Characterization of a managed aquifer recharge system using multiple tracers

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Abstract

Knowledge about the residence times of artificially infiltrated water into an aquifer and the resulting flow paths is essential to developing adequate groundwater-management schemes. To obtain this knowledge, a variety of tracers can be used to study residence times and gain information about subsurface processes. Although a large variety of tracers exists, their interpretation can differ considerably due to subsurface heterogeneity, underlying assumptions, and sampling and analysis limitations. The current study systematically assesses information gained from seven different tracers during a pumping experiment at a site where drinking water is extracted from an aquifer close to contaminated areas and where groundwater is artificially recharged by infiltrating surface water. We demonstrate that the groundwater residence times estimated using dye and heat tracers are comparable when the thermal retardation for the heat tracer is considered. Furthermore, major ions, acesulfame, and stable water isotopes (δ^2H and $\delta^{18}O$) indicate the various sources of groundwater extracted at the wells. Based on the concentration patterns of dissolved gases (He, Ar, Kr, N_2, and O_2) and chlorinated solvents (e.g., Tetrachloroethene (PCE)), three temporal phases are observed in the ratio between infiltrated surface water and regional groundwater during the pumping experiment. Variability in this ratio is significantly related to changes in the pumping and infiltration rates. The obtained results are discussed for each tracer considered and its strengths and limitations are illustrated. Overall, it is demonstrated that aquifer heterogeneity

and various subsurface processes necessitate application of multiple tracers to quantify uncertainty when identifying flow processes.

Keywords: Managed aquifer recharge, groundwater residence time, acesulfame, time series, noble gases, urban hydrogeology

1. Introduction

Due to increasing demand for water for residential and industrial uses, supplying drinking water in urban areas is challenging (Fletcher et al., 2013). Often, the availability of water is limited due to various groundwater contaminants (Baillieux et al., 2015; Schirmer et al., 2013). Managed aquifer recharge (MAR) is one way to meet water demands and operationally protect sites that produce drinking water (Asano and Cotruvo, 2004; Bouwer, 2002). The infiltration of surface water creates a water surplus and dilutes potentially contaminated groundwater (Dillon, 2005). Typically, physical, chemical, and biological degradation processes improve the quality of this infiltrated water during percolation through the vadose zone (Greskowiak et al., 2005; Henzler et al., 2014). In addition, MAR can be used to build up a local groundwater mound, which can serve as a hydraulic barrier to prevent inflow of contaminated water from areas upstream (Auckenthaler et al., 2010; Franssen et al., 2011; Moeck et al., 2016).

Knowledge about the residence times of artificially infiltrated water and its flow paths is essential to developing adequate groundwater-management and protection schemes (Bekele et al., 2014; Zoellmann et al., 2001). In addition, this information is prerequisite to efficient monitoring and risk assessment. The residence time indicates the travel time of a pollutant from the source to the drinking-water extraction well (Regnery et al., 2015). Short residence times might indicate that groundwater is vulnerable due to limited time for self-purification (Kralik et al., 2014).

Typically, various tracers are used to study residence times and gather information about subsurface processes. Tracers can be grouped into three general categories: 1) artificial tracers, including dye tracers (Ptak and Schmid, 1996, Runkel, 2015); 2) natural tracers, including heat tracers (Becker et al., 2013, Irvine et al., 2015), hydrochemistry data (e.g., major ions (Abou Zakhem and Hafez, 2012, Moeck et al., 2016), stable isotopes (e.g., $\delta\,^{2}H$

and δ ^{18}O (Clark et al., 2004, Demlie et al., 2008, Moeck et al., 2017), and dissolved atmospheric gases (Aeschbach-Hertig and Solomon, 2013, Clark et al., 2005); and 3) tracers of anthropogenic origin (Massmann et al., 2008), including persistent organic micropollutants (e.g., the artificial sweetener acesulfame (Hillebrand et al., 2015, Moeck et al., 2017) and pollutants present in surface and groundwater (e.g., chlorinated solvents (Urresti-Estala et al., 2015). According to Massmann et al. (2008) and Gasser et al. (2014), the application of multiple tracers is required to estimate the typically wide range of residence times and various subsurface processes that result from subsurface heterogeneity which can typically not be identified using one tracer. For instance, Batlle-Aguilar et al. (2017) show how major ions, isotopic tracers and dissolved gases can be used to study flow processes in semi-confined faulted aquifers. They show the advantages of several environmental tracers covering a wide range of residence times and highlight that in highly complex aquifer systems increasing data density is required to accurately characterize the flow system. Althaus et al. (2009) estimate groundwater travel times, mixing ratios and groundwater origin with $^{3}H/^{3}He$ dating method, supplemented by ^{85}Kr measurements. Müller et al. (2016) show that using multiple tracers is critical to for the final interpretation of a groundwater system where different tracers are applicable at different section along the flow direction. Clark et al. (2004) applied stable isotopes of water, tritium/helium dating and gas tracers to investigate groundwater dynamics in the vicinity of an artificial recharge facility. They were able to define flow patterns, however, whether the tracer was distributed vertically throughout the entire aquifer or only in layers, acting as preferential flow paths could not be definitely identified. It can be speculated that using more tracers in addition to the applied tracers would help to overcome the difficulties in the interpretation. After Zuber et al. (2010) and Newman et al. (2010) each tracer has specific constrains and complications. These limitations results from differences in the tracers transport characteristics in groundwater and the unsaturated zone. For instance, exchange with immobile zones and interaction with the aquifer matrix as well as unknown input functions and diffusion exchange of gaseous tracers with the atmosphere through processes in the vadose zone can occur. Moreover, natural production in the subsurface and artificial contaminations can make the use of specific tracers challenging (Cook and Herczeg 2012, Ekwurzel et al., 1994, Plummer et al., 2001).

