Environmental Pollution 173 (2013) 133–137

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Short communication

Occurrence and dynamics of micropollutants in a karst aquifer

Barbara Morasch [1]

Laboratoire de Chimie Environnementale, EPFL – ENAC – LCE, Bâtiment GR, Station 2, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form
4 October 2012
Accepted 10 October 2012

Keywords:
Karst aquifer
Micropollutants
Atrazine
Autochthonous endokarst microbial community
Drinking water quality

ABSTRACT

Karst systems represent important yet vulnerable drinking water resources. A wide spectrum of pollutants may be released into karst groundwater from agriculture, livestock farming, private households, and industry. This work provides an overview on the occurrence and dynamics of micropollutants in a karst system of the Swiss Jura. Ten months of intensive monitoring for micropollutants confirmed that the swallow hole draining an agricultural plain was the main entry path for pesticides into the karst system and the two connected springs. Elevated fungicide concentrations in winter and occasional quantification of pharmaceuticals suggested wood- or façade treatment and domestic sewer as additional sources of contamination. A continuous atrazine signal in the low ng/L range might affect the autochthonous endokarst microbial community and represents a potential risk for the human population through karst groundwater.

1. Introduction

Karst aquifers supply about 25% of the world population – in some European countries even 50% – with drinking water (Ford and Williams, 2007). Rain water reaches karst aquifers either by diffuse percolation via a thin soil cover or as surface runoff via swallow holes. The fast and almost barrier-free recharge of water makes karst systems highly vulnerable towards chemical and biological contaminations. Research on the mobility and attenuation of viruses, bacteria, and protozoa in groundwater has a long-standing tradition, e.g. (Mahler et al., 2000). In the meantime, numerical models are employed to evaluate the vulnerability of karst systems towards microbial contamination under varying recharge conditions (Butscher et al., 2011). The fate of chemicals in karst aquifers is less studied although the first reports on the occurrence of pesticides and fertilizers after storm events date from the 1980s, e.g. (Hallberg, 1989). Later it was observed that moderately hydrophobic agricultural chemicals like atrazine leached from the overlying soil or epikarst at high flow conditions and exhibited storm pulses in karst spring waters (Vesper et al., 2001). Innovative analytical multi-component methods for polar trace pollutants helped to gather more information on micropollutant contamination in karst, e.g. (Metcalfe et al., 2011). A deterioration of supposedly pristine water bodies through the human anti-inflammatory diclofenac was observed in a German karst landscape (Einsiedl et al., 2010). For that study site the authors concluded that intrakarstic biodegradation was only of minor importance. Assuming that its biodegradation was negligible, caffeine was used as indicator for untreated wastewater entering karst groundwater (Hillebrand et al., 2012). However, the conventional notion that contaminant attenuation is inefficient in conduit-rich karst with generally short water residence times was challenged (Heinz et al., 2009). The authors observed decreasing organic micropollutant concentrations between swallow hole and spring that could not be explained by dilution and hydrophobicity-dependent retention of the compounds. Thus, the near-elimination of several organophosphates was explained by biodegradation (Heinz et al., 2009).

To map the status quo of micropollutant distribution in Switzerland, a broad screening campaign for pesticides and pharmaceuticals in groundwater was performed (Hanke et al., 2007). However, for a more complete picture of micropollutant dynamics and fate in karst ecosystems there is still a great demand for regional surveys running over a period of time and going beyond single point measurements.

Main objective of this study was to provide time-resolved information on the occurrence and dynamics of micropollutants between the swallow hole and two main springs of a karst system in the Swiss Jura. With its large spectrum of micropollutants investigated, this study is unique among the few existing reports on the anthropogenic impact on karst ecosystems.

E-mail address: barbara.morasch@gmx.net.
[1] Present address: University of Tuebingen, Center for Applied Geoscience (ZAG), Sigwartstr. 10, 72076 Tuebingen, Germany.

0269-7491/$ – see front matter
http://dx.doi.org/10.1016/j.envpol.2012.10.014

2. Material and methods

2.1. Study site

In Switzerland 20% of the surface is covered by karst. The well-characterized karst system near Yverdon-les-Bains was chosen as study site (Fig. 1). Runoff from the agriculturally-dominated plain enters the karst aquifer via a swallow hole (*Feurtille*), which represents the major input path for fecal indicator bacteria into the karst system (Pronk et al., 2006, 2007). According to the hydrological model, the infiltrated water is diluted with deep groundwater and reappears at two karst springs (*Moulinet* and *Cossaux*) in 4.8 and 6.3 km distance after typical water transit times of ten to twelve days (Pronk et al., 2006, 2007). The contribution of water that infiltrated the karst system via the *Feurtille* swallow hole to spring waters varies with the discharge rates and characteristically is between 15–30% and 1–12% for *Moulinet* and *Cossaux*, respectively (Pronk et al., 2008). *Cossaux* supplies one third of the drinking water for Yverdon-les-Bains while the *Moulinet* source is of unsatisfactory sanitary water quality.

2.2. Water quality monitoring

Water temperature, turbidity, total organic carbon (UV extinction at 370 nm), electrical conductivity, and discharge were logged in 5-min intervals at the *Cossaux* reservoir. Apart from heavy rainfalls in the winter season, discharge and water properties were relatively constant throughout the study (Fig. 2).

