

## Assessment of the origin and transport of four selected emerging micropollutants sucralose, Acesulfame-K, gemfibrozil, and iohexol in a karst spring during a multi-event spring response

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### ABSTRACT

The assessment of vulnerability in karst systems reveals to be extremely challenging since it varies significantly with time and highly depends on the identification of diffuse and concentrated infiltration from surface karst features. The origin, consumed loads, and transport mode of selected micropollutants (MPs) including two artificial sweeteners (ASWs) Sucralose (SUC) and Acesulfame-K (ACE-K), in addition to other less investigated pharmaceuticals such as the lipid regulator Gemfibrozil (GEM), and the contrast media Iohexol (IOX) were investigated in a karst system under dynamic conditions. A detailed analysis of selected spring responses' chemograph and hydrograph following a multi precipitation event shows that three of the tracked MPs, especially ACE-K, and to the exception of IOX, can be used as specific indicators for point source domestic wastewater in karst systems. They have revealed to be persistent, source specific, conservative, and highly correlated with in-situ parameters easily measurable at the spring (chloride and turbidity). Even if the selected MPs are found in the system during low flow periods, they are mostly transported to the spring through fast flow pathways from flushed wastewater with surface water or flood rainwater. The highest mass inflow of ACE-K, IOX and GEM originated from a sinking stream, while SUC infiltrated exclusively through fast infiltration points (dolines). Their breakthrough curves coincide with the arrival of new waters and turbidity peaks. Unlike IOX, the mass fluxes of ASWs, and GEM to a lesser extent, can be linearly correlated with chloride mass fluxes and turbidity flux. Moreover, the variance of the normalized breakthrough curves of the MPs with respect to a mean transit time, increases in that order IOX < GEM < Turbidity < SUC < ACE-K indicating a higher restitution time for ACE-K with respect to other spring signals.

### 1. Introduction

Karst aquifers supply about 25% of the world population, and in some European countries even 50% with drinking water (Ford and Williams, 2007), especially in Mediterranean semi-arid regions. Karst systems' vulnerabilities are difficult to assess due to their duality of infiltration and flow. They are recharged through concentrated infiltration in dolines and/or dry valleys. Additionally, diffuse recharge also occurs through soil and epikarst forming a relatively thick unsaturated zone (Geyer et al., 2008; Perrin et al., 2003). A duality of flow is observed in the saturated zone, where a conduit system is draining low permeability matrix storage (Doummar et al., 2012; Geyer et al., 2007; Király, 2002). In the last few decades, emerging organic MPs on terrestrial and in aquatic environments are being investigated through continuous monitoring or grab sample analysis, not only to determine their occurrence and fate in the environment, (Daughton and Ternes,

1999; Halling-Sørensen et al., 1998; Kümmerer, 2009; Schwarzenbach et al., 2006; Stan and Linkerhagner, 1992; Stan et al., 1994) but also to assess their transport characteristics in various hydrological systems (Burke et al., 2013; Einsiedl et al., 2010). MPs include among others 1) pharmaceuticals such as antibiotics, anti-inflammatory, hormones, contrast media; 2) personal care products such as preservatives, antimicrobials, antibacterial; and 3) food additives: such as artificial sweeteners. Recent studies have documented the occurrence of artificial sweeteners Sucralose (SUC) and Acesulfame-K (ACE-K) in the aquatic environment (Brorström-Lundén et al., 2008; Buerge et al., 2009; Loos et al., 2009; Mead et al., 2009; Scheurer et al., 2009), along with the lipid regulator Gemfibrozil (GEM; Araujo et al., 2011, Bendz et al., 2005, Sanderson et al., 2003) and the contrast media Iohexol (IOX; Kormos et al., 2011, Putschew et al., 2000).

ASWs are ubiquitous in the human diet (Oppenheimer et al., 2012) and are not extensively metabolized by humans (Roberts et al., 2000).

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SUC, sold under the trade name Splenda®, is a chlorinated form of Sucrose. It is approved for use as an additive in over 4000 food products in over 80 countries (Torres et al., 2011). ACE-K is also a calorie free sweetener, sold under different commercial names, currently approved for use in the U.S.A and other countries (FDA, 2006). They are excreted unchanged in urine, flow into waste water treatment plants (WWTP) or untreated waste water, and are discharged directly to environmental waters. (Grice and Goldsmith, 2000; Hoque et al., 2014; Labare and Alexander, 1993; Roberts et al., 2000; Sang et al., 2014; Sims et al., 2000; Wood et al., 2000). Two percent (2%) or less of the consumed GEM is excreted unchanged (Zimetbaum et al., 1991), whereas IOX is released into urine largely unchanged after passing through the body (Kormos et al., 2010).

Concentrations of ACE-K reach 780 and 730 ng/l in surface water and groundwater respectively in Singapore (Tran et al., 2014a,b). Base flow concentrations of ACE-K (around 20 ng/l) were observed in a karst spring in Germany and were reported to increase with untreated waste water disposal on the catchment (Zirlewagen et al. 2016). Loadings of SUC into surface water in the US ranged between 120 and 10,000 ng/l (Oppenheimer et al., 2012). In Singapore, maximum concentrations of SUC in surface water reach 530 ng/l, while they fall below detection limit in groundwater (Tran et al., 2014a,b). In the US, concentrations of SUC in treated potable water ranged between 49 and 2400 ng/l (Wolf et al., 2012; Mawhinney et al., 2011). The ratio of ACE-K/SUC was estimated at about 40 in sampled waste water effluent in Germany and at only 3 in a site in Mediterranean country (Scheurer et al., 2009) indicating varying usage of the ASWs in different regions.

On the other hand, GEM was detected in surface water in the US at concentrations varying between 13 and 130 ng/l. Karnjanapiboonwong et al. (2011) showed that its concentrations in groundwater in the US can reach up to 2550 ng/l. This lipid regulator was found in groundwater in Spain at average concentrations of 165 ng/l (Barnes et al., 2008; Fram and Belitz, 2011). According to a study in western Greece by Stamatis and Konstantinou, 2013, the concentration of GEM in municipal waste water influents ranged between 470 and 1250 ng/l, while IOX was found at higher concentrations reaching 960 ng/l.

Due to their documented occurrence and persistence in surface water (Mead et al., 2009; Perkola and Sainio, 2014) and groundwater, SUC (Mawhinney et al., 2011; Oppenheimer et al., 2011) and ACE-K (Robertson et al., 2013) have been investigated as wastewater indicators of domestic wastewater pollution in groundwater (Buerge et al., 2009; Foolad et al., 2015; Oppenheimer et al., 2011; Stempvoort et al., 2011; Stempvoort et al., 2013; Wolf et al., 2012) and surface water (Liu et al., 2014; Nödlér et al., 2016; Spoelstra et al., 2013; Tran et al., 2014a,b).

