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# Assessment of presence, origin and seasonal variations of persistent organic pollutants in groundwater by means of passive sampling and multivariate statistical analysis

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ABSTRACT

The paper presents the use of passive sampling in combination with factor analysis to assess the presence of anthropogenic organic pollutants, and to determine the type of pollution and seasonal variability of contamination. This combined method enables the assessment of groundwater quality and the evaluation of pollution sources, and serves as the basis for recommended measures to improve the quality of groundwater. The method has been tested on the Vrbanski plateau aquifer near Maribor, Slovenia. Groundwater pollution was monitored at 15 observation points, and at one in the Drava River. Two sampling campaigns covered a period of roughly one year (May 2010–September 2010 and September 2010–March 2011). The data set of 54 samples with 12 variables (pollutants) was based on unbalanced nested hierarchical sampling design, and is expressed as intensity on an ordinal scale from 1 to 5. Nonparametric Kruskal-Wallis test for testing statistical significance of pollutants at various levels of sampling design, and factor analysis based on polychoric correlation, were used in this study. Results of the factor analysis show that groundwater contains organic pollutants from three different types of sources. Factor analysis split the group of pesticides into two factor-groups: Factor 1, representing pesticides which are indicators of agricultural activities, and Factor 2, including atrazine and desethyl-atrazine, which indicate old burdens or their illegal use. Pharmaceuticals and compounds of personal care products are loaded on Factor 3, which shows groundwater pollution from urban activities, while Factor 4 represents volatile aliphatic halogenated hydrocarbons, which are indicators of industrial contamination. Factor scores also revealed considerable differences between the two sampling campaigns at individual sampling points. The results show that the influence of pollution from various anthropogenic activities depends on the meteorological conditions in each sampling campaign. The passive sampling technique combined with multivariate statistical analysis has proved to be a useful approach to assessing groundwater quality, with a substantially cheaper and more effective monitoring design than the more commonly used monitoring methods.



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## 1. Introduction

During recent years intensive research on urban areas and on the impact of agriculture on groundwater has been conducted worldwide. This increased interest can be traced to the fact that large cities and other urban agglomerations are, as a rule, supplied by drinking water from the aquifers above which they are located, or from aquifers that have urban or agricultural zones within the vicinity of their recharge areas. Trends pointing to increased pollution in large aquifer systems continue to increase year by year. Studies have shifted from identifying pollutants to determining the origin of contamination. Researchers' attention today is focused on determining the presence of anthropogenic organic pollutants in the groundwater (Jurado et al., 2012; Stuart et al., 2012; Lapworth et al., 2015; Postigo and Barceló, 2015). These pollutants have been recognised as one of the important factors in environmental pollution (Wille et al., 2011). Anthropogenic organic pollutants have been found as contaminants in sewage, surface waters and groundwater, as well as in drinking water. This group of pollutants appears as pesticides and pharmaceuticals with metabolites, hormones, steroids, industrial additives, personal care products, water treatment by-products, fire retardants, surfactants and food additives (Stuart et al., 2012). Some of these contaminants can have a serious impact on human and environmental health, which underlines the need to better understand their role in the environment.

Groundwater source protection starts with improving drinking water quality and effective implementation of environmental protection policies. In order to realize these goals, the possible contaminants and their sources have to be determined. With the aim of effective water management, the European Union in 2000 adopted the Water Framework Directive (Directive 2000/60/EC) of the European Parliament and of the Council, establishing a framework for community action in the field of water policy (Ambrožič et al., 2008). In order to satisfy the requirements of legislative frameworks and directives it is necessary to monitor pollutants in the aquatic environment, as many of these compounds can pose a threat to both human health and ecosystems (Vrana et al., 2005). Commonly used monitoring techniques usually record only a limited number of chemical parameters and samplings of pollutant concentrations at specific points in time, which, however, substantially increases the cost of monitoring. Contrary to such techniques, passive sampling is less sensitive to accidental extreme variations in the concentration of organic pollutants in natural waters (Kot et al., 2000) and has been proved a useful monitoring tool in detecting a large range of contaminants in the aquatic environment (Seethapathy et al., 2008; Vermeirssen et al., 2009; Nyoni et al., 2011; Wille et al., 2011). A passive sampler can cover a long sampling period by integrating the pollutant concentration over time, and the analytical costs over the monitoring period can be reduced substantially. Several types of passive samplers are in use all over the world. Semipermeable membrane devices (SPMEs) have been used to monitor various persistent contaminants in sea and surface water (Bennett and Metcalfe, 2000; O'Toole et al., 2006; Metcalfe et al., 2000, 2008). Silicone rubber passive samplers were deployed to estimate concentrations of polycyclic aromatic hydrocarbons (PAHs) resulting from wildfires, in streams in Victoria, Australia (Schäfer et al., 2010). It is believed that silicone-based passive samplers represent a promising tool for determining organic toxicants. One of the most common substances in passive samplers for adsorbing organic contaminants from both air and water is activated carbon, which has been recognised and employed for decades (Rivera et al., 1987; Kadokami et al., 1990; Hale et al., 2009; Yu et al., 2009). This type of samplers was chosen precisely for general identification purposes in our research. Strategies for sampler design, calibration, in situ sampling and quality-control issues, and advantages and challenges associated with passive sampling in aqueous environments, are considered in various studies (Kot et al., 2000; Stuer-Lauridsen, 2005; Vrana et al., 2005; Seethapathy et al., 2008; Metcalfe et al., 2011; Nyoni et al., 2011; Wille et al., 2011). Research efforts are directed towards developing a passive sampling technology for monitoring organic and inorganic pollutants in water. New monitoring techniques and data processing procedures are being developed, enabling fast and cost-effective determination of the presence of pollutants and their origin.

Multivariate statistical analysis is a quantitative and independent approach to groundwater classification that allows for objective grouping of groundwater samples and establishing correlations between chemical parameters and groundwater samples for normally distributed data (Prasanna et al., 2010) on continuous scale. It has been successfully applied in a number of hydrogeochemical studies designed to identify contaminated aquifer zones using nonparametric statistical tests (Robinson and Ayuso, 2004) and multivariate analysis (Suk and Lee, 1999; Love et al., 2004; Suvedha et al., 2009; Yidana and Yidana, 2009; Prasanna et al., 2010). It has been shown that multivariate statistical analysis significantly helps to classify groundwater data and identify major mechanisms impacting the groundwater chemistry (Kim et al., 2005; Singh et al., 2005; Cloutier et al., 2008). The common factor analysis method has also proved to be an appropriate approach to analysing data on the ordinal scale (Basto and Pereira, 2012), and is used in our study. Many researchers demonstrated, based on theoretical models, that polychoric correlation should be used when performing factor analysis for ordinal data instead of Pearson's correlation matrix (Gilley