The objective of this study was therefore to develop a consistent process understanding and to determine the residence times of artificially infiltrated water at an important drinking-water supply site in northern Switzerland using seven different tracers. To date, the interpretation of residence times and subsurface processes that use all the seven aforementioned tracers (dye tracer, heat tracer, major ions, Acesulfame, ^{2}H and ^{18}O, dissolved gases and chlorinated hydrocarbons) have not yet been conducted and therefore a systematic comparison of the value of the information gained from the applied tracers is missing. It is evaluated whether mixing of artificially infiltrated water and water coming from the regional flow path occurred. Therefore, it was important to assess how the infiltrated water was distributed vertically throughout the aquifer. Knowledge about mixing of infiltrated water and water coming from the regional flow path is essential because the highest concentrations of chlorinated hydrocarbons are detected mainly in sampling locations where regional groundwater is present (Moeck et al., 2017). In addition to the distribution of various water types, the effects of changes in pumping and infiltration rates on the mixing ratio of artificially infiltrated water and that coming from the regional flow path is investigated. The seven tracers are applied and it is indicated which subsurface processes could not be identified when a certain tracer was omitted. The applied tracers were chosen because they have no or very low background concentration at the study site, behaves mostly conservative (nonreactive and no sorption occur) in the saturated zone and apart from the dye tracer no artificial injection is required. Furthermore, these tracers are relatively inexpensive. After Clark et al. (2005), tracers which can be economically introduced should be used to ensure a sufficient concentration when artificially injected to taken into account the typically large volume of recharge water, as it is the case at the investigated study site (artificial recharge rate ~ $3.5e^{7}$ m^{3}/a). This is even more the case for naturally occurring tracers that do not require artificial injection. To use the tracers under controlled flow conditions, a pumping experiment was carried out in which groundwater was extracted from an aquifer adjacent to landfills and industrial areas. Using this unique dataset, the value of the information gained from the applied tracers was systematically compared and their similarities and differences are illustrated.

2. Materials and Methods

2.1 Study site

The study site is located in northwestern Switzerland and has an area of approximately 10 km^{2} (Fig. 1). The annual average precipitation and temperature is 730 mm/a and 11.5 °C, respectively. Highest temperature occurs during the months June-August, whereas the lowest temperature is occurred typically between January and March. The wettest (driest) month is May (February) with average values of 99 mm (45 mm) of rain.

Within this site, two main aquifers exist: the Quaternary Rhine gravel and the underlying karstified Upper Muschelkalk limestone aquifer. The Quaternary aquifer consists of fluvialglacial gravel of up to 50 m in thickness (Spottke et al., 2005). The thickness of the aquifer in the vicinity of the main drinking-water extraction wells (33 wells, referred to as the pumping-well gallery) is about 20 to 40 m. The second aquifer is the Triassic Upper Muschelkalk. The thickness of the Upper Muschelkalk, is about 70 to 80 m. In some places, the Quaternary and Triassic aquifers form a continuous aquifer. The region's most prominent tectonic feature is the southeastern portion of the Upper Rhine Graben main border fault, which is represented by a flexure zone and a large number of faults, exhibit a NNE–SSW strike, and resulting in faulted blocks, horsts, and grabens (Spottke et al., 2005). A geological plan view and cross-section are provided in the supporting information, figure S1 and S2.

The Quaternary aquifer is unconfined and primarily used to produce drinking water in combination with a groundwater artificial-recharge system, due to the high average hydraulic conductivity of $3.1*10^{-3}$ m/s (Spottke et al., 2005). The Upper Muschelkalk aquifer represents a highly fractured, karstified limestone aquifer with an average hydraulic conductivity of $1.3*10^{-4}$ m/s (Gürler et al., 1987), which ranges between $1*10^{-3}$ m/s and $2*10^{-6}$ m/s (Affolter et al., 2010).The hydraulic conductivities of the fault zones are unknown and might be spatially variable. In the western part of the study area, the structurally deformed zones allow an exchange of groundwater between the bedrock aquifer and the Quaternary aquifer (Moeck et al., 2016).

Historically, the infiltration system was designed to maintain a hydraulic gradient toward areas of potential risk in which contaminated groundwater exists. For this purpose, to build up an increased groundwater mound, the volume of infiltrated water is typically about twice that of the groundwater being extracted at the pumping-well gallery. The infiltrate is Rhine River water that is pumped to an excavated system of channels and seven infiltration ponds having a combined infiltration rate averaging 95,000 m^3/day. In the study area, various patterns of contaminants have been observed in previous studies (MBN, 2008; Moeck et al., 2016), mostly close to landfills. The most commonly found contaminants are Tetrachloroethene (PCE) and Trichloroethene (TCE), two of the most widely used cleaning and degreasing solvents worldwide (Doherty, 2000), and Hexachlorbutadiene (HeCBD) and 1,1,4,4 Tetrachlorbutadiene (TeCBD), which are by-products of the production of chlorinated solvents (Fields, 2004). TeCBD can also form as a result of HeCBD dechlorination (Bosma et al., 1994). Overall, the highest concentrations of chlorinated hydrocarbons were detected in the south western part of the study area, where mainly regional groundwater is present. Regional water with higher concentrations of chlorinated hydrocarbons is coming most likely from the south (Moeck et al., 2016). A trend towards decreased concentration has been observed in areas where the influence of surface-water infiltration is increased (Moeck et al., 2017a).