SUC is highly soluble in water (Li et al., 2010); its mineralization is reported to occur in soils, lake sediments, sewage, and estuarine water. (Labare and Alexander, 1993). Additionally, biodegradation of SUC in water is not significant (Sharma et al., 2014). For instance the breakdown of SUC is unfinished and does not occur over a short time scale under natural conditions (Tollefsen et al., 2012).

A new study showed that ACE-K can be biodegraded in WWTPs only under oxic and denitrifying conditions (Castronovo et al., 2017); however, it is not eliminated in conventional wastewater treatment plants (WWTPs) (Brorström-Lundén et al., 2007; Buerge et al. 2011; Minten et al., 2011; Robertson et al., 2013; Scheurer et al., 2009; Soh et al., 2011; Subedi and Kannan, 2014; Torres et al., 2011). Furthermore, ACE-K revealed to be poorly removed by biodegradation and adsorption processes under both oxic and anoxic conditions in saturated soil (Foolad et al., 2015). In septic tanks, SUC was proven not to be a good marker for wastewater (James et al., 2016; Oppenheimer et al., 2011), because of its several years half-life and its thermal stability and resistance to metabolism and decay (Scheurer et al., 2009). It was suggested by Oppenheimer et al., 2011, that the evaluation of the environmental transport of SUC and their concentration in groundwater and surface water is still needed. GEM is used as lipid regulator under

various commercial names, and has a high persistence in the natural environment (Araujo et al., 2011). IOX is a water soluble, low chemo-toxic, and low osmolality contrast agent used for medical imaging (drugs.ca). Both IOX and GEM are not degraded by conventional WWTP processes (Ternes and Hirsch, 2000; Putschew et al., 2001); therefore they are considered indicators for domestic waste water or potentially, hospital waste in the case of IOX.

Various studies have identified waste water indicators in karst groundwater for water quality monitoring purposes. Some pharmaceuticals such as carbamazepine have revealed to be suitable waste water indicators (Clara et al., 2009; Doummar et al., 2014; Gasser et al., 2010) for long term contamination or old stored waste water. Other investigated MPs such as caffeine were considered as indicative of short term contamination because of their biodegradability potential (Hillebrand et al., 2015; Reh et al., 2015). Based on continuous monitoring of its concentrations in a karst spring, ACE-K was reported to be persistent and a suitable waste water indicator (Zirlewagen et al., 2016) in karst systems.

Nevertheless, there is an urgent need to investigate the occurrence and fate of other selected MPs under specific hydrological conditions (Lim et al., 2017), before assessing their suitability as waste water indicators in the environment especially in challenging karst systems, especially in the case of the least investigated GEM, IOX, and SUC.

In this work, four MPs: SUC, ACE-K, GEM, and IOX are monitored in spring responses following rain events. The occurrence of these MPs is compared and contrasted to other easily in-situ measured parameters at the spring such as chloride (Cl), electrical conductivity (EC), and turbidity (TU) to test their efficiency as waste water indicators in karst systems, under variable flow conditions.

## 2. Field site

Qachqouch Spring, located in the Metn area in Lebanon 18 km north from Beirut, is draining a catchment of about 50 km<sup>2</sup>. It originates from the Jurassic karst aquifer at about 64 m above sea level (asl; Fig. 1). The Jurassic formation is mainly formed of limestone; with intertonguing dolostones in the lower parts of the formation because of diagenetic dolomitization (Nader et al., 2007). The spring is highly polluted due to excessive non sorted solid waste and untreated waste water disposal on its urbanized catchment upstream. During low flow periods, the spring is used to complement water shortage in Beirut and its surrounding areas. The total yearly discharge of Qachqouch Spring reaches 60 Mm<sup>3</sup>, based on high resolution monitoring of the spring (2014–2017). Its flowrate is about 2 m<sup>3</sup>/s during high flow periods on average and recedes to 0.2 m<sup>3</sup>/s during recession, with a maximum recorded value at 17 m<sup>3</sup>/s for a short period of time following flood events. The total yearly precipitation is estimated at 1000 mm on average, from one station deployed over the Qachqouch catchment at 950 m asl. (2014–2017 local high resolution monitoring).

Raw wastewater is either directly discharged into the river system or stored onto the catchment in bottomless septic pits or abandoned boreholes, as there are no effective WWTPs on the studied catchment area. A sample of waste water effluent discharged into the river collected on the groundwater catchment revealed concentrations of 210,000 ng/l of ACE-K, and 760 ng/l of SUC, 3500 ng/l of GEM, and 290 ng/l IOX in untreated waste water. Therefore in typical local wastewater samples, the concentrations of MPs increases in the following order: IOX < SUC < GEM < ACE-K.

Tracer experiments show that about 2% of river water infiltrates rapidly in one location on the highly polluted El Kalb River, and reaches the Qachqouch spring with velocities varying between 0.02 and 0.04 m/s according to the base level of the River (2–4 h).

