Integrative Passive Samplers to Detect Chlorinated

Hydrocarbon Contamination in Karst

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Abstract

A large number of former industrial sites and landfills are responsible for aquifer contamination with chlorinated solvents in Switzerland. 16.7 % of them are located in karstic areas. But, the detection of such contaminations in springs or boreholes can be difficult because concentrations are often varying highly and rapidly. Measuring low concentrations during a few measurement campaigns is not sufficient to prove the absence of contamination. To overcome this difficulty, the performances of integrative passive samplers were investigated in the framework of the Chlorokarst project funded by the Swiss Federal Office for the Environment. Three types of devices were tested. They allow measuring time-weighted average concentrations of pollutants over long periods. Experiments in karst springs show that the Sorbicell samplers developed by the Sorbisense company were capable of measuring average concentrations over a 2-month period, matching the averages of the concentrations measured in daily snapshot samples collected with an automatic sampler taken as reference. Equipment of the springs with the Sorbicell devices was found to be easy. More difficulties were encountered when exposing the Sorbicell samplers in piezometers, because of the impact of the high fluctuations of the water column above the sampler on the filling rate. Adaptation of the device was thus carried out with the manufacturer, to reduce the effect of the water column, using air-vents and cartridges of high resistance. Satisfactory results were then obtained in terms of sampling rate. Uncertainty still remains on the estimated concentrations provided by the system since they can vary by a factor of two depending on how the volume of water that passed through the cartridge is estimated. Two other types of passive samplers were tested, the ceramic dosimeters developed at the University of Tübingen and commercialized by IMW, and the Tips developed by the AGI company. They were both found to be inappropriate to estimate reasonably well the mean concentrations in chlorinated solvents in these types of environment, even if they can still be used to detect the presence of contamination.

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23.1 Introduction

Contaminated sites resulting from former industrial and urban activities are responsible of soil, air, and water chemical contaminations that may endanger human beings and ecosystems. In Switzerland, a large number of registered polluted sites are located in karstic areas, most of them in the Jurassic Arc, which is not surprising, given that karst covers 24.5 % of the total surface of the country (ISSKA 2012). Contamination with chlorinated solvents is also a specificity of Switzerland, due to the watchmaking and microtechnology industries. As a consequence, 26,502 sites are suspected to be contaminated with chlorinated solvents, 16.7 % of which implemented in karstic regions (Bapst et al. 2012).

The particular flow conditions in karstic aquifers and the specific chemical properties of chlorinated hydrocarbons (CHCs) make difficult both characterization and assessment of the impact of these contaminated sites on groundwater. The standard procedure, consisting of collecting snapshot samples downstream of the polluted sites for laboratory analyses, may be inefficient, because of high fluctuations of contaminant levels in karstic aquifers. Automatic water samplers allow to sample water at regular intervals over a long period, but the cost of repeated laboratory analyses may be prohibitive. Development of in situ monitoring techniques of volatile organic compounds in groundwater has been attempted, but without any operational and commercialized device up to now (Patterson et al. 1999, 2000).

Integrative passive samplers have been developed since the beginnings of the 2000s, to measure averaged contamination levels in water over long periods, without any energy source (no pumping) (Vrana et al. 2005; Rollin 2011a, b, c). They are expected to be able to detect the sporadic inputs of chemicals in springs and piezometers in karstic aquifers, since they continuously accumulate the compounds over the exposure time.

The performances of three commercialized integrative passive samplers were tested for the purpose of the Chlorokarst project, funded by the Swiss Federal Office for the Environment (FOEN). Started in 2014, Chlorokarst involves 2 consulting companies, eOde and MFR, and the Centre d'Hydrogéologie et de Géothermie of the University of Neuchâtel. The project includes experimental works on various tools and techniques selected for their potential interest to characterize site contamination in karst, as well as methodological works to define a tailored approach for assessing contaminated sites in the current Swiss regulatory context.

The goals of the experiments on the passive samplers were (1) to check the validity of the concentrations they measure, comparing them to reference concentrations measured with a standard sampling and analytical procedure, and (2) to test their suitability and resistance to the specific conditions encountered in the springs and boreholes located in karst.