Fig. 1. a) Study area Hardwald with pumping wells and both single and clustered piezometers (Clusters 1 and 2). The green and the red-gray dots show the injection locations of the tracers. Dashed black lines indicate the location of a SW–NE cross-section. b) Simplified cross-section between the infiltration channels and the Rhine River. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Methods

2.2.1 Experimental setup

The pumping experiment was carried out at extraction well 21.A.17, which is centrally located in the well gallery (Fig. 1). This well was chosen because a previous study found that it has a different hydrochemistry andisotope composition as well as higher concentrations of organic micropollutants than most of the other wells (Moeck et al., 2016). The pumping regime of the well was divided into three phases: 1) a pre-phase before the injection of the dye tracers (-250 to 0 h, in which t = 0 represents the time of tracer injection); 2) the pumping experiment (0 to 560 h after tracer injection); and 3) the post-phase (560 to 996 h after tracer injection), when the pumping regime returned to the regular one used by the water supplier (Fig. 2). Hourly extraction rates and water-table values at well 21.A.17 were recorded for all three phases of the experiment (Fig. 2), during which the extraction rates maintained a constant value of 176 m^3/h, while wells in the direct vicinity were turned off (in detail wells 21.A.16, 21.A.18, 21.A.19 and 21.A.32, see Figure 1). Before and after the experiment, the daily pumping-rate cycles were between 0 and 176 m^3/h, with a maximum duration of 11 h of water extraction. The infiltration rate of Rhine River water into the channels and ponds averaged 3700 m^3/h, but it ranged from 0–5632 m^3/h. Due to an accidental spill of methyl-tert-butylether (MTBE) that occurred upstream in the Rhine River, the infiltration was interrupted between 363 h and 403 h. This interruption resulted in an immediate decline in the groundwater table of about 0.8 m (Fig. 2). The influence of this interruption on the hydrochemistry and contaminant patterns is addressed in detail in the discussion.

Fig. 2. Time series at well 21.A.17. a) Pumping rate. b) Total infiltration rate. c) Electrical conductivity (EC). d) Groundwater table elevation. Times between -250 h and 0 h indicate the fluxes, EC, and water table before the experiment. Times between 0 h and -560 h indicate the duration of the experiment. Times between 560 h and 996 h indicate the post-experiment phase.

For the dye-tracer test, fluorescein (300 g) and naphtionate (5 kg) were injected at t = 0 h ,respectively in a pond and the channel (Fig. 1). The pond and the channel were drained before the tracer injection. After injection channel and pond were flushed immediately. A point wise injection can therefore be assumed. The injection points were chosen because the highest infiltration occurs in these sections (Moeck et al., 2017a). Then, samples were taken at 27 sampling locations distributed along the direction that the dye tracers were expected to flow in the groundwater and comprising 3 regular piezometers; 2 clustered piezometers, the first having 3 and the second having 4 different filter-screen depths available for sampling; and 15 extraction wells (Fig. 1and Table 1). The screen depths and geological stratigraphy are presented in the table S1. The artificially infiltrated surface water was also sampled. Table 1 shows the sampling locations and frequency for each tracer.The groundwater samples were collected from the piezometers using submersible pumps (COMET-COMBI 24-4T) and from the extraction wells directly from the sampling ports. Surface-water samples were taken as grab samples from the infiltration system. Note, it is assumed due to the high infiltration rates and infiltration capacity (Moeck et al., 2017a) that the infiltrated water is well mixed and spatial gradients in the concentration between the different channels and ponds are insignificant, not changing the outcomes of this study. At study locations where slow mixing and significant gradients in the tracer concentration exist, the estimated travel times between tracer injection point and extraction wells might be influenced, as demonstrated by Clark et al. (2004) and Clark et al. (2005).To prevent cross-contamination, every piezometer was equipped with its own submersible pump. The water samples were analyzed for the dye tracers, major ions, organic micropollutants, water isotopes ($\delta\ ^{2}H$ and $\delta\ ^{18}O$), and chlorinated hydrocarbons. The dye tracers were analyzed using a PerkinElmer LS 50B Fluorescence Spectrometer. The analyses for major ions, organic micropollutants, and chlorinated hydrocarbons were conducted at the accredited laboratories of the Environmental Agency of the Canton Basel-Landschaft (Resort Environmental analytic, Major ions analysis with ICP; Micropollutants analysis with LC-MSMS; Chlorocarbons analysis with Purge & Trap GC-MS). Stable isotope analysis was performed using cavity ring-down laser spectroscopy (Picarro L1 102-I). The measurement errors for all mentioned tracers are provided in table S2 (supporting information). In addition to the abovementioned compounds, time series of dissolved gas concentrations (He, Ar, Kr, N_2, and O_2) were acquired at extraction well 21.A.17 using an onsite, standalone system based on a membrane inlet mass spectrometer (MIMS) (Mächler et al., 2013; Mächler et al., 2014). The temperature data used as a heat tracer (Table 1) were continuously recorded both in the infiltrated water and at each extraction well, and a three-year dataset was used to statistically analyze this temperature data.

Table 1. Sampling location and sampling frequency for all tracers.