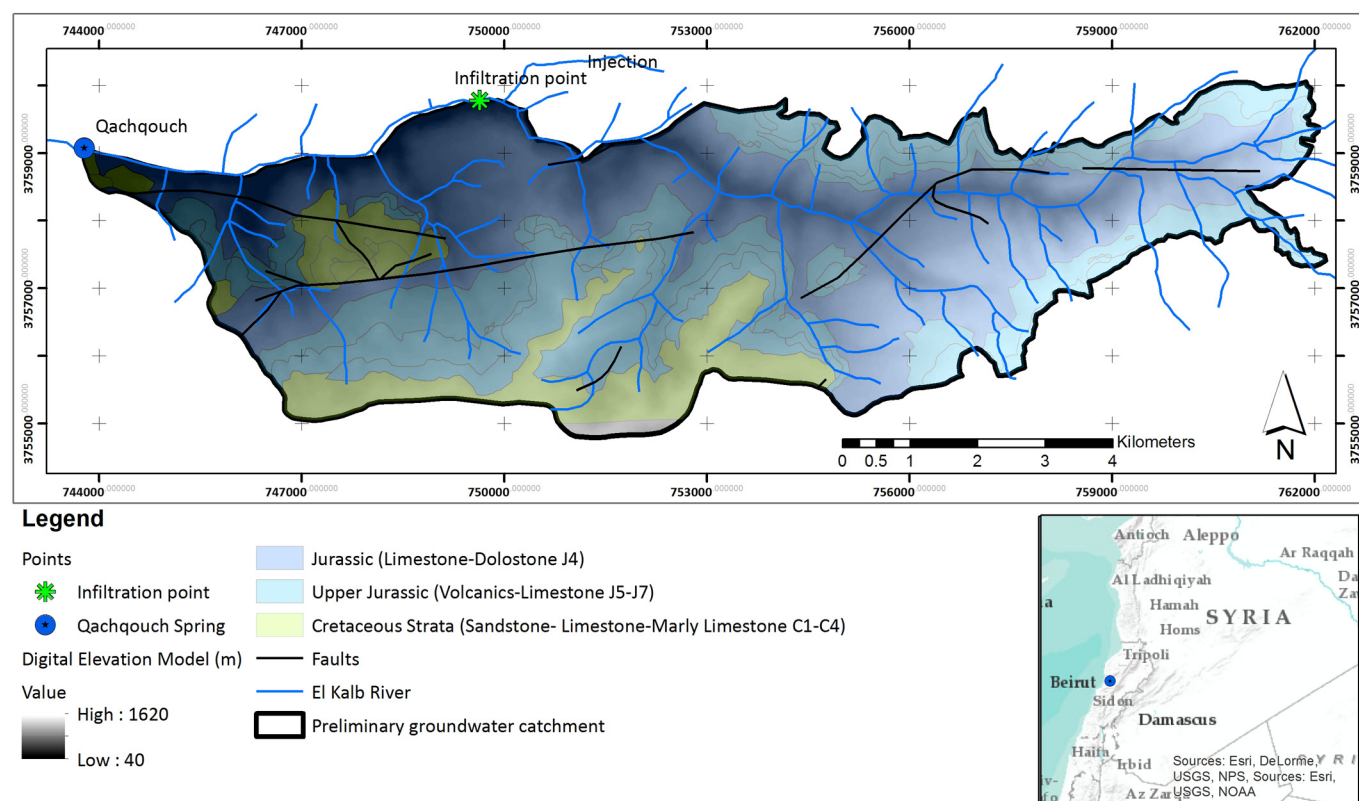


Fig. 1. Overview map of the field site showing the catchment and geology of the Qachqouch Spring. Tracer experiments reveal a fast pathway connection between the River and the spring.

### 3. Materials and methods

#### 3.1. Event monitoring

A total of 20 samples from Qachqouch Spring were collected at varying time intervals (4–8 h) following the beginning of three consecutive events between December 30th 2015 and January 9th 2016. Two rain samples were collected on January 5th at 600 m and 900 m asl respectively for the estimation of calcium (Ca), Cl, and stable oxygen and hydrogen isotope concentrations in rain water. EC, Cl, TU, and water levels were monitored every 20 min in-situ with a multi parameter probe installed at the spring mounted with a Cl sensitive electrode. Based on a rating curve, discharge rates were estimated from the water level data measured at the spring. A total of sixteen additional samples were collected in 2015 and 2017 from the Nahr El Kalb River before and after the sinking stream to assess the concentrations of the tested micropollutants in the River under varying flow conditions (Doummar and Aoun, 2018).

#### 3.2. Sample collection

MP samples were collected in 40 mL amber glass vials and preserved in the field in a cooler with a 3 mg sodium omadine and 5 mg ascorbic acid (Oppenheimer et al., 2011). The samples were then transported on ice and preserved in the fridge at temperature < 6°C until they were shipped to Eaton Eurofins Laboratories in California in coolers, a week after collection. The analyses date is two weeks after collection. Both preservatives have been shown to be effective for stabilizing many pharmaceuticals and personal care products (PPCPs) for 28 days or more under these conditions. All sample containers were provided by the laboratory and sampling was performed with chain-of-custody documentation (Oppenheimer et al., 2011).

#### 3.3. Chemical analysis

The 20 samples were further analyzed in the laboratories of Eaton Eurofins in California in the laboratory according to the method detailed in Oppenheimer et al. (Oppenheimer et al., 2011). It consists of a standard operating procedure using an online SPE coupled with a high performance liquid chromatographic separation with tandem mass spectrometric detection (SPE-HPLC-MS/MS). For extraction, Oasis HLB cartridges (2.1 × 10 mm 25 μ) were used and conditioned with 5 mL acetonitrile and 5 mL HPLC grade water acidified to pH 3 (Oppenheimer et al., 2011). Solid Phase Extraction column (SPE) allows complete extraction with good recoveries from aqueous matrices. The investigated MPs were analyzed in Electropray Ionization (ESI) negative mode where an XBridge-C18 (2.1 × 150 mm 3.5 μm particle size) column (Waters, Milliford, MA) was used for this purpose (Oppenheimer et al., 2011). The seven replicate of daily Minimum Reporting Limits Check – MRL\_CHK, based on 2.5 mL of spiked solution by using an online enrichment and back flush column switching method. The main analyzed MPs include wastewater indicators such as ASWs, lipid regulators, stimulants, analgesics, antibiotics, and anti-oncuvulants and anti-inflammatory drugs. In this work the two ASWs; Sucralose, Acesulfame –K, Gemfibrozil and Iohexol are of major interest for the interpretation. The method quantification limit for SUC, ACE-K, GEM, and IOX were 100 ng/L, 20 ng/L, 5 ng/L, and 10 ng/L respectively, while the relative standard deviation for the compounds is 8.1%, 3%, 3.9%, and 4.5% respectively.

Ca was determined by means of ion chromatography (IC). A Dionex LC 20 with suppressor and conductometric detection, a Dionex CS12A column and a 20 mM methanesulfonic acid eluent at a flow rate of 0.45 mL/min were used for the cations analysis. Additionally, prior to the analysis, 125 μL methanesulfonic acid 99% were added to each of the samples and stirred in a shaker for 2 h. The Cl sensitive electrode was calibrated using three point calibration solutions in the field with a

limit of detection of 1 mg/l).

Stable isotopes were analyzed using the high Temperature Conversion Elemental Analyzer (TC/EA) method for water analysis, with a standard deviation of 0.2‰ for <sup>2</sup>H and <sup>18</sup>O.

### 3.4. Analytical methods

#### 3.4.1. Quantification of the volume of new waters

The volume of new waters and percent of total discharge was estimated using a two- end mixing model (Eq. (1)) based on both Cl and Ca concentrations. It should be noted that the use of Ca underestimates the amount of new waters because of the water-rock interaction, especially in three consecutive events. The mass of Cl originating from waste water in each event is considered negligible given the significant dilution.

$$\int C_n Q_n dt + \int C_b Q_b dt = \int C_m Q_m dt \tag{1}$$

with  $Q_m = Q_n + Q_b$  where  $C$  is concentration of Cl in rainwater ( $C_n$ ), in mixed spring water ( $C_m$ ) and pre- event spring water ( $C_b$ ),  $Q_n$  is newly infiltrated waters,  $Q_b$  is baseflow, and  $Q_m$  is the mixed spring discharge water.

