



Occurrence and spatial distribution of organic micro-pollutants in a complex hydrogeological karst system during low flow and high flow periods, results of a two-year study

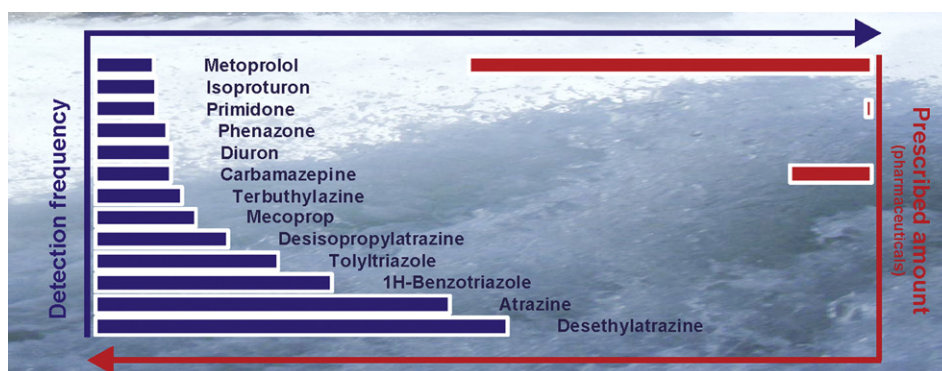
Roland Reh ^{*}, Tobias Licha, Tobias Geyer, Karsten Nödler, Martin Sauter

Geoscience Center of the University of Göttingen, Dept. Applied Geology, Goldschmidtstr. 3, 37077 Göttingen, Germany

HIGHLIGHTS

- ▶ Fifty-four micro-pollutants are studied in a large and complex aquifer system.
- ▶ Forty-four organic compounds are detected in groundwater.
- ▶ Most frequently detected are triazoles and triazines.
- ▶ Comparison of prescribed doses with detection frequency refers to persistence.
- ▶ First reported detection of tamoxifen in a fractured karstified aquifer.

GRAPHICAL ABSTRACT



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ABSTRACT

Fifty-four different organic micro-pollutants (OMPs) including pharmaceuticals, pesticides, corrosion inhibitors and other typical wastewater compounds such as caffeine are repeatedly analyzed in approximately fifty groundwater observation points in a complex faulted and fractured carbonate aquifer system consisting of three spring catchment areas. With the applied HPLC–MS/MS method, achieving method quantification limits (MQL) of 1.2–28 ng L⁻¹, forty-four of the OMPs are detected in groundwater. Regarding the vertical distribution in the aquifer system the highest variety of OMPs occurs in the shallow aquifer. Most frequently detected compounds are atrazine together with the metabolites of several triazines, desethylatrazine (DEA) and desisopropylatrazine (DIA), the corrosion inhibitors 1H-benzotriazole and tolyltriazoles and as pharmaceutical residues the anti-epileptic drug carbamazepine as well as the analgesic drug phenazone. Median OMP concentrations are in the range of 20–40 ng L⁻¹ with occasionally and locally higher concentrations of up to 6000 ng L⁻¹. Defined combinations of OMPs occur repeatedly in the same observation wells and allow to distinguish different input functions. The comparison of detection frequency with the number of prescribed doses gives information about the specific persistence of pharmaceuticals. The analgesic phenazone exhibits a peculiar high detection frequency, although it is recently not prescribed in significant amounts. The detection of the estrogen antagonist tamoxifen (6–17 ng L⁻¹) in a groundwater flow system is reported for the first time.

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1. Introduction

Organic micro-pollutants (OMPs) such as pharmaceuticals and pesticides are widely distributed in the aquatic environment (Ternes, 1998;

^{*} Corresponding author. Tel.: +49 56131097273; fax: +49 56131097277.
 E-mail address: reh@geonik-gmbh.de (R. Reh).

Kolpin et al., 2002; Schwarzenbach et al., 2006). The vast majority of studies on the occurrence and fate of OMPs in the environment focus on surface waters. Studies on groundwater, especially karst and fractured aquifers, are still heavily underrepresented. Groundwater flow and OMP transport in karst and fractured aquifers are mainly affected by the interaction of rapid conduit flow and slow flow within fissured matrix blocks (e.g. White, 1969; Atkinson, 1977). Therefore, these aquifer systems are very complex regarding flow and transport parameters. Although OMPs are potential and suitable environmental tracers (Clara et al., 2004; Müller et al., 2012) comprehensive and systematic studies on the occurrence and distribution of OMPs taking into account the spatial and/or temporal variation of OMPs in such aquifers are still scarce (Nödler et al., 2012; Estévez et al., 2012). Previous studies mostly target special problems of discrete conduits (Heinz et al., 2009) and are either limited in number and character of OMPs or sampling points (Metcalf et al., 2011). Study periods mostly represent hours or days and therefore specific discharge situations (Hillebrand et al., 2012). Longterm observations of an extended spectrum of analytes at all available sampling points within a catchment are uncommon so far.

However, as karst and fractured aquifers are very important but vulnerable drinking water resources this gap of knowledge must be bridged.