Tracer/ Sampling location	**# of samples**						
	Dye tracer	**Heat tracer**	**Major ions**	**Acesulfame**	**Stable isotopes**	**Dissolved gases**	**Chlorinated hydrocarbons**
21.A.17	27	69	8	6	18	every 10 min	19
21.J.105	24	0	6	7	17	0	16
21.J.106	25	0	6	7	18	0	0
21.J.107	25	0	6	7	18	0	9
21.J.108	25	0	6	7	18	0	16
21.J.109	24	0	6	7	18	0	16
21.J.110	24	0	6	7	17	0	0
21.J.111	26	0	6	7	17	0	15
21.J.112	0	0	1	0	1	0	1
21.A.12	13	67	2	0	0	0	2
21.A.13	12	76	4	0	1	0	3
21.A.14	13	44	0	0	0	0	2
21.A.15	18	78	0	0	0	0	2
21.A.16	7	62	0	0	0	0	2
21.A.18	7	67	0	0	0	0	2
21.A.19	7	72	0	0	0	0	2
21.A.20	19	74	0	0	0	0	2
21.A.21	19	67	0	0	0	0	2
21.A.22	19	64	0	0	0	0	2
21.A.23	19	79	0	0	0	0	2
21.A.26	16	47	0	0	0	0	2
21.A.31	19	61	0	0	2	0	2
21.A.32	7	60	0	0	2	0	2
21.C.210	13	0	0	1	2	0	2
21.C.219	15	0	2	4	1	0	4
21.C.234	15	0	2	4	1	0	4
Surface water	0	156	2	3	13	0	4

2.2.2 Analysis of tracer data

2.2.2.1 Dye tracer

Dye tracers have a long history of application for estimating residence times (Kim et al., 2010; Neumann et al., 2009; Runkel, 2015). In addition, spatial variability of the hydraulic conductivity and sorption-related aquifer properties can be estimated based on breakthrough data at multiple observation points (Ptak and Schmid, 1996). In this study, the residence times of artificially infiltrated water were calculated based on the breakthrough curves of the two dye tracers, fluorescein and napthionate, at the extraction wells. Both tracers can be considered ideal for an application in groundwater, as both are not or only minimally adsorbed at the matrix (Leibundgut et al., 2009). An analytical solution of the one-dimensional (1D) convection-dispersion equation was inversely fitted to the acquired data by using the TRAC software program (Gutierrez et al., 2012). Velocity and dispersivity were estimated by minimizing an objective target function that consisted of the sum of squared differences between observed and fitted concentrations.

2.2.2.2 Heat tracer

Temperature data can be used as a natural heat tracer for the interaction between surface water and groundwater (Becker et al., 2013; Hoehn and Cirpka, 2006; Vogt et al., 2009). Time shifts in the heat signals between the surface-water input and the groundwater observation point indicate retarded travel times (Engeler et al., 2011; Irvine et al., 2015; Langston et al., 2013).

Here, aquifer residence times were assessed based on the time shift of the maximum correlation of heat fluctuations between artificially infiltrated Rhine River water and heat measured at selected extraction wells. The cross-correlation methodology of Hoehn and Cirpka (2006) was applied, assuming that the heat recorded at two locations belongs to the same stream tube and that all heat-transfer properties are uniform along the length of the flow path. For the cross-correlation calculations, the raw heat data were fitted to a sine curve (T_{calc}) to fill data gaps in the time series.

$$T_{calc} = (A + T_{min}) + A \sin\left(\frac{2\pi}{\omega} * t + \Delta t\right) \qquad (1)$$

where A is the amplitude (°C), T_{min} is the minimum observed temperature (°C), ω is the sine curve period (time), and Δt is the phase shift (time). The parameter ω was set to 365 days and T_{min} was set to the minimum observed temperature, and all other parameters were calibrated using the statistical solver feature in Microsoft Excel and employing the least-squares concept. The travel time of the seasonal heat fluctuations between the infiltrated water and the wells was computed from the time shift of the maximum correlation of heat fluctuations between artificially infiltrated Rhine River water and heat measured at selected extraction wells and then converted to an estimate of aquifer residence time using a thermal retardation factor (R_T).

$$R_T = \frac{n_e \rho_w C_w + (1-n_e)\rho_s C_s}{n_e \rho_w C_w} \quad (2)$$

R_T is related to the following: effective porosity (n_e); heat capacity per unit volume of bulk granular medium ($C_b\, \rho_b$), as expressed by the product of specific heat capacity (C_b) and gravimetric density (ρ_b); and the specific heat capacity (C_w) and gravimetric density (ρ_w) of water (Hoehn and Cirpka, 2006). Since the $C_b\, \rho_b$ is related to the specific heat capacity (C_s) and gravimetric density (ρ_s) of the aquifer sediments. In the present study, an effective porosity (n_e) of 0.12 was used for the sand-gravel aquifer. This value was based on a value estimated for the study site in a numerical groundwater model application (Affolter et al., 2010). In addition, a ρ_w of 1000 kg m^{-3} and a C_w of 4.19 J kg^{-1} K^{-1} were used (Bekele et al., 2014). For the sand-gravel aquifer, a quartz mineralogy with a specific heat capacity (C_s) of 740 J kg^{-1} K^{-1} and a gravimetric density (ρ_s) of 2.65 kg m^{-3} was applied (Bekele et al., 2014, Waples and Waples 2004) leading to an R_T value of 4.4. A discussion of uncertainty in R_T calculation is included in the discussion and demonstrated by a sensitivity analysis in the supporting information (Table S3).

The following formula relates the linear-flow velocity of solutes to that of convective heat (Hoehn and Cirpka, 2006).

$$\bar{v}_w = R_T * \bar{v}_T \quad (3)$$

The flow velocity for heat ($\bar{v}_T$) was calculated as the ratio of time shift to linear distance between the infiltration system and the observation well. To compare the flow velocity based on the heat data with the results obtained from the dye tracers, $\bar{v}_w$ was calculated from the product of R_T and $\bar{v}_T$.

2.2.2.3 Hydrochemistry

Classically, hydrochemical data are used to understand processes such as subsurface water mixing (Abou Zakhem and Hafez, 2012; Dilsiz, 2006; Lakshmanan et al., 2003). The present study compared artificially infiltrated surface water and groundwater from piezometers and extraction wells to identify differences in the composition of major ions. Ratios between the sampling locations and infiltrated surface water were used to identify trends in water chemistry, including mixing of different water types.