Based on  $Q_n$  and  $Q_b$  calculated above, the total mass of SUC and ACE-K referred to as  $M_{MP}$  was estimated using a three end mixing model as follows (Eq. (2)):

$$\begin{aligned} M_{MP} + \int C_n Q_n dt + \int C_b Q_b dt &= \int C_m Q_m dt \\ C_{MPm} V_m &= C_{MPn} V_n + C_{MPb} V_b + M_{MP} \\ M_{MP} &= C_{MPm} V_m - C_{MPb} (V_m - V_n) \end{aligned} \tag{2}$$

where ( $C_{MP}$ ) is the concentration of the artificial sweetener (ACE-K and SUC) in the volume of mixed spring water ( $V_m$ ), Volume of precipitated newly infiltrated water ( $V_n$ ), and pre event waters ( $V_b$ ).  $M_{MP}$  is the new mass of artificial sweetener introduced to the spring. The concentration of MP in precipitation water is considered nil.

Moreover, a mean transit time ( $t_m$ ; the time between the start of the rain event and the time where 50% of the mass flux had elapsed at the spring) was calculated for each of the four MPs and turbidity in events 1 and 2. The variance of the signals mass fluxes with respect to a mean transit time was estimated using Eq. (3). A low variance is indicative of a higher skewness of the breakthrough curve while a higher variance would imply a longer duration of the compound's breakthrough.

$$\sigma^2 = \frac{(t_i - t_m)^2 \int C_i(t) Q_i(t)}{\int C(t) Q(t) dt} \tag{3}$$

where  $\sigma^2$  is the variance [ $T^2$ ] of the mass flux breakthrough curve with respect to a mean transit time ( $t_m$ : [T]).  $\int C_i(t) Q_i(t)$  is the mass between time  $t_i$  and  $t_{i+1}$  [M],  $\int C(t) Q(t) dt$  is the total mass [M].

The mass flux of the MPs, TU, and Cl were cross correlated to identify the relationship among spring signals using a cross correlation function (CCF; where a good correlation was implied when a correlation coefficient  $R^2$  is between 0.7 and 1 and a lag correlation of 0).

## 4. Results

Concentrations of the four investigated MPs in River water samples

**Table 1**  
Baseline analysis of River water and one waste water sample on the catchment area.

Samples	MRL (ng/l)	Units	NK4-1	Waste water	NK 2-0	NK 1-0	NK4-0	NK 6-0
Sampling date			17:00		6/4/2015	6/3/2015	6/4/2015	6/5/2015
Analysis			25/04/2017	6/16/2015				
Gemfibrozil	5	ng/l	20	3500	15	19	25	10
Iohexal	10	ng/l	0	290	13	13	0	12
Acesulfame-K	20	ng/l	51	210,000	110	67	53	110
Sucralose	100	ng/l	0	760	0	0	0	0

and one waste water sample (Table 1; Doummar and Aoun, 2018) reveals a higher loading of ACE-K in the River (53–110 ng/l) and in waste water (210,000 ng/l) in addition to IOX and GEM found at varying concentrations in River and waste water. Sucralose was not detected in surface water, despite its presence in waste water effluents (760 ng/l).

Following the four monitored precipitation events, four spring responses with varying peak discharges were detected (characteristics of the spring responses in the four events are summarized in Table 2 and Fig. 2). The pre-event flow rate was 0.29 m<sup>3</sup>/s; during the events, the maximum discharge at the spring varied between 2.0 and 11 m<sup>3</sup>/s, with total discharged volumes ranging between 0.3 Mm<sup>3</sup> to 4 Mm<sup>3</sup>. The higher the response time at the spring (with respect to start of rain event), the lower the percentage of newly infiltrated waters, indicating a lower transit time of phreatic or diffuse waters.

Newly infiltrated waters during the three events constituted between 3.0% and 24% from the total discharged volume. In every spring response, a turbidity peak is observed simultaneously with a decrease of Cl concentrations indicating newly infiltrated waters arriving at the spring. In the third event two turbidity peaks can be discerned; a primary peak and a secondary peak attributed to a sinking river (Fig. 2; River flood level exceeds baseline level). Depletion in Deuterium (<sup>2</sup>H) and heavy Oxygen (<sup>18</sup>O) accompanies the first turbidity peaks in all of the events, whereas enrichment in the heavy stable isotopes is observed with the secondary turbidity peak.

Out of the 27 tested MPs, only five were detected in all of the samples (including GEM, IOX, SUC, ACE-K, and the cleaning agent 4-nonylphenol) possibly due to the high dilution effect. It is worth mentioning that substances characterized by a relatively short half-life such as diclofenac and ibuprofen were below detection limits (5 and 10 ng/l respectively).

The four investigated MPs (SUC and ACE-K, GEM and IOX) are found in the pre -event waters at concentrations 120, 78.0, 6.10, and 19.0 ng/l, equivalent to mass fluxes of 0.035 0.023, 0.002, 0.003 (10<sup>-3</sup> g/s) respectively. In the first three events, three different breakthrough of the artificial sweeteners ACE-K, SUC, Gem, and IOX can be observed (Fig. 2). Maximum concentrations of SUC varied in the three events between 290 and 320 ng/l, while that of ACE-K varied between 150 and 200 ng/l. The total mass of ACE-K and SUC arriving at the spring in the three events is shown in Table 2; reaching 316 and 430 g of ACE-K and SUC respectively. Similarly, three distinct breakthrough curves of IOX and GEM can be observed in the spring multi-response (Fig. 2 and Table 2). The major increase of mass flux for GEM and IOX occurs during the third event along with the secondary turbidity peak, while that of the ASWs occurs with the primary turbidity peaks.

In the three events about 10–32 g of SUC and 7–15 g of ACE-K arrived with fast infiltrated waters with the primary turbidity peaks through fast pathways to the spring. During event 3, an additional amount of 37 g of ACE-K was introduced by infiltration from the river, while 0 g of SUC (out of a total of 55 g) arrived to the spring with the secondary turbidity peak.

During the three events, 1.0–24 g of GEM and 0.5–15 g of IOX were estimated at the spring. Not > 1.5 g of IOX and 3.5 g of GEM arrived with the first three primary peaks. The significant load of around 13 g of IOX and GEM coincided with the secondary turbidity peak in the third

**Table 2**

Summary of the spring response to the monitored events in terms of time to response, volumes of rapid newly infiltrated water, total volumes, percent of new volume to total volume, mass loads of SUC, ACE-K, GEM, and IOX in the spring.