23.2 Materials and Methods

23.2.1 Springs and Piezometers Tested in the Jurassic Arc

The passive samplers were tested in 2 karstic springs and 3 piezometers in the Jurassic Arc. The Betteraz spring is the main outlet of the catchment basin of the Malm regional aquifer, northeast of Porrentruy in the Canton of Jura. The watershed includes old landfills and industrial sites that may have released chlorinated solvents in soil. Perchloroethylene (PER) and trichloroethylene (TRI) are found in the spring since the 1980s. Concentrations ranged from 1 to 15 μ g/L for PER and 0.06 to 9 μ g/L for TRI, during the two main exposure periods of the integrative passive samplers, in 2014 and 2015 (**□**Fig. 23.1). This spring was selected because of numerous data collected since decades on contamination, redox conditions and water discharge, and for the facility to equip it with measuring instruments.

The Reconvilier spring is located 20 km north of Bienne, in the Canton of Bern, a few ten meters downstream from an old landfill responsible of groundwater contamination in CHCs, especially in PER. The spring is an outlet of fractured sandstones whose water catchment includes the landfill. The response of the passive samplers to higher concentrations in CHCs than in the Betteraz spring could be tested with this spring.

Piezometers located close to pollution sources of former industrial sites and landfills in the Betteraz catchment basin were equipped with passive samplers. Boreholes are 10–40 m depth, with groundwater columns ranging from 0.5 to 13.5 m above the passive samplers (placed in the screen area of the boreholes). Groundwater is highly contaminated, including several tens of thousands μ g/L of halogenated volatile organic compounds. Note that despite that only PER and TRI levels are shown in the followings, various other chlorinated compounds were quantified with the passive samplers; they lead to the same conclusions than those deduced from the PER and TRI levels.

23.2.2 Integrative Passive Samplers

Three types of passive samplers were selected (Sorbicell, ceramic dosimeter, and Tips) because of their ability to be immersed over long periods, and their commercial availability (easy access to practitioners).



(a) From 17 July to 17 September 2014

Fig. 23.1 Variations of PER and TRI concentrations in the Betteraz spring over the 2 main exposure periods of the integrative passive samplers

The Sorbicell sampler (DFig. 23.2) consists of a reservoir that contains one or two cartridges permeable to water (De Jonge and Rothenberg 2005; Rozemeijer et al. 2010). The porous material constitutive of the cartridges adsorbs the solutes when the water passes through the cartridges (advective flow). The cartridges contain also a tracer compound (salt: calcium citrate) that is released progressively over the exposure period, depending on the flow rate. The volume of water that passes through the cartridges can thus be deduced from the quantification of tracer loss in the laboratory, or be directly measured in the field, since water is accumulating in the reservoir. The ratio of the total mass of adsorbed solutes and the volume of water provides an estimate of the average concentration of adsorbed solutes during the entire sampling period. Filling rate of the reservoir is mainly governed by the resistance of the cartridge material to the water flow, and the hydrostatic pressure gradient of the water column above the Sorbicell and the interior pressure (atmospheric) inside the reservoir. The higher the water column above the sampler, the higher the filling velocity.

Various cartridges are commercialized by the manufacturer, to measure either organic or inorganic com-



Fig. 23.2 Pictures of the constitutive elements of a Sorbicell sampler. **a** *White* GWS40 reservoir, **b** *Black* WW50 reservoir, and **c** details on the cartridges, plugs, air-vent, and insertion holes

pounds. Sorbicell VOC samplers of different resistances (VOC101, VOC102, and VOC103) provided by Sorbisense were tested. Two types of reservoirs were also experimented: The black WW50 designed for surface water and only one cartridge were used in the springs, whereas the white GWS40 designed for groundwater and two cartridges were tested in the boreholes (note that a dedicated plug may be used to close the insertion hole when only one cartridge is exposed in a GWS40 reservoir).

The ceramic dosimeter (**F**ig. 23.3) is made of a ceramic tube operating as diffusion-limiting barrier, filled with a sorbent showing a high affinity with the solutes to be detected (Weiss et al. 2007; Bopp et al. 2005; Martin et al. 2003; Cristale et al. 2013). The contaminants accumulate by diffusing from the contact water through the ceramic membrane into the adsorbent bed. The contaminants accumulate linearly with time, depending on the concentration gradient and the masse transfer diffusion across the ceramic membrane. Solutes can be accumulated continuously if the diffusion gradient is maintained

over extended periods. Time-weighted average contaminant concentrations can thus be deduced from Fisk's first law. Ceramic dosimeters provided by IMW Innovative Messtechnik Dr. Weiss were used.

