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Passive sampling as a tool for identifying micro-organic compounds in groundwater

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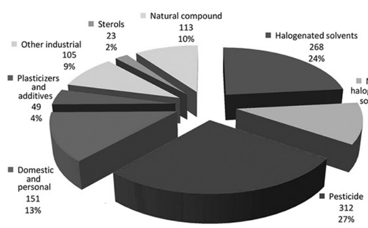
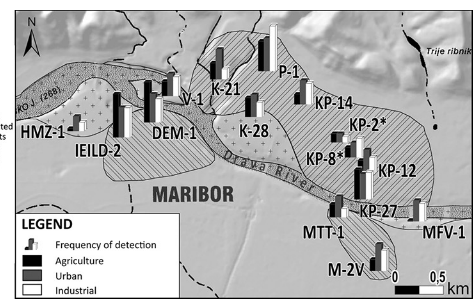
HIGHLIGHTS

- Passive sampling is an appropriate tool for identifying MOs in groundwater.
- Based on the detected MOs in groundwater, seasonal variations can be observed.
- Micro-organic contaminants can be used as markers to identify sources of pollution.
- Using passive sampling enabled the team to optimize monitoring.

GRAPHICAL ABSTRACT





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ABSTRACT

The paper presents the use of a simple and cost efficient passive sampling device with integrated active carbon with which to test the possibility of determining the presence of micro-organic compounds (MOs) in groundwater and identifying the potential source of pollution as well as the seasonal variability of contamination. Advantage of the passive sampler is to cover a long sampling period by integrating the pollutant concentration over time, and the consequently analytical costs over the monitoring period can be reduced substantially. Passive samplers were installed in 15 boreholes in the Maribor City area in Slovenia, with two sampling campaigns covered a period about one year. At all sampling sites in the first series a total of 103 compounds were detected, and 144 in the second series. Of all detected compounds the 53 most frequently detected were selected for further analysis. These were classified into eight groups based on the type of their source: Pesticides, Halogenated solvents, Non-halogenated solvents, Domestic and personal, Plasticizers and additives, Other industrial, Sterols and Natural compounds. The most frequently detected MO compounds in groundwater were tetrachloroethene and trichloroethene from the Halogenated solvents group. The most frequently detected among the compound's groups were pesticides. Analysis of frequency also showed significant differences between the two sampling series, with less frequent detections in the summer series. For the analysis to determine the origin of contamination three groups of compounds were determined according to type of use: agriculture, urban and industry. Frequency of detection indicates mixed land use in the recharge areas of sampling sites, which makes it difficult to specify the dominant origin of the compound. Passive sampling has proved to be useful tool with which to identify MOs in groundwater and for assessing groundwater quality.

1. Introduction

Micro-organic (MO) compounds have been recognized as an important factor in environmental pollution (Wille et al., 2011). Research in

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the past has been dedicated to the detection of classical pollutants in water, e.g. pesticides, nitrates and PCBs, while today the aim of studying the presence of MOs in groundwater is also to determine the presence of hormones, pharmaceuticals, personal care products and other household and industrial chemicals (emerging contaminants). Determining the presence of MO compounds in groundwater (Stuart et al., 2012; Lapworth et al., 2015; Pitarch et al., 2016), development of sampling (Verreydt et al., 2010; Allinson et al., 2015; Křesinová et al., 2016; Mirasole et al., 2016) and analytical methods (Locatelli et al., 2016) have become the focus of present research.

Drinking water is often pumped from the aquifers that are subject to the influence of urban and agricultural pressures. This fact has led to increased interest in research on the determination, fate, transport and degradation processes of anthropogenic organic pollutants in the environment, particularly where groundwater is the most important source of drinking water. The presence of MOs in aquatic environment has given rise to an increased demand for sensitive and reliable monitoring tools (Wille et al., 2011; Vrana et al., 2005). Strict legislation concerning drinking water quality in the EU requires the optimization of analytical methods for organic pollutants in order to gain accurate and precise results at ppt levels. In the groundwater, most pollutants are usually present in concentrations below the limit of quantification (LOQ), and several of them also below the limit of detection (LOD) at ppt and sub-ppt levels. Developments in assessing water quality also require the appropriate accompanying sampling technologies to support the monitoring programs.