	P (mm)	Response lag (t <sub>so</sub> -t <sub>p0</sub> )	Q <sub>max</sub>	V <sub>n1</sub> (Mm <sup>3</sup> )	V <sub>t1</sub> (Mm <sup>3</sup> )	C <sub>max</sub> (ng/l)	C <sub>max</sub> (ng/l)	New Mass (g)	Total Mass (g)	New Mass (g)	Total Mass (g)
		(hours)	(m <sup>3</sup> /s)	% of V <sub>T</sub>		[SUC]; [ACE-K]	[GEM]; [IOX]	SUC; ACE-K	SUC; ACE-K	GEM; IOX	GEM; IOX
Event 1 (E1)	53	12.5	2.05	0.01–3.0%	0.27	300; 180	16; 18	28; 14	58; 34	1.00; 0.46	2.04; 1.95
Event 2 (E2)	33	19.0	2.95	0.01–3.4%	0.29	290; 150	9.5; 12	10; 7.0	70; 40	0.64; 0.00	1.72; 1.08
Event 3 (E3)	29	4.50	10.8	0.36–24%	1.56	320; 200	38; 47	55; 74	302; 242	24.0; 15.0	29.0; 24.0
River (E3)	–	–	7.97	0.1–6.4%	1.56	150; 200	38; 47	0.0; 37	302; 242	13.4; 13.0	29.0; 24.0
Event 4 (E4)	53	6.00	9.80	0.2–5%	4.00	NA	NA	NA	NA	NA	NA

T<sub>p0</sub> = Time since precipitation started.

T<sub>so</sub> = Time of first response.

V<sub>n</sub> = Total volume of newly infiltrated waters.

V<sub>t</sub> = Total volume of water per event.

event.

Concentrations of SUC and ACE-K detected at the springs are not well synchronized in the observed breakthrough curves as shown in (Fig. 2). Moreover, EC and Cl concentrations do not correlate well with the ASWs, GEM, or IOX (Fig. 3). Nevertheless, the breakthrough curves of mass fluxes (Q<sub>i</sub> [C<sub>i</sub>]) of ASWs are very well correlated with primary turbidity peaks in each of the events, except for the secondary turbidity. A maximum correlation between ASWs and TU (R<sup>2</sup> = 0.99 for ACE-K and R<sup>2</sup> = 0.97 for SUC) and ASWs and Cl mass fluxes (SUC R<sup>2</sup> = 0.99 to ACE-K R<sup>2</sup> = 0.97) is observed a time lag = 0; Table 3; Fig. 4). However, the other MPs mass fluxes correlate with those of Cl and TU with a lag time equals to -1 (Table 3; Fig. 4). A negative lag indicates that the predictand precedes the predictor by one lag (equivalent to 4–8 h).

ACE-K and SUC mass fluxes are less correlated with those of GEM while they poorly relate to IOX. Despite a lower ratio of ACE-K to SUC in the waste water sample, the ratio of ACE-K to SUC consumption during the three events on the catchment is 0.77 (Fig. 5), indicating higher loads of SUC with respect to ACE-K and a possible similar origin of both compounds except when the origin is infiltrated surface water. The relationship between of GEM and IOX mass loads at the spring during the different events can be described linearly by GEM = 0.86 [IOX] + 1.19 (R<sup>2</sup> = 0.97; Fig. 5), because IOX can decrease to below detection limits in the spring.

Furthermore a relationship was established between new masses of GEM, IOX, and ACE-K, introduced to the spring and the total mass of each MP calculated in each event (Fig. 6). The latter was less applicable in the case of SUC.

The variance of MPs breakthrough curves with respect to a mean transit time in events 1 and 2 was evaluated (Eq. 3; Fig. 7). As a result, the variance of ACE-K breakthrough curve with respect to a mean transit time is slightly higher (σ<sup>2</sup> = 0.71 and 0.16 h<sup>2</sup>) than that of SUC (σ<sup>2</sup> = 0.68–0.16 h<sup>2</sup>), TU (σ<sup>2</sup> = 0.64–0.15 h<sup>2</sup>), GEM (σ<sup>2</sup> = 0.57–0.09 h<sup>2</sup>), and IOX (σ<sup>2</sup> = 0.31–0.07 h<sup>2</sup>) respectively (Fig. 6). Event 3 was excluded because of the secondary turbidity peak indicating a varying flux of ASWs from the River.

## 5. Discussion

### 5.1. Origin and mass loads of the selected MPs

Both ASWs, as well as GEM are found in the spring during baseline (where no active recharge is occurring), during the events, and post events. This indicates that despite the significant dilution, the three MPs are persistent in the fissured matrix/epikarst at high concentrations (e.g., SUC > 100 ng/l), corresponding to daily loads of 3.0, 2.0 and 0.2 g of SUC, ACE-K, and GEM respectively.

Despite the presence of SUC, GEM, and ACE-K in phreatic waters, the mass of the four investigated MPs increases substantially during the

inflow of fast infiltrated flood waters. In the three events, varying percentages of newly infiltrated water (between 3.0% and 24% from the total volume discharged) were accompanied by varying mass loads of MPs. In the first and second events, the fast flow pathways were saturated with highly mineralized pre-event water that gets flushed away in the spring's first and second responses. The latter can explain the relatively low percentage of new water reaching the spring in the first two events. As fast flow pathways become less saturated with stored water, a higher volume of flood water is able to infiltrate through sinkholes and dolines to reach the spring in the third event. The depletion in stable isotopes (e.g., deuterium) observed with every spring response confirms that the origin of the fast flow is located on the dolines' plateau on the highlands of the catchment between 1200 and 1500 m. In the third event, a significant enrichment in deuterium and heavy oxygen observed during the secondary turbidity peak, implies an infiltration of additional new waters from a lower recharge area on the catchment (800 m) corresponding to the river input via the sinking stream. The correlation of turbidity and breakthrough of MPs allows the identification of the waste water origin (hospital and domestic) and the mode of infiltration (River versus dolines). While SUC is arriving mostly through dolines, important mass loads of ACE-K, GEM, and IOX are also infiltrating along with surface water from a karst sinking stream along the Kalb River. The absence of SUC in the sinking stream is due either to its absence in the wastewater effluent in the river, to SUC concentration falling below its relatively high detection limits in river water (100 ng/l), or to mineralization of SUC in soils or river sediments (Labare and Alexander, 1993). It is worth mentioning that sucralose was found in the waste water effluent on the catchment area (Table 1) and in spring water (Table 2), indicating its high consumption on the catchment area. Therefore, its presence in river samples infiltrating to the spring cannot be completely ruled out. On the one hand, it has been reported that SUC is characterized by a lower likelihood for detection (Kokotou and Thomaidis, 2013; Subedi and Kannan, 2014) especially in sludge material typical of non-treated wastewater. Despite that fact, Oppenheimer et al. (2011) considered SUC as a very suitable wastewater indicator in septic tanks, but suggested the evaluation of SUC transport under natural conditions.

