



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

and Uhlig, 1993; Holgado-Tello et al., 2010; Basto and Pereira, 2012). But there is a shortage of studies that use ordinal data and factor analysis in hydrogeochemistry and in other studies related to the natural sciences. Only a few studies were found to use polychoric correlation of ordinal data in the natural sciences (Souter et al., 2010; Norris and Michalski, 2010; Cavallero et al., 2012). Variables characterized by an ordinal scale are more common in many empirical investigations within the social and behavioural sciences (Onyx and Bullen, 2000; Cutter et al., 2003; Basto and Pereira, 2012).

Using multivariate statistical analysis with ordinal data from a passive sampling technique to solve problems related to groundwater management presents a challenge. Therefore our study is focused on verifying the suitability of a methodology in which the results of groundwater passive sampling on the ordinal scale are supported by various statistical methods that could provide additional information on the studied subject.

The goal of the presented study was to assess the presence of anthropogenic organic substances in the Vrbanški plateau (Maribor, Slovenia) aquifer, to study the relationships between them, and to determine their origin and seasonal variations depending on the type of anthropogenic activity using effective monitoring (passive samplers) and multivariate statistical methods to interpret the results. The factors indicating contamination according to different types of pollution should be defined using multivariate statistical methods. With this methodology we tried to explain the detected substances in groundwater in terms of hydrogeological conditions, in the framework of the dynamics of water and land use. The obtained results should provide a quick and transparent overview of potential pollution loads linked to the type of pollution (agricultural, urban or industrial). The presented methodology should be used in groundwater management for an effective assessment of the state of groundwater quality as a basis for determining the measures necessary to improve the status of groundwater.

2. Study area

The city of Maribor is the capital of the north-eastern region of Slovenia. The greater municipality area comprises 147 km² with 94,809 inhabitants (SORS, 2014). In the past the economy was based on heavy industry, which left behind traces in the environment. Former

industrial areas, which could be contaminated with various pollutants, have now largely been transformed into commercial districts with many new businesses. The urban area is very diverse and has a relatively well-regulated public utility. The problem is an old sewage system in some places, or lack thereof in the outlying settlements. The city's outskirts are covered by forest and farmland with intensive agriculture, which also represent potential sources of groundwater pollution.

The Vrbanški plateau aquifer is situated beneath the city of Maribor, and is the most important source of drinking water in the region (Fig. 1). Overexploitation of the aquifer (about 40 m³/day) causes problems with water quality. Pollution, which is a consequence of the city's expansion and industrial development, has become a major problem. The spread of polluted water from any part of the city or its surroundings poses a potential danger for the water supply. The Vrbanški plateau aquifer is particularly at risk of contamination owing to intensive land use. It is evident from previous studies of the aquifer that the groundwater is polluted with pesticides and their metabolites (atrazine, desethyl-atrazine, metolachlor, terbutylazine, desethyl-terbutylazine, prometryn, bentazone), with pharmaceuticals and personal care products (carbamazepine, caffeine), and with volatile aliphatic halogenated hydrocarbons (trichloroethene, tetrachloroethene) (Mali and Auersperger, 2013; Koroša et al., 2013).

Approximately 68% of the region's drinking water supply is pumped from the Vrbanški plateau recharge area in the northern part of the city (Juren et al., 1996). There are two pumping stations: one on the Vrbanški plateau (VP), where 400–500 L/s of water are pumped, and the other at Maribor Island (MI), with 150 L/s of water pumped for the artificial recharge of groundwater in the Vrbanški plateau aquifer. The aquifer is formed from Quaternary gravel deposits of the Drava River, which now crosses the aquifer area twice. The aquifer can be classified as an intergranular aquifer of good permeability with unconfined groundwater table (Mali et al., 1995). The area of the present study extends over the entire aquifer area.

The aquifer is recharged from the Drava River, from precipitation infiltration, and from the small streams that flow down from the surrounding hills (Mali et al., 1995). The coarse gravel deposit is about 40 m thick on the plateau and 10 m near the Drava River. The groundwater table is found at an average depth of 25 to 37 m below the surface, thus the saturated layer along the aquifer is 13 m thick in the deepest