2.2.2.4 Artificial sweetener - Acesulfame

Surface-groundwater studies increasingly use chemically persistent anthropogenic markers, including artificial sweeteners (Hillebrand et al., 2015; Lee et al., 2015; Robertson et al., 2016). The use of these indicator substances enables determination of specific pathways in the water cycle (Moeck et al., 2016; Van Stempvoort et al., 2011). For example, elevated concentrations of anthropogenic markers are typically present in treated wastewater effluents, and thus can be used to estimate the interaction between surface water and groundwater (Mawhinney et al., 2011; Moschet et al., 2014). In this experiment, concentrations of the artificial sweetener acesulfame in both the Rhine River infiltrate and the groundwater from the various sampling locations were used to identify potential mixing of artificially infiltrated water and groundwater from the regional flow path.

2.2.2.5 Water-isotope data

Variations in stable water isotopes are used to obtain information on the origin(s) of groundwater (Demlie et al., 2008). This commonly applied data can be used to understand mechanisms of groundwater circulation and mixing (van Geldern and Barth, 2012).

2.2.2.6 Dissolved gases

Atmospheric gases dissolved in water provide an alternative to more traditional tracers (Aeschbach-Hertig et al., 1999; Aeschbach-Hertig and Solomon, 2013; Beyerle et al., 1999). The recent development of onsite analysis of dissolved gases in groundwater provides a new analytical opportunity to trace flow processes at high temporal resolutions using the miniRUEDI instrument (Brennwald et al., 2016; Gasometrix GmbH, Mächer et al., 2012; Mächler et al., 2014). In the present study, because the high temporal resolution of 10 min of gas measurements was associated with noise in the dataset, a change-point analysis (Killick and Eckley, 2014) was applied, seeking to identify the location of multiple change points in the times series and link the corresponding periods with possible changes in the regime of the subsurface flow. Change points were identified based on changes in the mean and variance of the time series of each of the dissolved gas concentrations measured.

2.2.2.7 Chlorinated hydrocarbons

Pollutants in surface water and groundwater, including chlorinated solvents, can be used to understand subsurface flow and transport processes (Urresti-Estala et al., 2015; Widory et al., 2004). The present study used the observed temporal patterns of the chlorinated hydrocarbons PCE, TCE, TeCBD, and HeCBD to identify changes in the concentration pattern that were due to variations in the pumping regime and the infiltration rates. This was similar to the use of dissolved gases, except that it lacked the change-point analysis because of its lower temporal-data resolution.

3. Results

3.1 Dye tracer test

This section describes the breakthrough curves for napthionate and fluorescein at two piezometer clusters and extraction well 21.A.17. At Cluster 1, close to the infiltration system, the breakthrough curves indicated a vertical gradient in the distribution of the injected tracers (Fig. 3). The highest concentration occurred at the top-most sampling location, 21.J.111, which had a first-arrival time of 72 h for both substances and reached maximum peak 96 h and 216 h for fluorescein and napthionate, respectively. The lowest peak concentration for fluorescein was measured at the bottom-most sampling location, 21.J.109, where the first-arrival time was measured at 72 h (fluorescein) and 96 h (napthionate), but the peaks were reached later than at 21.J.111, (192 h and 264 hfor fluorescein and napthionate, respectively.

Fig. 3. Napthionate and fluorescein breakthrough curves at piezometer Cluster 1 and extraction well 21.A.17, of which Cluster 1 is located closer to the infiltration system. The well screens are located at depths of 253.7 masl (21.J.111), 248.0 masl (21.J.110), 242.8 masl (21.J.109), , and 231.3 masl (21.A.17).

The fluorescein and napthionate concentration at Cluster 2, which is in close proximity to the extraction well, was less than an order lower than that observed at Cluster 1 (Fig. 4). Nevertheless, a vertical gradient in the distribution of the tracers were observed in the data. Again, the highest concentration for both substances was measured at the top-most sampling location, 21.J.108, which had a first-arrival time of 96 h (fluorescein) and 216 h (napthionate) and reached a peak at 264 h and 432 h for fluorescein and napthionate, respectively. The lowest concentration was measured at the bottom-most sampling location, 21.J.105, which had a first-arrival time of 120 h (fluorescein) and 288 h (napthionate) and reached a peak at 288 h and 456 h for fluorescein and napthionate, respectively.

In terms of breakthrough and peak, the breakthrough curve of extraction well 21.A.17 was similar to the breakthrough of the deeper sampling location. Again, the first-arrival time was 120 h and 168 h, and the peak was reached at 288 h and 672 h for fluorescein and napthionate.

Fig. 4. Napthionate and fluorescein breakthrough curves at piezometer Cluster 2 and extraction well 21.A.17, which are close to each other. The well screens are located at depths of 251.5 masl (21.J.108), 245.4 masl (21.J.107), 240.1 masl (21.J.106), 232.0 masl (21.J.105),and 231.3 masl (21.A.17).

All obtained first-arrival and peak times were between 91 h and 288 h for fluorescein and between 211 h and 672 h for napthionate (Table 2). However, the first-arrival time was much less, being about 1/3 of the maximum peak time.