Additionally, the added ASWs' mass loads/event through direct rain infiltration (except for the infiltrated surface water) correlate linearly indicating that they have the same origin, infiltrating from point source waste water (with a definite ratio of SUC to ACE-K), and a rapid infiltration to the saturated zone. In all of the events, the persistence of ASWs, more specifically ACE-K in the phreatic zone, could also originate from slow continuous infiltration from the river into groundwater through bank filtrates, which is enhanced during high flow periods (Engelhardt et al., 2013). The correlation between mass fluxes of GEM and IOX may indicate a similar origin for the two MPs as well.

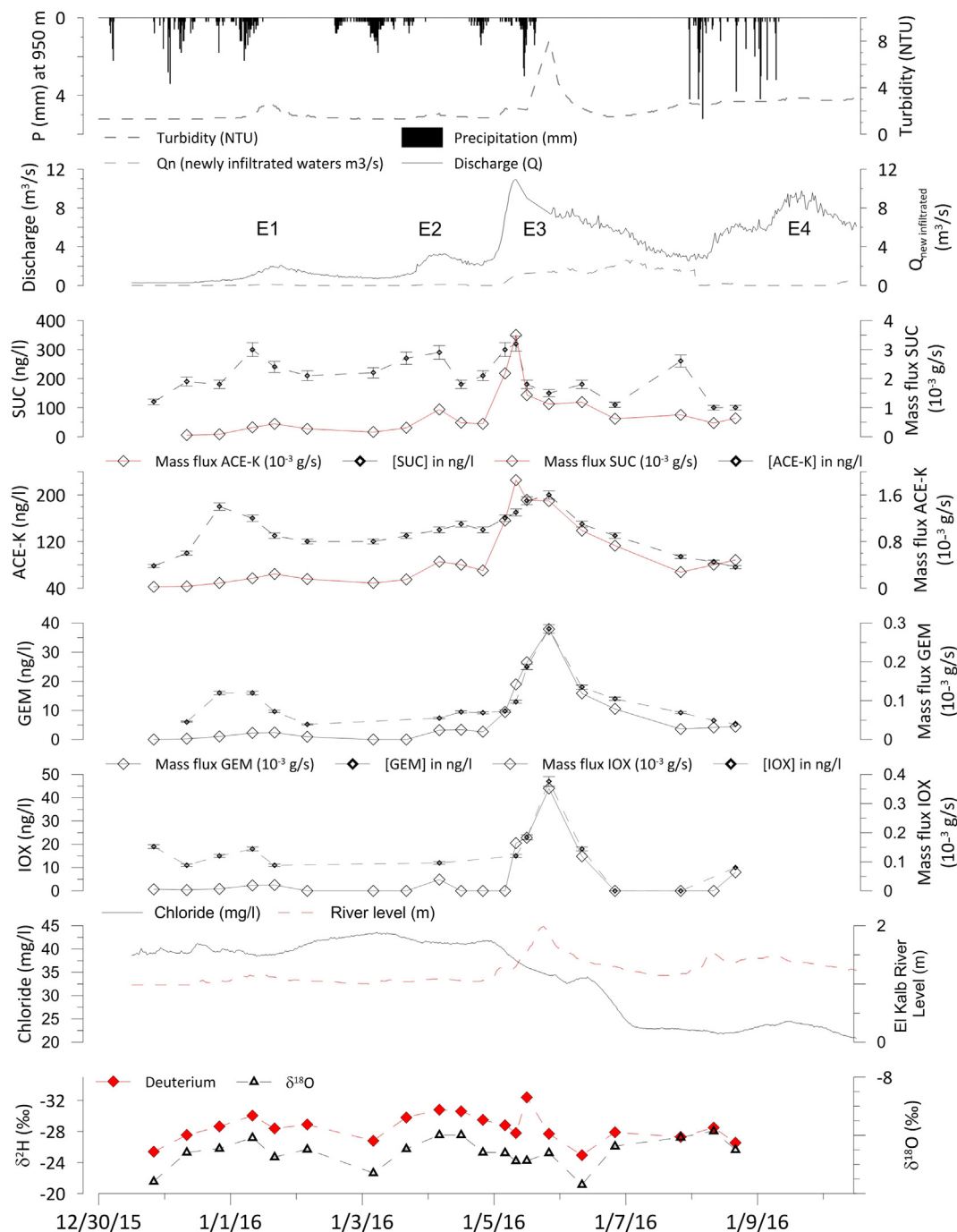


Fig. 2. “Chemograph showing the variation of physico-chemical parameters and concentrations and mass fluxes of investigated micropollutants as a response to three consecutive precipitation events (E1 to E3; 15-min precipitation data). E1 to E4 refer to the four consecutive occurring events”.

5.2. Correlation of MPs and in-situ parameters measured at the spring

Since the ASWs' mass fluxes and those of Cl correlate to a high extent, Cl (corrected for flow rate) could allow the quantification of the mass flux/concentrations of the two ASWs at the spring. Cl mass and TU fluxes correlate less with GEM and almost at no time with IOX; indicating a less conservative behavior of IOX with respect to the three other MPs. The short-term breakthrough of the contrast media is most probably related to sporadic point source hospital effluents and its limited release on the catchment.

The comparison of the normalized breakthrough curves with respect to peak concentration and transit time) for the first two events show that the breakthrough of turbidity, ACE-K, SUC, and GEM are well

synchronized. The slightly higher variance of ACE-K breakthrough curve with respect to that of SUC and turbidity could be reflective of a longer duration of breakthrough, potentially attributed to varying transport processes (e.g, dispersion). Moreover even if not detectable in the chemograph or hydrograph, an additional input of mass flux from a point source contamination such as the River (in the case of ACE-K) could also explain the tailing effect observed in events 1 and 2. Studies have shown that ACE-K showed no retardation in porous aquifers with respect to Carbamazepine (Stempvoort et al., 2013) or in karst aquifers with respect to another ASW such as Cyclamate and Sodium fluorescein (Hillebrand et al., 2015). However, a higher sorption to suspended particulate matter of ACE-K was observed by Subedi and Kannan (2014). Nevertheless, since the breakthrough curve is resulting from

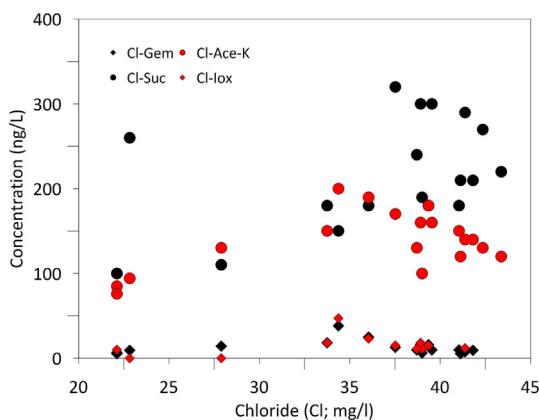


Fig. 3. Correlation between concentrations of the four MPs (ACE–K, SUC, GEM, IOX) and Chloride showing that the breakthrough of the four MPs is not simultaneous at the spring at all times.