The Tips¹ passive sampler is also composed of a semipermeable membrane and a sorbent with a strong affinity to the contaminants, with a sampling rate governed by the diffusion flux through the membrane (Hodny et al. 2009). The membrane is flexible, unlike the ceramic tube of the dosimeters. Tips samplers were provided by Amplified Geochemical Imaging.

23.2.3 Field Experiments

A first series of tests was carried out in the Betteraz spring between July and April 2015, to test the capacities of the samplers and to compare their performance.

¹ Exact commercial reference: SPG0008 (Tips 7).



Fig. 23.3 Pictures of **a** a ceramic dosimeter (Bopp et al. 2005) and **b** a Tips sampler

Multiple exemplars of the 3 types of samplers were placed in the spring at the same date. Duplicates of each of the 3 types were removed at regular intervals (after 2 weeks and then every month), up to a 6.5-month exposure period. An automatic water sampler specific to CHC contamination (ISCO 6100 volatile organic sampler) was installed over the entire period, to collect one grab sample every 24 h or 36 h. Water level, temperature, conductivity, turbidity, and organic matter content were also continuously monitored.

A second series was performed in the Reconvilier spring in autumn 2014. The same protocol was applied to the samplers, removing duplicates of the 3 types after 2 weeks, 1 month, and 2 months. Standard snapshot water samples were collected by pumping, at each time passive samplers were removed, so that a time series of 4 punctual sample analyses was available in the end.

A third series occurred in the second half of 2015. Duplicates of Sorbicell samplers were exposed for 2 months in various piezometers located in contaminated sites of the Betteraz catchment area. These tests occurred after unsuccessful attempts that led to adapt the passive sampler equipment to the characteristics of the boreholes (cartridges of higher resistance and use of air-vents). Furthermore, one Tips was immersed in every borehole during the same exposure time. No snapshot samples were collected during the exposure period, because the validity of the results provided by the samplers was already checked by the two first series of tests. Analytical results of previous and later sampling campaigns provided by the Jura Canton were nevertheless used as indicative CHC concentration levels.

23.2.4 Laboratory Analyses

CHCs adsorbed in the passive samplers were analyzed in the laboratories usually employed by the manufacturing companies: Danish Eurofins laboratory for the Sorbicell samplers, University of Tübingen for the ceramic dosimeters, and Amplified Geochemical Imaging (AGI) itself for the Tips. Laboratories provide both the desorbed mass of chemical in μ g and the concentration of chemical in μ g/L.

The punctual water samples collected with the automatic sampler in the Betteraz spring were analyzed in the laboratory of the Centre d'Hydrogéologie et de Géothermie (CHYN) at the University of Neuchâtel.

The punctual water samples collected in the Reconvilier were analyzed (duplicates) by both the CHYN laboratory and the private Swiss Wessling laboratory.

CHCs were analyzed using a GC-MS² technique in the Eurofins, AGI, and CHYN laboratories. AGI follows a modified version of the US EPA 8260C method, including a thermal desorption of the pollutants from the adsorbent constitutive of the Tips. CHCs were extracted from the dosimeters using acetone by the University of Tübingen. CHCs were extracted from the Sorbicell by organic solvents through DANAK accredited method M 0337, by the Eurofins laboratory.

The Wessling laboratory applied the OFEV E-8 protocol of the Swiss federal guideline on the analytic methods

2 Gas chromatography-mass spectrometry.

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Table 23.1 Accumulated masses of PER and TRI by the integrative passive samplers as a function of the exposure duration in the Betteraz spring—from July 17 to November 26, 2014

Type of sampler	ype of sampler 2 weeks		1 month 2 months		4 months	
Tips						
PER	8.88 (0.30)	11.96 (0.20)	14.17 (0.10)	62.09 (0.18)	82.10 (<i>0.57</i>)	
TRI	2.25 (0.15)	4.36 (0.06)	7.08 (0.14)	7.85 (0.06)	7.11 (0.03)	
Sorbicell VOC101						
PER	1.25 (<i>0.35</i>)	1.1 (1.41)	2 (0.28)	-	-	
TRI	0.56 (0.21)	0.39 (0.48)	0.57 (0.08)	-	-	
Volume	358 (0.7)	305 (<i>77</i>)	287 (95)	-	-	

PER, Mass of perchloroethylene in µg; *TRI*, Mass of trichloroethylene in µg; *Volume*, Volume of water passed through the Sorbicell cartridge in mL, deduced from salt dissolution. Average values measured in duplicate (standard deviation in brackets)

for contaminated sites and wastes, using a FID-ECD³ or MS^4 technique (OFEV 2013).