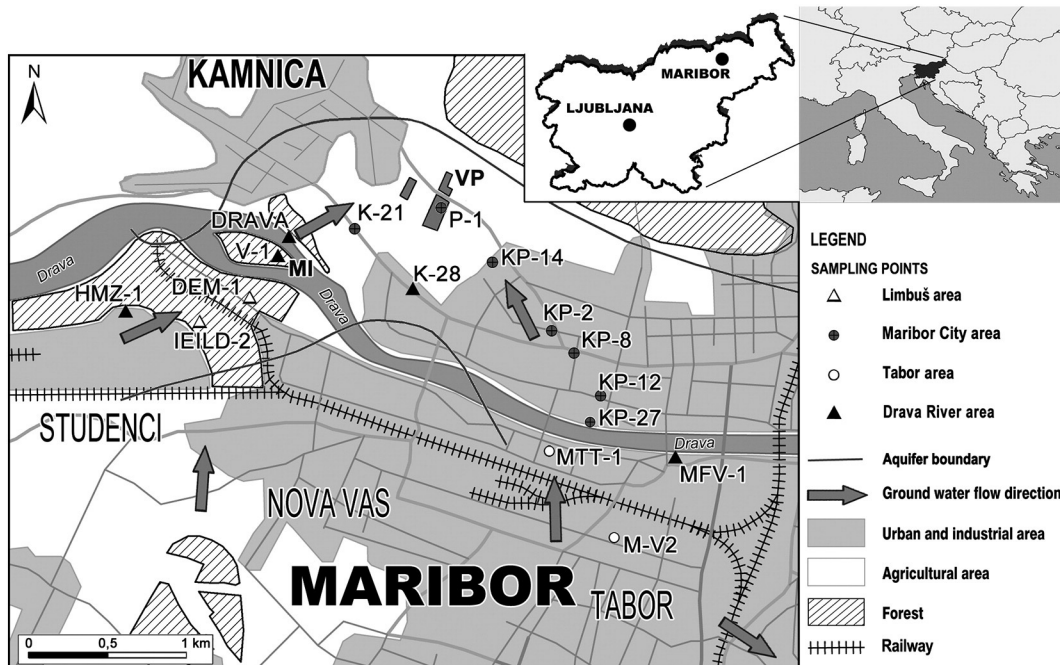


Fig. 1. Location map of study area and groundwater sampling points.

sections. Reported hydraulic conductivity of the principal aquifer ranged from 5×10^{-3} to 2×10^{-2} m/s (Mali et al., 1994, 2003). The study area belongs to the moderate continental climate of north-east Slovenia, which has a typical continental precipitation regime and an average yearly precipitation of 800 to 1000 mm. The average annual air temperature varies between 10 and 11 °C (SEA, 2013).

3. Materials and methods

3.1. Sampling design

The monitoring network was established on the basis of previously collected data on the geological and hydrogeological characteristics of the aquifer and a review of facilities in the field. Sampling points were selected in the recharge area of the active pumping stations, at Maribor Island on Drava River, and at the Vrbanski plateau. The sampling design network covered the entire aquifer area with a focus on those sampling points located in regions with more intensive land use, where, based on the groundwater dynamics, increased levels of pollutant substances were expected. All samples were classified into four levels:

3.1.1. Locations

4 groups of sampling points were determined based on their positions in the studied area and on the main components of groundwater recharge (see also Fig. 1):

1. Limbuš area, recharged by precipitation and inflows from surrounding hills: IEILD-2 and DEM-1;
2. Maribor City area with mixed recharge components: K-21, P-1, KP-27, V-1, KP-14, KP-2, KP-8, and KP-12;
3. Tabor area, recharged by precipitation: M-V2 and MTT-1;
4. near the Drava River: Drava, HMZ-1, K-28, and MFV-1.

3.1.2. Sampling points

Passive sampling devices were installed in 15 observation wells in the aquifer and one in the Drava River, which is one of the aquifer's recharge components.

3.1.3. Sampling depth

At 9 monitoring points, passive samplers were applied at different depths of the saturated zone, where contact with groundwater is constant, thus enabling the identification of organic contaminants along the depth profile:

1. 2 m above the aquifer base,
2. 4–5 m above the aquifer base,
3. 7–9 m above the aquifer base.

3.1.4. Sampling campaign

Two long-term sampling campaigns (app. 6 months) covered a period of roughly one year in order to integrate the pollutant concentration over time:

1. Summer (May–September 2010 with 423 mm of total precipitation),
2. Winter (September 2010–March 2011 with 313 mm of total precipitation).

The amount of precipitation during both sampling campaigns was measured at the climatological station Maribor–Tabor (SEA, 2013). In both campaigns a total of 54 samples were collected. Due to damaged samplers at the sample location KP-8, KP-2 and Drava River, only one sampling campaign was performed.