Part of the process of ensuring good groundwater is an effective monitoring system. One of the associated challenges is how to improve the monitoring of groundwater quality. One obstacle in connection with MOs is that they are present in the environment as mixtures at sub-ppb concentrations, and at variable times and locations. Spot sampling is usually used to collect water samples, with which contamination at a given time and place can be determined. However, this method may not take full consideration of the temporal variations in the concentrations due to fluctuations in flow, precipitation, or episodic inputs (e.g., combined sewer overflows or sewage lagoon release) (Kreuger, 1998; Carlson et al., 2013). Another disadvantage of classical monitoring methods is the small volume of water typically used for analysis, resulting in relatively high detection limits (Gunold et al., 2008). In tracking the above objectives the concept of monitoring is very important, where the first preliminary qualitative methods are used to assess the situation, and are later supported by precise and accurate quantitative analytical methods. Passive sampling has been proven to be a useful monitoring tool for a range of different contaminants in aquatic environments (Wille et al., 2011; Seethapathy et al., 2008; Vermeirssen et al., 2009; Nyoni et al., 2011; Ahrens et al., 2015), which allows for continuous monitoring over an extended period of time and to determine time-weighted average (TWA) water concentrations of MOs (Alvarez et al., 2004; Vrana et al., 2014). It is based on the situ deployment of devices/sorbents capable of accumulating contaminants freely dissolved in the water (Ahrens et al., 2015). Compared to classical sampling methods, the cost of analysing the passive sampler is lower, due to relatively simple sample treatments, limited matrix interferences, and considerably lower detection limits (Vrana et al., 2005).

Recently, numerous studies all over the world have described the development and use of Polar Organic Chemical Integrative Samplers (POCIS) to screen MOs in groundwater (Soulier et al., 2016; Metcalfe et al., 2011; Berho et al., 2013) as well as in various aquatic systems (Tapie et al., 2011; Ibrahim et al., 2013). Polyethylene devices (PEDs) are used for assessing hydrophobic organic compounds (HOCs) in aquatic environments (Adams et al., 2007). Also semipermeable membrane devices (SPMDs) have been used to monitor polycyclic aromatic hydrocarbons (PAHs) in water columns (Amdany et al., 2014; Bourgeault and Gourlay-Francé, 2013), and PAHs and/or polychlorinated biphenyls (PCBs) in aqueous systems (Schäfer et al., 2010; Prokeš et al., 2012; Monteyne et al., 2013; Uher et al., 2016), all of which indicate a promising tool for determining organic toxicants. One of the most common passive samplers used to adsorb organic contaminants from water and air is activated carbon, which has been known for decades (Rivera et al., 1987; Kadokami et al., 1990; Hale et al., 2009; Yu et al., 2009; Verreydt et al., 2010), but recently we have seen a lack of studies where it has been used for monitoring MOs in aquatic systems.

For passive sampling different type of sorbent with different polarity depending from the purpose of sampler are used. Principle of choice is very similar to those at solid-phase extraction or micro-extraction techniques. However, most of sorbents from organic material (e.g. different modified styrene-divinylbenzene copolymer type) or modified inorganic sorbents (e.g. modified alumina type) are very hard to prepare free of interfering compounds (e.g. plasticizers). Active carbon is broad range adsorbent, which could be easily cleaned by a heating in clean environment. After heating, deactivation of the surface could be done by a water steam. Therefore active carbon as a sorbent has been chosen in our study for general identification of MOs in groundwater.

The aim of the present article is as follows: (1) determine the presence of MO contaminants in groundwater by means of passive sampling; (2) test the applicability of the passive sampling method in monitoring groundwater quality; (3) investigate those hydrogeological conditions that have an influence on the emergence of contaminants in groundwater; (4) identify the source of MOs for every sampling site.

2. Site description

Maribor is the second largest city in Slovenia, and is located in the northeast of the country. It is situated on the banks of the Drava River, which has a mean discharge of 300 m^3/s. Our study area (Fig. 1) covers 18 km^2. The Vrbanski plateau aquifer is situated under the city of Maribor, and is the most important drinking water resource for Maribor and its surrounding municipalities. Approximately 68% of the region's drinking water supply is drawn from the aquifer (Juren et al., 1996).

The aquifer is formed from old coarse gravel deposits of the Drava River some 20 to 40 m thick, and can be classified as an intergranular aquifer of good permeability with an unconfined groundwater table, and as highly vulnerable to contamination derived from the surface. The groundwater table is found at an average depth of 25 to 37 m below the surface, the thickness of the saturated aquifer is 13 m in the deepest sections. Based on previous studies, the hydraulic conductivity of the aquifer is estimated at between 5×10^{-3} and 2×10^{-2} m/s. The aquifer is recharged from the Drava River (20%), from precipitation infiltration, and from small streams from the surrounding hills (Mali et al., 1996). General direction of groundwater flow is from west to east (Fig. 1), determined based on previous isotopic studies (Mali et al., 1995, 2003).

The Maribor area has a moderate continental climate typical of central Slovenia, with an average annual temperature of between 8 and 10 °C and a typical continental precipitation regime. The average yearly precipitation is between 800 and 1000 mm (SEA, 2013).

In the past, industry, which has constituted the main source of economic activity of Maribor, left traces in the environment, thus the industrial areas could be contaminated with various pollutants. The urban area is very diverse and has a relatively good regulated sewage system, though in some places presents a problem due to old or leaking sewers or lack thereof in the outlying settlements. The city's outskirts are covered by forest and farmland with intensive agriculture, which also represents a potential source of groundwater pollution.

3. Materials and methods

3.1. Sampling design

The sampling design network covered the entire aquifer area of the city of Maribor, with a focus on regions with different types of intensive land use, where, based on the groundwater dynamics (Mali et al., 2012)