23.3 Results and Discussion

23.3.1 Getting a 2-Month Exposure Period in Springs

A 2- or 3-month exposure period is targeted to integrate seasonal fluctuations of contaminant release observed in karst. Accumulation of CHCs by the 3 types of passive samplers was then measured over increasing exposure periods in the Betteraz spring, between July 17 and November 26, 2014. Results (Table 23.1) show that PER and TRI are progressively adsorbed in the Tips samplers, reaching a sill between 2 and 4 months. CHC accumulation was also observed in the Sorbicell samplers, but water flux was stopped, and thus pollutant adsorption, as soon as 2 weeks after immersion (volume of water recovered in the reservoirs or deduced from the dissolution of salt is indeed stable, around 300 mL, whatever the exposure period between 2 weeks and 2 months). The incoming flow was believed to be too fast, due to the low resistance of the samplers (VOC101 type) and the height of the water column above them $(\sim 1 \text{ m})$.

Complementary experiments were then conducted during a second period between February 6 and April 6, 2015, exposing Sorbicell samplers of low and median resistance, either at 0.5 m depth or just below the water

4 Mass spectrometry.

surface. The tests indicate that cartridges of medium resistance (VOC102) immersed at a depth of 0.5 m favor a progressive accumulation of PER and TRI in the Betteraz spring over the targeted period of 2 months (**Table 23.2**). Note that the low levels of accumulated masses are consistent with the concentration evolution observed during that period, with a strong decrease between February and April 2015.

Finally, ceramic dosimeters were not found to be suitable to the purposes of the Chlorokarst project: The quantification limits of the CHC compounds, which decrease with the exposure duration, remain high, even after a 4-month period; they do not allow quantification of low mass levels such as those found in the karstic Betteraz spring, and more generally in the karstic springs.

Table 23.2 Optimized conditions for progressively accumulating PER and TRI over a 2-month exposure period with the Sorbicell samplers in the Betteraz spring: cartridge of medium resistance (VOC102) and 0.5-m-depth immersion—tested from February 6 to April 6, 2015

Sampling conditions	2 weeks	1 month	2 months			
Sorbicell VOC102—0.5 m depth						
PER	1	2.1	1.6			
TRI	0.39	0.71	0.46			
Volume	164	240	296			

PER, Mass of perchloroethylene in μ g; TRI, Mass of trichloroethylene in μ g; Volume, Volume of water passed through the Sorbicell cartridge in mL

³ Flame ionization detector–electron capture detector.

Spring	Period	Duration	Sampler	PER	TRI
Betteraz	17.07-17.09	2 months	ISCO 6100	7.58	3.28
			Sorbicell VOC101	7.54 (3.48)	2.05 (0.38)
			Tips	0.76 (0.00)	0.52 (0.01)
	17.07–26.11	4 months	ISCO 6100	10.75	3.83
			Tips	5.09 (0.16)	2.93 (0.01)
Reconvilier	04.09–27.10	21/2 months	Snapshot	29.25	0.65
			Sorbicell VOC102	29.77 (9.66)	1.12 (<i>0.29</i>)

2014 experiments *PER*, Concentration of perchloroethylene in μ g/L; *TRI*, Concentration of trichloroethylene in μ g/L. Average values measured in duplicate in passive samplers (standard deviation in brackets), in daily snapshot samples using the ISCO 6100 automatic sampler, in 4 snapshot samples in the Reconvilier spring

23.3.2 Validity of the Passive Sampler CHCs Concentrations

Validity of the time-averaged CHC concentrations provided by the passive samplers was estimated by comparing them to the mean of the daily concentrations analyzed in the samples collected by the ISCO 6100 automatic sampler, over the period July 17-November 26, 2014, in the Betteraz spring. In the Reconvilier spring, concentrations of snapshot samples collected at each of the 4 control visits over the period September 4-November 26, 2014, were averaged and compared to the passive sampler concentrations (Table 23.3). Averaged daily concentrations provided by the automatic sampler in the Betteraz spring are obviously more representative of the mean concentrations, than the average obtained from only 4 grab samples in the Reconvilier spring. It should also be noted that high demand is placed on the passive samplers in that project, since the concentrations levels they should measure are very low. Taken these reserves, Tips samplers are found to measure the same order of magnitude of PER and TRI concentrations in the Betteraz spring after a 4-month exposure period; but they fail to find the concentration levels after a shorter period of 2 months. The Sorbicell samplers provide a good prediction of the time-averaged concentrations after a 2-month or 2 1/2-month period, either in the Betteraz spring or in the Reconvilier spring showing higher PER concentrations.