2.3. Water sampling and analysis of micropollutants

From the beginning of November 2009 to the end of August 2010, water was sampled in monthly intervals at the swallow hole and the two karst springs. In April and May, at the beginning of the agricultural season, eight additional samplings were performed (Fig. 2). Weather conditions during the period of intensified monitoring were characterized by occasional rain illustrated in a slightly increased discharge rate at *Cossaux*. Grab water samples were taken with autoclaved amber glass bottles that had been rinsed with acetone, hexane, and methanol and heated to 250 °C for 6 h. For the analysis of micropollutants, 1 L of freshly-sampled water was filtered through glass fibre filters (<1 μm pore size; Whatman) and adjusted to pH 2.5 with 5 N HCl. The same morning, organic analytes were extracted using hand assembled cartridges of 6 mL volume filled with a mix of four different solid phase extraction matrices. Subsequent elution was performed at <0.5 mL/min according to established protocols (Morasch et al., 2010). Prior to the analysis by UPLC-MS/MS (Ultra-performance liquid chromatography coupled with tandem mass spectrometry) the extracts were diluted 1:5 with UPLC eluent containing 10,11-dihydrocarbamazepine as internal standard. The UPLC gradient method was operated with H_2O and methanol both amended with 1% of formic acid and 5 mM of NH_4 formate as eluents. The flow rate was 0.3 mL/min, and the HSS T3 column (2.1 × 100 mm, 1.8 μm; Waters) was maintained at 30 °C. The injection volume was 7.5 μl and each sample was analysed in duplicate. The UPLC-MS/MS multi-component method that had been described in detail before (Morasch et al., 2010) was modified and allowed the analysis of 36 micropollutants of domestic or agricultural origin in the low ng/L range in a single UPLC-MS/MS run (Table S1).

3. Results and discussion

3.1. Occurrence of micropollutants in the karst system

Based on intensive monitoring, micropollutants of different classes could be identified at the in- and outlets of the karst aquifer. Ten different pharmaceuticals were occasionally quantified by the multi-component method with median concentrations <10 ng/L. Pharmaceuticals, among them the anti-inflammatory drugs paracetamol, ketoprofen, and diclofenac and the antibiotic sulfamethoxazole, occurred more frequently in the springs than at the swallow hole (Table 1). It is assumed that the pharmaceuticals in karst groundwater were of domestic origin which would be consistent with previous findings (Heinz et al., 2009; Einsiedl et al., 2010; Hillebrand et al., 2012).

Moreover, ten different corrosion inhibitors/pesticides could be quantified at a three times higher frequency than the pharmaceuticals (Table 1). Median concentrations of pesticides, which were more frequently found at the swallow hole than in karst spring waters, were usually higher than the concentrations of the pharmaceuticals (Table 1).

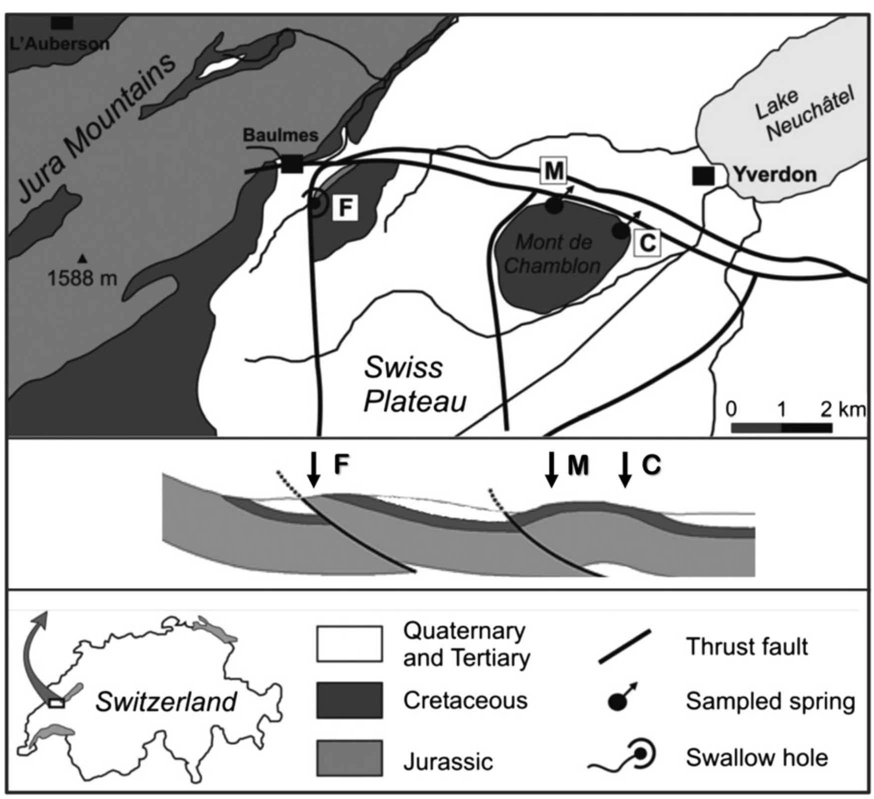

Fig. 1. Geological map of the sampling sites close to Yverdon-les-Bains, Switzerland, depicting the *Feurtille* swallow hole (F) and the two karst springs *Moulinet* (M) and *Cossaux* (C) in 4.8 and 6.3 km distance. The three locations are situated at the contact zone between the Jurassic-Cretaceous karst aquifer system and the overlying Tertiary–Quaternary formations (Modified after Pronk et al., 2006).