3.2. Analytical methods

The preparation of passive samplers and all analyses was carried out by the accredited laboratory of Ljubljana Water Works and Sewerage in Slovenia according to standards ISO 5667–23:2011 for sampling, and

EPA 625 modified for chemical analysis. Quantitative analysis of selected compounds was performed according to the EPA 525.2 method.

3.2.1. Passive samplers

In the research, passive sampling devices with granular activated carbon were applied (Fig. 2) (Kadokami et al., 1990; Yu et al., 2009). Prior to installation, active carbon from Merck (1.5 mm, extra pure, food-grade quality) was heated in glass vials for 3 h at 300 °C. Before cooling, a few droplets of ultra-pure water were added to generate steam, which reactivates active carbon. Vials with active carbon fibres were filled with ultrapure water. At this step, the addition of Ag salt could be used to prevent microbiological activity after installation. Vials with active carbon in ultra-pure water were closed in an additional flask with ultrapure water and active carbon on the bottom of the flask. The activated carbon (app. 3 g) was inserted into the passive sampler made of 1 mm mesh pouches fixed to 1-mm thick wire. All devices were made of stainless steel. The active carbon was transported thus and installed in screened borehole sections.

3.2.2. Chemical analysis

Immediately after sample collection, granular active carbon was transferred to a vial filled with ultra-pure water and transported to the laboratory. Ultra-pure water was removed from the vial and the granular active carbon was dried in an oven at 100 °C for 1 h. The adsorbed material on the passive sampler was eluted from the activated carbon with dichloromethane. The extract was further transferred to chromatographic vials and concentrated in a stream of nitrogen, which was then analysed using the gas chromatography–mass spectrometry (GC–MS – Perkin Elmer) analytical method. The installation method and analysis of passive samplers is accredited according to ISO/IEC 17025 standard (accreditation certificate LP-023). All the preparation steps have been validated.

For the interpretation of chromatograms the AMDIS (Automated Mass Spectral Deconvolution and Identification System) deconvolution was used. The deconvolution was covered by the GC–MS library with retention times for 921 organic contaminants from Agilent, USA, as well as the NIST 2008 library of mass spectra (Auersperger et al., 2011). Although the method is qualitative, GC–MS chromatograms were interpreted by estimating peak intensities on a scale of 1 to 5 and considered as “tentative identification” or “confirmed identification” according to ASTM D 4128–01 standard. Estimated peak intensity is connected with certainty of identification (EURACHEM/CITAC, 2003). In addition to the qualitative monitoring with passive samplers, current samplers for chemical analysis of different organic compounds were taken (Koroša et al., 2016). Based on these results, the parallels between detection limits for the analysis of current samplers were determined; similarly the detection limit of individual compounds with passive sampling was evaluated. Fig. 3 shows the example of determination of atrazine and terbuthylazine in groundwater based on passive sampling. Moreover, the comparison with quantitative monitoring data suggested that the method could identify the majority of compounds of interest at concentration levels of 1 ng/L or less (see Fig. 3). A good correlation between the results of quantitative monitoring data and the results of qualitative monitoring data from passive sampling was observed (Auersperger et al., 2015). From calculation of signal-to-noise ratio (S/N), which compares the level of a desired signal to the level of background noise, there is noticeable clear evidence, that method of passive sampling is more sensitive than regular methods for pesticide analysis, where typical LODs are at 0.001 ng/L. From Fig. 3 it could be seen that estimated LODs (S/N > 3) for terbuthylazine for passive sampling method are app. 0.00001 µg/L and for atrazine app. 0.00002 µg/L. Those LODs could be also addressed to all similar chemical compounds.

3.2.3. Quality control (QC)

Organic compounds are often found in personal care products and medication, therefore rigorous quality control of sampling should be

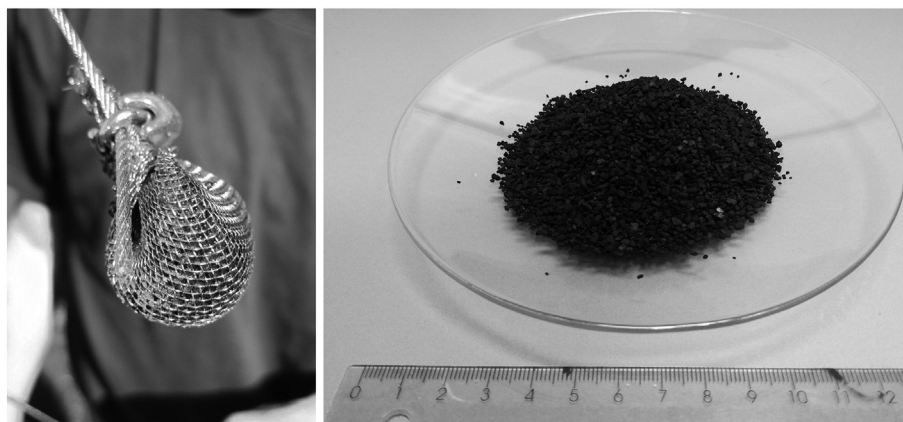


Fig. 2. Left - Passive sampler with granular activated carbon; right - granular activated carbon.