The Tips samplers show nevertheless a better reproducibility than the Sorbicell measurements, since the standard deviations provided by the duplicates are lower with the first samplers. Despite this drawback, the Sorbicell samplers were found to fulfill most of the requirements for monitoring the karstic springs, unlike the other samplers. The Sorbicell samplers were kept for the need of the Chlorokarst project, because they allow to quantify the concentration levels over a 2-month period, provided an adequate equipment and immersion height. The Tips samplers were kept as sentinels able to detect the presence of CHCs, in the form of pollutant masses, but unable to provide a satisfactory quantification of concentration levels in their current state of development.

23.3.3 Equipment of Piezometers in Karst

The suitability of the Sorbicell samplers was demonstrated for the springs, but not for the piezometers, which implies another type of reservoir recovering the water passing through the cartridges, as well as other water flow conditions. The first trials of exposing Sorbicell samplers in piezometers were unsuccessful. Duplicates of VOC102 cartridges were placed in GWS40 reservoirs in 13 boreholes of height varying from 10 to 80 m, under water columns of 1-3.5 m depth. The first check made after 1 exposure month revealed that most of the reservoirs were full, with some of the plugs and cartridges ejected from their insertion hole. These issues were thought to come either from a too rapid water flux in the cartridges or from bypassed water entry in the reservoirs, due to an imperfect sealing around the insertion holes. The second hypothesis of bypassed water in the reservoirs could be rejected, after laboratory experiments showing that nearly no water was filling the reservoirs when insertion holes were closed only with the plugs (no cartridges). It was thus tried to reduce the water velocity by using cartridges of higher resistance (VOC103) and air-vents. The air-vents consist of HDPE tubes (a few dm length) fitted with a metal air-valve to allow air exit, but no intrusion of water. They are connected to the reservoirs in order to reduce the pressure gradient at a fixed level, and thus reducing the flow rate of groundwater passing through the cartridges. Moreover, the immersion depth of the samplers was reduced.

Experiments were then repeated in 3 of the 13 piezometers, where the immersion depth of the samplers was ranging from from 0.5 to 3.35 m (Table 23.4). The results show that the reservoirs are progressively filled over a period of ~2 months, without any saturation, allowing the continuous adsorption of the chemicals in the cartridges. The lower depths, the use of VOC103 cartridges, and air-vents appear thus to reduce the flow velocity to an appropriate level. However, a supplementary problem emerges: The volume of water measured in the field in the reservoirs differs significantly from the amount deduced from the salt dissolution in the laboratory, creating a big discrepancy between the 2 related estimated pollutant concentrations. As an example, the volume of water recovered during a 7-week exposure period (23.10.2016-13.12.2015) is estimated to 182 mL from the analysis of the salt tracer in the E19 C piezometer, whereas the direct field measurement provided 345 mL. As a result, the PER and TRI concentrations are about twice when the volumes deduced from salt dissolution are used to compute the concentrations (respectively

420 and 15000 μ g/L with the "salt" volume, 220 and 7971 μ g/L with the "field" volume). Note that the concentrations deduced from the "field" volumes are closer to the concentrations measured in snapshot samples collected at dates close to the exposure period (240 and 390 μ g/L of PER, 4700 and 5000 μ g/L of TRI).

It is found that the volumes measured in the field are systematically higher than those deduced from the salt dissolution. The same trend was observed in the Betteraz spring with 10 WW50 reservoirs and VOC102 cartridges exposed during a 2-month period without or without airvents, in a complementary series of tests: The difference of estimated volumes was higher with air-vents, systematically with higher values for volumes measured in the field.

No clear explanation is currently found to explain these differences. As already discussed, infiltration of water outside the cartridge was first thought to be responsible of the higher volumes measured directly in the field. But the laboratory experiment conducted with the GWS40 reservoirs in a water column tends to put aside this hypothesis. Another explanation could be searched in the chemical composition of water; it cannot be excluded that salt interacts with the solutes of water, or that the redox conditions impact the dissolution rate of the salt. High levels of calcium may indeed be found in karst systems, which can reduce the solubility of the tracer salt, made of calcium citrate.