Table 2. First-arrival and peak times for well 21.A.17 and piezometers of Clusters 1 and 2Tracer	ID	First arrival [h]	Maximum peak [h]
Napthionate	21.A.17	168	672
	21.J.109	91	259
	21.J.110	91	259
	21.J.111	67	211
	21.J.105	283	449
	21.J.106	283	403
	21.J.107	163	451
	21.J.108	211	427
Fluorescein	21.A.17	120	288
	21.J.109	67	187
	21.J.110	67	187
	21.J.111	67	91
	21.J.105	115	283
	21.J.106	91	283
	21.J.107	65	283
	21.J.108	91	259

3.2 Heat tracer tests

Figure 5 shows the time series of heat data for infiltrated Rhine River surface water and five extraction wells for the last three calendar years. The fitted sine function represents the measured data well, although a small underestimation of the summer temperatures of the Rhine River water occurred in the second and third years. Because calculating residence times requires only the time shift of the maximum correlation of heat fluctuations between infiltrated surface water and measured heat at extraction wells, a mismatch in the absolute data does not affect our results and can therefore be ignored.

Fig. 5. Time series of heat data for five groundwater wells in the pumping gallery and infiltrated Rhine River water. The lines represent the resulting fit of the heat data based on equation 1.

The time series were used in a cross-correlation function to calculate the time shift between heat data from infiltrated water and heat measured at the wells (Table 3). The obtained time between the surface-water input signal and the observed heat signal at the observation wells was between 2496 h and3408 h. Taking into account the calculated thermal retardation factor (R_T), this corresponds to a travel time of between 576 h and 768 h. This is similar to the peak time for the dye tracer napthionate at the wells.

Table 3. Calculated time shift for five wells based on heat observations and travel time

	Unit	21.A.16	21.A.17	21.A.18	21.A.19	21.A.21
Travel time without thermal retardation factor	**hours**	**2544**	**3408**	**3024**	**2496**	**2520**
Travel time with thermal retardation factor	**hours**	**576**	**768**	**696**	**576**	**576**
VT	**m/day**	**3.95**	**2.95**	**3.28**	**3.97**	**3.35**

3.3 Hydrochemistry

Overall, only small differences in major ions concentrations were observed between infiltrated water and sampled groundwater. Only extraction well 21.A.17 showed higher concentrations, especially of SO_4^{2-}, Ca^{2+}, and Na^+. Although well 21.A.17 and Cluster 2 are separated by a distance of only 25 m, their concentrations of cations and anions differ remarkably, as shown by the example for Ca^{2+} and SO_4^{2-} (Fig. 6). For the nested wells at the clusters, no distinct differences in concentrations were observed, apart from those at observation well 21.J.105, where the filter screen was located at the bottom of the aquifer. There, the concentrations were more similar to those measured at the extraction well than to those at all other sampling locations.

Fig. 6. Boxplot of Ca^{2+} and SO_4^{2-} concentration [mg/l] for Rhine River water infiltrate (0 m) and sampling locations. The distance [m] from the infiltration channel is illustrated at the top of the graph. Cluster 1 is located closer to the infiltration system.

3.4 Artificial sweetener – Acesulfame

As expected, the concentration of acesulfame was higher in the Rhine River infiltrate, which had a mean of 0.39 µg/l, than in the groundwater samples (Fig. 7). The concentration decreased slightly between the infiltration system and piezometers 21.C.219 (70 m) and 21.C.234 (228 m), which had mean values of 0.31 and 0.33 µg/l, respectively,however, at Cluster 1 (distance 277 m), a marked decrease in acesulfame concentrations was observed. The concentrations were less than 40% of the mean concentration of the infiltrated surface water. At this cluster, the highest concentration was measured at the top-most sampling location, 21.J.111, and the lowest concentration at the bottom-most sampling location, 21.J.109. Subsequently, the concentrations remained low for piezometer 21.C.210 and Cluster 2. Also at Cluster 2, a vertical concentration gradient was observed. Although the concentration differences were smaller between the top-most and bottom-most sampling locations, the trend was the same as that for Cluster 1: the highest acesulfame concentration was found in the top-most sampling location, 21.J.108, and the lowest concentration was measured at the bottom-most location. The lowest concentrations of all were measured at extraction well 21.A.17.

Fig. 7. Boxplot of acesulfame concentration [µg/l] for Rhine River water infiltrate (0 m) and sampling locations. The graph provides the distance [m] from the infiltration system. Cluster 1 is located closer to the infiltration system.

3.5 Water-isotope data

Stable isotope data ($\delta^{18}O$ und $\delta^{2}H$) are used to identify subsurface processes. For all groundwater sampling locations, the observed isotope range was between -11.3 and -10.7‰ ($\delta^{18}O$) and -83.0 and -80.1‰ ($\delta^{2}H$). For the surface-water samples, the range was between -11.5 and -11.0‰ ($\delta^{18}O$) and -81.6 and -79.0‰ ($\delta^{2}H$) (Fig. 8). As expected, the isotope compositions of the infiltrate and the nested wells of Cluster 1 (close to the infiltration system) were quite similar. In comparison, Cluster 2, which is in close proximity to extraction well 21.A.17, showed values similar to those of that well. Generally, the isotope composition changed from infiltrated surface water to Cluster 1 and changed more so in Cluster 2 and extraction well 21.A.17. However, the differences among the various sampling locations were quite small, and interpretation must be done with caution.

Fig. 8. Isotopic composition ($\delta^{18}O$–$\delta^{2}H$) of groundwater and surface-water infiltrate. The black line shows the Global Meteoric Water Line (GMWL). Colors indicate the various sampling locations. Note that between 2009 and 2013, the water-isotope composition of the Rhine River varied in a relatively small range: between -11.5 and -10.3‰ for $\delta^{18}O$ and between -81.9 and -74.1‰ for $\delta^{2}H$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.6 Dissolved gases

Figure 9 shows the time series of dissolved gases. The 24-hour moving average (in orange) indicates three phases during the pumping experiment, which are validated by the change-point analysis (red lines). The behavior of the gases during the experiment and their relationship to changing fluxes in the pumping and infiltration rates are discussed using the concentration of krypton as an example. The time series of all other dissolved gases measured showed very similar behavior during the three phases.