Table 3

Maximum cross correlation coefficient between the various spring signals (mass fluxes) obtained for correlation lag times between predictand and predictor. One positive lag indicates that the predictand lags the predictor by one lag.

	Predictor (mass fluxes; CQ)						
		GEM	IOX	SUC	ACE-K	TU	Cl
Predictand (mass fluxes; CQ)	GEM	1	0.92 (0)	0.96 (1)	0.96 (1)	0.95 (1)	0.95 (1)
	IOX	0.92 (0) <sup>a</sup>	1	0.92 (1)	0.91 (1)	0.92 (1)	0.89 (1)
	SUC	0.96 (–1)	0.92 (–1)	1	0.94 (0)	0.97 (0)	0.97 (0)
	ACE-K	0.96 (–1)	0.91 (–1)	0.94 (0)	1	0.99 (0)	0.99 (0)
	TU	0.95 (–1)	0.92 (–1)	0.97 (0)	0.99 (0)	1	0.99 (0)
	Cl	0.95 (–1)	0.89 (–1)	0.97 (0)	0.99 (0)	0.99 (0)	1

<sup>a</sup> Coefficient of correlation  $R^2$  (lag time between predict and predictor for a maximum  $R^2$ ).

convolved multiple peaks of ASWs' mass fluxes, transport parameters such as dispersion cannot be calculated for each of the MPs.

IOX appears to be poorly synchronized with the Cl mass and turbidity fluxes, therefore TU and Cl could be considered less associated with the breakthrough of the contrast media, especially with the observed lag time. Finally, the secondary turbidity peak originating from

the river input coincided solely with a breakthrough of ACE-K, GEM and IOX, showing that SUC is a poor indicator of infiltrated river water in this case.

### 5.3. Suitability of the MPs as waste water indicators

A suitable waste water indicator is characterized by 1) its persistence against degradation and decay in an aquifer system and in treatment plants, 2) its common usage for specific purposes, and 3) its occurrence above detection limits (Clara et al., 2009). Based on spring baseline concentrations, ACE-K, GEM and SUC are persistent in the aquifer during baseflow and during the events. Moreover, this study reveals that ACE-K can be considered a good domestic waste water indicator in the natural environment, because its breakthrough is concordant with all the turbidity signals and the arrival of infiltrating waste water into the spring from both surface water and fast infiltration pathways after a precipitation event. For the same reasons, SUC appears also to be a suitable waste water indicator except for surface water effluents due to its high detection limits. Additionally, GEM appears to be a suitable waste water indicator, especially for transport of river water into groundwater in this particular case. Finally, the breakthrough of IOX is relatively short at the spring with respect to the other investigated MPs, indicating a rather limited release in waste water. Therefore it can be regarded as an indicator of hospital effluents for short term breakthrough events.

On the other hand, ACE-K and SUC correlate very well with Cl mass and TU fluxes, therefore, the combination of easily monitored parameters at the spring such as Cl and TU can be used to predict concentrations and duration of breakthrough of these ASWs as waste water indicators, which is essential for contamination management purposes. Mass fluxes of GEM and IOX correlate less with Cl and TU, thus these two parameters cannot fully portray the breakthrough of the lipid regulator and contrast media as domestic or hospital waste water indicators.

## 6. Conclusions

In this work, the concentrations of the two artificial sweeteners (SUC and ACE-K) along with a contrast media (IOX), and lipid regulator (GEM) were monitored following three consecutive rain events. Most of the investigated MPs are persistent in the matrix during low flow periods. They are further introduced with infiltrated flood waters through fast flow pathways e.g., dolines, which explain the observed peaks of MPs despite the relative high dilution. An additional secondary peak of GEM, IOX, and ACE-K was observed in the third event, indicating rapid infiltration of waste water from contaminated River water. Given that a suitable waste water indicator is defined by its persistence in

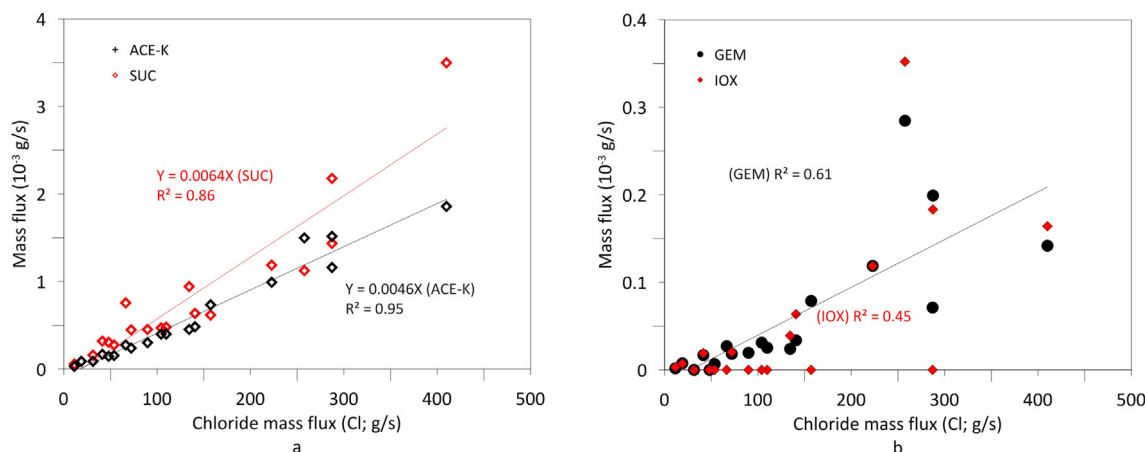


Fig. 4. Correlation between mass fluxes of Chloride and mass fluxes of a) SUC and ACE-K and b) IOX and GEM in each of the three events.