Table 23.4 Sorbicell concentrations and snapshot samples concentrations of PER and TRI in 3 piezometers of the Betteraz catchment area

Borehole	Period	Duration	Sorbicell depth	Volume of water		PER	TRI
E19 C—10 m	23.10.15- 13.12.16	7 weeks	3.35 m	Labo Field	182 mL 345 mL	420 (<i>57</i>) 220 (<i>33</i>)	15,000 (<i>1414</i>) 7971 (<i>615</i>)
Snapshot	28.07.15					240	4700
	18.01.16					390	5000
F2 M—35 m	23.11.15– 05.01.16	6 weeks	0.5–1 m	Labo Field	<50 mL 120 mL	> 41,000 (4243) 17083 (1768)	>92,000 (2828) 38,334 (1179)
Snapshot	29.10.14					12000	56,000
F3 M—36 m	23.10.15– 05.01.16	10 weeks	0.5 m	Labo Field	<50 mL 275 mL	>27,000 (4243) 4910 (771)	>14,700 (2121) 2673 (386)
Snapshot	29.10.14					6500	30,000

2015-2016 experiments with VOC103 cartridges and 20-cm air-vents *PER*, Concentration of perchloroethylene in μ g/L; *TRI*, Concentration of trichloroethylene in μ g/L. Average values measured in duplicate in passive samplers (standard deviation in brackets), with volumes estimated either in the laboratory (salt) or in the field

Finally, due to the high fluctuations of water levels in the karstic system, we had to face another difficulty in the exposure of the samplers in the boreholes. Within the exposure period, the samplers may be out of water or on the contrary immersed under a water column which was much higher than at the date of equipment of the boreholes, due to the drastic change of the static level. A compromise must then be found between immerging just below the surface water to get rid of the pressure gradient effect on the sampling rate, or at a high depth to avoid the device to be out of the water.

23.4 Conclusion

The experiments conducted within the Chlorokarst project to assess the capabilities of 3 integrative passive samplers to quantify CHC concentrations in karstic aquifers lead to the following conclusions. The ceramic dosimeters are practical to use and robust, allowing to expose them either in springs or in piezometers over severalmonth periods. But they were found to be not adequate to the purpose of quantifying low levels of chlorinated concentrations in 2- or 3-month periods, as targeted in the project. The Tips samplers are also very easy to use and convenient for both springs and piezometers. Moreover, they allow to detect the presence of chlorinated hydrocarbons, even at low levels within the targeted exposure periods. But the laboratory of the AGI company that provides the samplers is currently unable to quantify CHC concentrations with a satisfactory accuracy level. Currently, they can thus only be used as sentinels. The Sorbicell samplers require a more sophisticated equipment, including a reservoir to collect the water penetrating the cartridge that contains the adsorbent, and a tube (or an air-vent) to induce water entry under the effect of a pressure gradient. But comparison tests show that these samplers reproduce correctly the weighted average reference concentrations, obtained with an automatic sampler collecting daily samples over the total exposure period, even if the concentration values are low (a few μ g/L of each of the chlorinated compounds). Implementation of the Sorbicell samplers in the springs is rather easy, and appropriate analytical results are obtained provided that the type of cartridge and the immersion depth are adapted to the water height found in the springs. Exposure in piezometers is more difficult. Cartridges of high resistance to the water flux and air-vents have to be used to slow down the leaching of the cartridge, and thus to extend the exposure period to the required 2 months. Immersion of the device at low depths reduces the material failure (such as cartridge ejection). On the other hand, the device has to be

immersed at sufficient depth to avoid being out of water during the exposure period, especially in karstic context where the water level may strongly fluctuate. In the end, the high discrepancy between the volumes of water measured in the reservoirs in the field and those estimated from the dissolution of the tracer salt in the laboratory is questioned. The 2 volume estimates provide the right order of magnitude of chlorinated concentrations, from the adsorbed mass of pollutant. But the concentration level may be up to twice higher with the directly measured volumes than with the volumes deduced from salt dissolution. These differences may cause problem when concentration levels have to be compared to regulatory values. Further experiments would then be required to define the estimation method that provides the closer to the real leaching volume.

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