The first phase showed the concentration before the constant pumping of the pumping experiment (time < 0 h). Before this phase, the pumping rates were variable (see Section 2.1, Experimental setup). As a result of this constant pumping (time ~ 0 h), decreased krypton concentrations were observed. These decreases were relatively fast until they reached a plateau (time > 0 h). Due to a detected spill of MTBE in the Rhine surface water, an infiltration interruption occurred between 363 hours and 403 hours, during which time, krypton concentrations increased rapidly until they reached a plateau. Note that the pumping rate was constant during this time, although the infiltration rate fluctuated.

Fig. 9. Time series of dissolved gases (He, Ar, Kr, N_2, and O_2) showing 24-hour moving average (orange line) and three estimated change-point intervals (red line). The green rectangle indicates the infiltration interruption due to the spill of MTBE into the surface water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.7 Chlorinated hydrocarbons

Figures 10a and 10c show the normalized concentration patterns for Clusters 1 and 2. To normalize the data, the concentration for each observation point was divided by the maximum concentration for that observation point. Similar to the trend observed with the dissolved gases, three distinct phases were observed for chlorinated solvent patterns. The following explanation of these patterns uses PCE as an example. The first point of the normalized concentration patterns shows the concentrations before the constant pumping of the experiment (time < 0 h). For all observations, the normalized concentration was 1 or close to

1. Then, constant pumping with continuous infiltration led to decreased concentration (time ~ 0 h) until a plateau of approx. 0.7 was reached. Due to the aforementioned infiltration interruption, the concentration increased until it reached a plateau. After 560 h, intermittent pumping occurred, which led to fluctuations in the concentration pattern of all observations, especially those for Cluster 2, which is in close proximity to the extraction well. The short term cessation of the pumping leads to fluctuations in the concentrations but are less pronounced compared to the concentration variation due to the infiltration stop or constant pumping.

Figures 10b and 10d show as boxplots the absolute concentrations of PCE for the various observations. The concentrations at Cluster 2 were the lowest, less than half those at extraction well 21.A.17. Cluster 1 is in close proximity to the infiltration system, and therefore the amount of artificially infiltrated surface water was high, which led to lower concentrations through dilution. At lower depths, there was a trend toward increased concentration of chlorinated hydrocarbons. The lowest concentration was measured at observation point 21.J.111 (the top-most one), and the highest concentration was measured at observation point 21.J.109, at the bottom of the sand-gravel aquifer. In addition, although the differences were small, the amount of infiltrated water seemed to vary with depth. At Cluster 2, no clear concentration differences were observed between the extraction well and the observation points. Finally, the concentrations at Cluster 2 were clearly higher than at Cluster 1, indicating that the amount of regional groundwater was higher.

Fig. 10. a and c: Normalized PCE concentration patterns for Clusters 1 (top left) and 2 (bottom left) and extraction well 21.A.17. Normalization was carried out by dividing the concentration of each observation point by the maximum concentration for that observation. b and d: Boxplot of the PCE concentration ranges for Cluster 1 (top right) and 2 (bottom right), extraction well 21.A.17, and Rhine River infiltrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Discussion

4.1 Assets and drawbacks of the various tracers

Some assets and drawbacks can be elucidated based on the experiments. In the following, the obtained results are discussed for each tracer considered and its strengths and limitations are illustrated. We discuss which tracers are well suited for answering specific research questions and which other tracers has to be chosen when another task has to be carried out.

Travel time

One major requirement is that the time shift of heat or concentration fluctuations between two locations must be large enough to calculate a shift between the input and output signals. Moreover, suitable tracers for estimating travel times should be measurable with a high sampling frequency and show a sufficient variability among the samples. For the study site, only the dye and heat tracers were satisfying these requirements. For the remaining tracers sampling frequency was limited by sampling logistics and techniques as well as laboratory restrictions. Currently, there are efforts to develop high-resolution, onsite measurement tools for stable isotope analysis (Tweed et al., 2016; von Freyberg et al., 2017), but such applications still require a great deal of labor and have been applied only to surface water so far. The high temporal resolution of onsite gas measurements in groundwater provides certainly new analytical opportunity for dynamic processes using the miniRUEDI instrument (Brennwald et al., 2016, Gasometrix GmbH). In the presented work, however, only the output was measured. Although, important information about flow and transport during changing infiltration and pumping rates were identified in the output signal, no time shift between input and output signal could be used to estimate the travel time. Even though currently only a few onsite-measurement devices are available, anticipated developments in dissolved-gas analysis should increase their availability.

For the study site the residence times resulting from the dye tracer and the heat tracer were very similar (Figs. 3–5), although times obtained from the heat tracer were somewhat higher. The different residence time for fluorescein compared to napthionate might be related to the flushing in the pond, in which, due to increased hydraulic gradient, a high volume of water forced the infiltration process in contrast to napthionate where a lower infiltration rate existed in the channel compared to the ponds (Moeck et al., 2017). The small differences observed between the dye and the heat tracer might also be related to the forced flow field during the dye-pumping experiment (Ptak et al., 2004). Furthermore, a few studies have shown faster transport for mass tracers due to preferential subsurface flow paths (Seibert et al., 2014), whereas heat tracers show transport times more dependent on thermal retardation and diffusion with the aquifer matrix (Colombani et al., 2015).