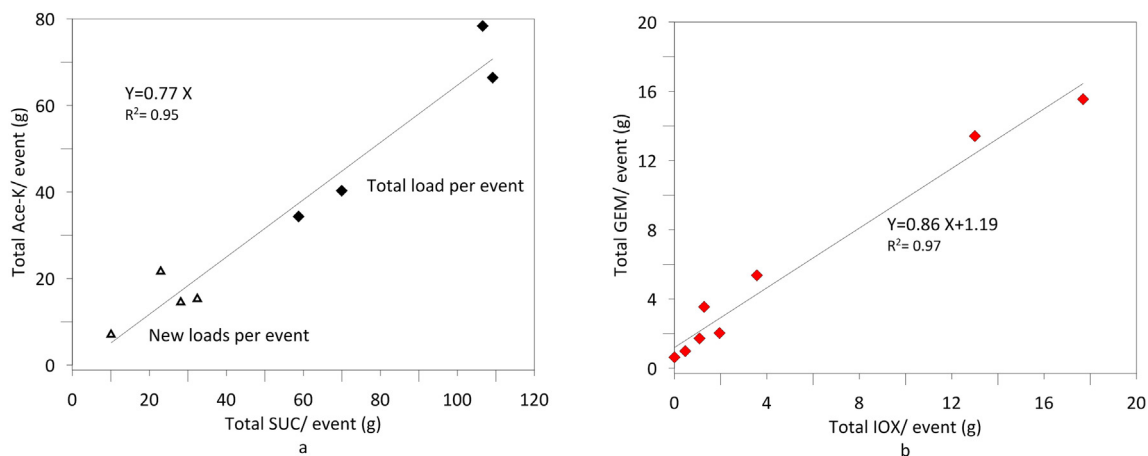


Fig. 5. A linear correlation between total and additional mass loads of a) SUC and ACE-K retrieved during the three monitored events showing that the ratio of ACE-K to SUC loads in waste water is around 0.77. b) A linear correlation between total and additional mass loads of GEM and IOX, showing that the ratio between masses of GEM to IOX is 0.86.

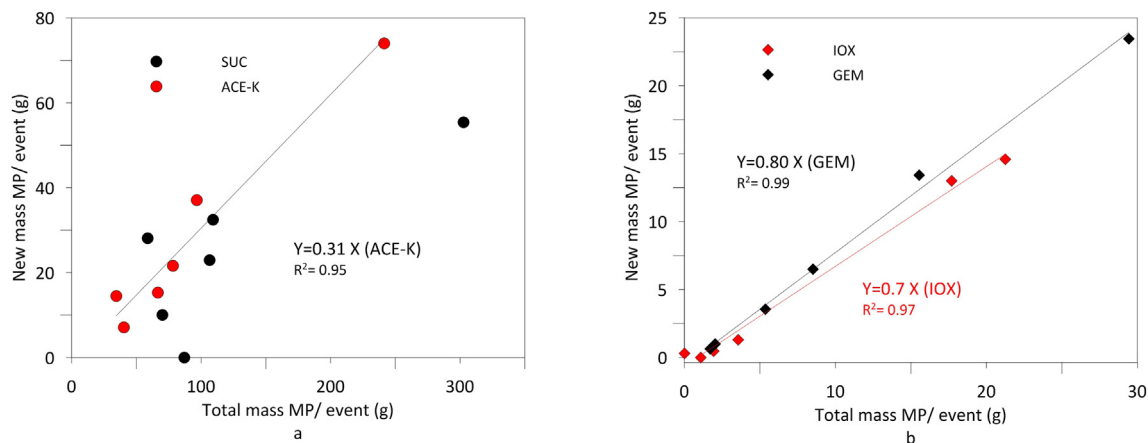


Fig. 6. Correlation between total mass and newly introduced masses of each of the investigated MP per event showing a relationship between the new masses arriving through fast flow pathways and total masses calculated at the spring.

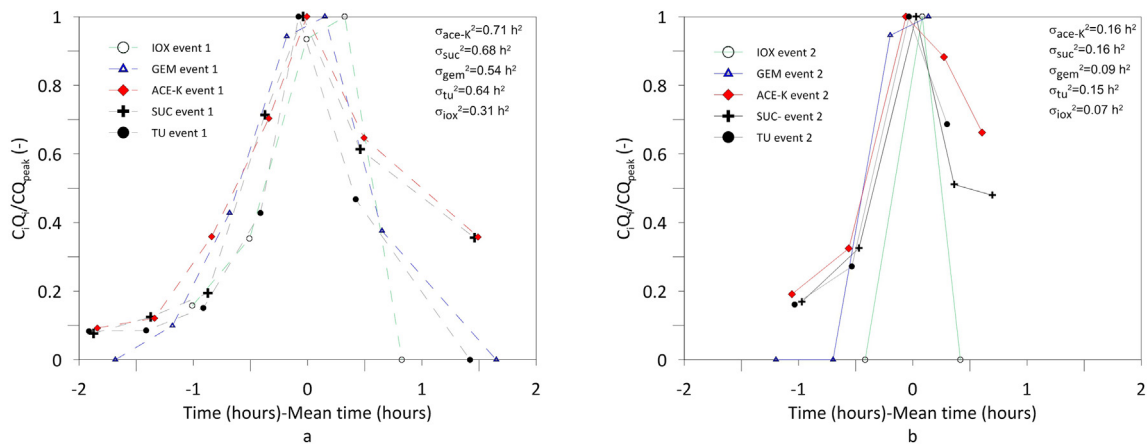


Fig. 7. Comparison of the shape of normalized turbidity and MPs' mass flux  $C_iQ_i$  (with respect to peak mass flux  $(CQ)_{max}$ ) as a function of normalized time (with respect to transit time;  $t_i-t_m$ ) for the evaluation of the duration of MPs' retrieval at the spring for event 1 (a) and 2 (b).

groundwater storage and its particular origin (such as hospital waste for IOX); therefore, the four MPs ACE-K, SUC, GEM, and to a lesser extent IOX can be envisaged as indicators of waste water originating from various sources (autochthonous versus allochthonous sources). However SUC breakthrough curve fails to reflect the infiltration of contaminated river water into the spring, either because SUC falls

below the detection limits or because of its controversial absence in surface water samples. Additionally, a good waste water indicator is characterized by a high likelihood of detection because of its predominant usage on the catchment or high resolution of detection. The analytical limits of each of GEM, ACE-K, and IOX are below 10.0 ng/l, while that of SUC is 100 ng/l, thus decreasing its likelihood of detection

unless present at relatively high concentrations (high mass fluxes). Nevertheless, SUC is to become a promising indicator for fast infiltrated groundwater given its increasing usage on the GW catchment area over other artificial sweeteners.

The MPs slightly varying transport behaviors, consumption loads, and potential origin, are reflected in their breakthrough's concentrations (peak concentrations) and duration at the spring. The mass flux of TU and Cl are strongly correlated with those of the two ASWs and to a lesser extent with GEM, while IOX appear to be less reliable because of its sporadic and short breakthrough. Additionally this correlation between ASWs and parameters that are easily measured in-situ at the spring can be used to predict the breakthrough of SUC and ACE-K as waste water indicators and thus be reflective of the specific variable spring vulnerability. Finally, a long term monitoring of these selected MPs and parameters such as Chloride, Turbidity, or bacteriological contamination can help validate the results under varying flow periods.

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