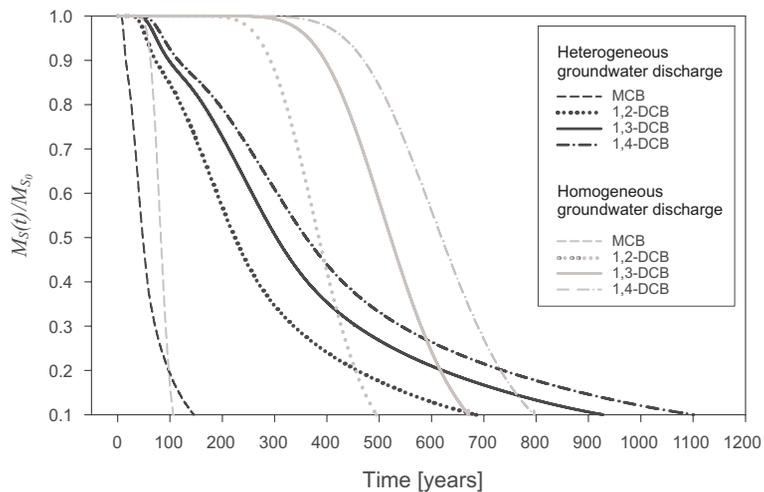


Fig. 7. Normalized contaminant mass flow rates along the studied reach for homogeneous and heterogeneous groundwater discharge as a function of time.

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