In this study the occurrence and distribution of 54 different OMPs in a complex and karstified aquifer system are presented. Many of the chosen OMPs have already demonstrated high detection frequencies in the aquatic environment in previous studies. Additionally, substances with limited data on their occurrence and fate in the environment (e.g. pantoprazole, cetirizine and tamoxifen) were also included. The chosen study area, characterized as well by the influence of an urban area with industrial sites and waste disposals as by surrounding agricultural uses, exhibits a complex system of several karstified carbonate aquifers. Consequently a high yield of OMPs with different applications was expected, more so than in sparsely populated areas.

The results from four water sampling campaigns during a two year period (2010–2011) are presented. Considering specific information about the land use and the amount applied in the catchment (e.g. the prescribed daily dosage of the analyzed pharmaceuticals, analysis of a banned herbicide) the abundance and persistence of the compounds in the investigated area are evaluated.

2. Material and methods

2.1. Field site

The investigation area covers approximately 65 km², with a city with approximately 24,000 inhabitants and its industrial area located in the center, surrounded by agricultural and forested land uses. The urban area is characterized by intensive industrial applications and exhibits several disused waste disposal sites (Fig. 1). Therefore, the release of corrosion inhibitors from industrial applications and pharmaceuticals from the waste disposals are expected.

Concurrently, nearly the complete investigation area is located in a water protection zone. Roughly 10% of the replenished groundwater is abstracted for public water supply and industrial use. The waste water is discharged to a treatment plant 3.5 km south of the study area.

The investigated aquifer system is developed within an alternating sequence of shale rocks, fractured aquiferous carbonates and sandstones of the Zechstein formations which are exposed to the surface at the eastern rim of the Rhenish massif (Kulick, 1997). The stratigraphic classification (Table 1), based on the stratigraphic table of Germany (“Deutsche Stratigraphische Tabelle”) (Mennig and Hendrich, 2002) distinguishes seven Zechstein formations (z1–z7). In this study the aquifers of the z3–z7-formations are united as “upper

aquifers” while the z1-aquifer is distinguished as “lower aquifer”. For the z2-carbonate no wells or sampling points are existent. The fractured carbonate aquifers of the z1- and z3-formation show partial characteristics that are typical for karstification such as ponors and discrete springs. Through north striking tectonic faults the investigation area is divided into two main tectonic blocks (Kulick, 1997), Ense-Scholle in the western part and Meininghausen-Scholle in the East (Fig. 1).

The investigation area is restricted by two main spring areas, which are located in the North and in the South. The total discharge of each spring area, consisting of a number of contiguous single springs, amounts about 75 L s⁻¹. East of the fault “Westheimer Abbruch” a number of small springs feed a river with a discharge of 100 L s⁻¹. Due to the positions of the main spring areas and the hydraulic head subsurface water divides are expected within the study area (Hölting and Matthes, 1963) leading to preferential north and south directed groundwater flow.

2.2. Sampling

Samples were taken from 51 sampling points consisting of observation and abstraction wells, springs, and rivers. 44 of the sampling points represent groundwater (Fig. 2). The number of sampling points associated to the different aquifer levels is displayed in Table 1. Natural springs are correlated to the outlet position of highly permeable subsurface flow pathways (e.g. solution enlarged fractures). Two of the observed springs are located in carboniferous shale west of the investigation area.

Most groundwater wells are established in either the z1- or the z3- aquifer. Additionally some well screens hydraulically connect different aquifer levels. In total, the sampling points represent 46 locations.

The samples were taken during four sampling campaigns in spring and late summer in 2010 and 2011 representing high and low flow periods respectively. Between spring and late summer groundwater levels decline by 0.2–2.0 m and the discharge of the main springs decreases by 30–60%. Additional samples were taken 2 weeks after snow melt in January 2011 representing a special recharge event. According to the types of sampling points, different sampling methods were applied. Samples from spring water and from surface water were directly taken as grab samples (500 mL glass bottles, screw cap). Wells for regular groundwater abstraction were sampled directly from the rising main during their continuous production. In observation wells a submerged pump was installed for well purging purposes and the sample was taken immediately afterwards using a PTFE bailer. The samples were transported in 500 mL glass bottles to the laboratory in a dark, cooled box and extracted within 24 h after sampling.

2.3. Chemical analysis

A multi-residue analytical method based on solid phase extraction (SPE) and high-performance liquid chromatographic separation with tandem mass spectrometric detection (HPLC-MS/MS) was used for the analysis. Details regarding the methodology and analytes were published previously (Nödler et al., 2010). The method quantification limits (MQL) reported therein are between 1.2 and 28 ng L⁻¹. The analytes cotinine (nicotine metabolite), atenolol acid (metabolite of atenolol and metoprolol), haloperidol (antipsychotic), tamoxifen (estrogen antagonist for breast cancer treatment), terbuthylazine (herbicide), 4-OH-diclofenac (diclofenac metabolite), desamino-SMX, and 4-nitro-SMX (both sulfamethoxazole metabolites, see Nödler et al., 2012) were included in the presented study. The MS/MS parameters of the additional analytes were added to the methodology of Nödler et al. (2010). Further information can be found in Table 2.

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