Although a forced-gradient tracer test was conducted, the recovery rate of the dye tracers was low (typically less than 10%) and therefore might have limited its utility and interpretation. The heat tracer seems to be a valuable alternative to dye tracers because it typically has no issues related to recovery rate, thanks to the spread of the thermal signal and its natural occurrence. In addition, temperature measurements are robust and easy to record (Irvine et al., 2016; Shanafield et al., 2016). However, temperature time series still present a few drawbacks when used to estimate residence times. Apart from the requirement that the time shift between two locations must be large enough, the assumptions that the temperature recorded at both locations belongs to the same stream tube and that all heat-transfer properties are uniform along the length of the flow path are not always true. Uncertainty arises from the fact that aquifer-matrix parameters, including effective porosity, are difficult to measure and significantly affect the calculated thermal-retardation factor, R_T, which relates the travel time of solutes to that of the convective heat tracer (Schmidt et al., 2006) (see also Table S3).

Origin and lateral transport

Tracers identified as suitable for estimating the origin and mixing of sampled groundwater included major ions, stable water isotopes, and organic micropollutants (e.g., acesulfame and chlorinated hydrocarbons). All indicated differences between the sampling locations and helped to identify mixing between artificially infiltrated water and regional groundwater. For instance, at extraction well 21.A.17, the major ions indicated that the extracted groundwater was a mixture of infiltrated water and groundwater from a different origin (Fig. 6), and higher ion concentrations were measured at this site. Most likely, regional groundwater from the underlying limestone aquifer, which is enriched with Ca^{2+}, Mg^{2+} , SO_4^{2-}, and HCO_3^- (Moeck et al., 2016) was extracted in addition to the artificially infiltrated surface water. However, in the case of the major ions, rock-water interaction might biasing the estimation of mixing ratios (Moeck et al., 2017). Acesulfame and the stable isotopes δ^2H and $\delta^{18}O$ are more attractive candidates for identifying groundwater mixing due to their typically persistent behaviour for the flow field and residence times considered. The spatial-concentration pattern of the artificial sweetener acesulfame (Fig. 7) shows a significant decrease in acesulfame concentration in the extraction well compared to the infiltrated water, especially in an area 228–277 meters from the infiltration channels. In this area, upwelling through the fractures might have been localised, and an amounts of water from the lower part of the limestone aquifer—which has smaller concentrations of acesulfame—may dilute the groundwater in the upper aquifer. However also in the uppermost piezometer of cluster 1, acesulfam concentration is reduced to about half of the concentration of the infiltrating water. Given the hydrogeological situation, beside dilution there must be another process reducing the acesulfam concentration.

Nevertheless, at this study site, the differences observed between concentrations in infiltrated surface water and groundwater were very small (e.g. Fig. 7-8). In addition, uncertainty was introduced due to the variability of the surface water's input. The load of organic micropollutants in surface water can vary daily and seasonally (Musolff et al., 2009; Ruff et al., 2015). This might be less important when only a snapshot of the spatial distribution is required, but, for accurate mixing-ratio calculations, time series with small sampling intervals are necessary. However, they are typically limited by technical restrictions.

Stratification of the flow system

Suitable tracers to estimate differences in the vertical distribution included dye tracers, acesulfame and stable isotopes. For instance, the largest share of the infiltrated dye tracer was found at the top of the aquifer (Figs. 3–4).Similarly, the highest acesulfame concentrations in the clusters were found at the top-most sampling locations, whereas the lowest concentrations were observed at the bottom-most ones (Fig.7).

Temporal changes of the flow system

Typically, changes in mixing ratios due to changing boundary conditions cannot be investigated with the sampling frequencies commonly available with the tracers applied in this study. As demonstrated, at our study site, only the time series of chlorinated hydrocarbons and dissolved gases provided important information about flow and transport during changing infiltration and pumping rates, which highlights the importance of data with high temporal resolution. Both tracers yielded comparable results (Figs. 9-10). During constant pumping rates (time > 0 h), more artificially infiltrated surface water was extracted, which led to a higher dilution of the regional groundwater and to all concentrations decreasing rapidly. However, the infiltration interruption caused the ratio to change and more regional groundwater to be extracted, which led to an increase in all concentrations. These effects could not be identified with remaining tracers due to sampling and laboratory restrictions.

Artificial tracers and Intrinsic tracers

Overall, the use of artificial tracers (e.g., dye tracer) has several disadvantages compared to intrinsic tracers. An artificial, injected tracer can be used over only a short period of time, which might reduce the recovery rate and validation of the results obtained. When the higher field-work demands involved in planning, preparing, and injecting the artificial tracer are taken into account, it becomes obvious that natural, intrinsic tracers are preferable for many applications.

5. Conclusions

Seven tracers were considered in analyzing a pumping experiment at a site where drinking water is extracted from an aquifer located close to landfills and industrial areas and where groundwater is artificially recharged by infiltrating surface water. It was demonstrated that dye and heat tracers were useful for estimating the residence time of the artificially infiltrated water. The results obtained might be biased by issues related to the recovery rate (dye tracer) and uncertainty in the required aquifer-matrix parameters (heat tracer) needed to calculate the thermal retardation factor.

Tracers identified as suitable for estimating the origin and mixing of groundwater included major ions, stable water isotopes, and organic micropollutants (e.g., acesulfame and chlorinated hydrocarbons). All indicated differences among the sampling locations and helped to identify mixing between infiltrated water and regional groundwater. However, because of the small differences in observations between infiltrated water and groundwater, measurement errors and variable input require sampling to have high temporal resolution. The effects of changing infiltration and pumping rates on groundwater flow and transport were observed only for data on the time series of chlorinated hydrocarbons and dissolved gases. For many applications, using artificial tracers rather than intrinsic tracers has several disadvantages,however, overall, it could be demonstrated that the application of multiple tracers was beneficial to minimizing uncertainties and to uncovering subsurface processes that would not have been identified by the application of only one tracer.

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