conducted both in the field and also in the laboratory. Sampling personnel should avoid drinking coffee and consuming other products containing caffeine (Fram and Belitz, 2011).

In each series of passive samples, regular blank tests and control samples spiked with compounds of interest were used, including benzene, atrazine and carbamazepine, and were parallel-processed using the same procedure. Before validation, analytical parameters (e.g. passive sample exposure time, drying procedure and elution procedure) were optimized. Compounds that were identified in the blank tests were excluded from reports. Active carbon for quality control procedures was stored in a laboratory in ultra-pure water for the entire duration of the installation and analysed at the same time as the collected passive samplers. During the analytical procedure, quality control samples showed that there was no diffusion of the material from the filter into the water before the ultrapure water was removed from the vial.

Field blanks according to the EPA 525.2 method (chapter 3.6) for quantitative method were prepared from ultrapure water that was sequentially transferred from one bottle to another at each sampling site. The Laboratory Fortified Sample Matrix (according to the EPA 525.2 definition) was used to calibrate the overall procedure and the QC. Regular spiked QC samples were analysed at each chromatographic run, including blanks of spring water used for calibration.

3.3. Statistical methods

Data obtained from laboratory analysis was used as a variable input for statistical analysis. The data set of 54 samples was based on an unbalanced nested hierarchical sampling design. Values are presented as intensities ranked on a scale from 1 to 5, while a 0-value was assigned to observations with no detectable pollutants. For statistical data processing, all samples for all four levels were used: locations (4), sampling points (16), sampling depth (3) and sampling campaign (2).

Because the data for observations were on the ordinal scale, non-parametric tests and multivariate statistical procedures were used. In this study the non-parametric Kruskal-Wallis test was used to determine the significance of differences between various categories at various levels of applied design as defined by location, sampling campaign, sampling depth and sampling point. Data was analysed using Statistica software, version 6.0 (StatSoft, 2001). The multivariate statistical method of factor analysis for nonparametric ordinal data was applied to identify the relationships between various chemical parameters based on the type of pollution. In performing factor analysis for ordinal data the polychoric correlation (Polycor package developed by John Fox in R) was used to estimate the associations between chemical organic compounds in groundwater. The polychoric correlation matrices and multivariate analysis were performed with R statistical software, version 3.0.2 (R Core team, 2013).

3.3.1. Kruskal-Wallis test

The non-parametric Kruskal-Wallis test is executed by ranking the data and performing a parametric test on the ranks to determine whether all groups have the same median, or whether at least one median is different. However, when the null hypothesis is rejected, the test does not indicate which group is significantly different from the other groups. In addition to Kruskal-Wallis test the nonparametric Mann-Whitney *U* test could be used, for testing to which group the differences can be attributed (Helsel and Hirsch, 1992).

In this study the tests are used to determine whether the intensity of each chemical constituent in groundwater occurs at significantly different frequencies in sample subgroups. These are defined as sampling campaign, sampling depths, sampling points and location categories. The null hypothesis for both tests is that there is no significant median difference between categories in each subgroup. Rejection of the null hypothesis at the 95% confidence level ($\alpha = 0.05$) was considered evidence supporting the alternative hypothesis that (at least) one category in each subgroup significantly differs from the others by its median.

3.3.2. Polychoric correlation

The polychoric correlation coefficient is an alternative to the standard Pearson's correlation coefficient for the relation between two variables. An ordinal variable can be thought of as a crude representation of an unobserved continuous variable. Polychoric correlation is estimated strongly under the assumption that the ordinal variables reflect underlying continuous bivariate normal distribution. These types of correlations extrapolate what the categorical variable distributions would be if they were continuous, adding tails to the distribution (Olsson, 1979; Flora and Curran, 2004; Basto and Pereira, 2012). The correlation coefficient can range from 1.0 perfect positive association, through zero, no association, to -1.0 perfect negative association and is interpreted analogously to the Pearson's correlation coefficient (Cavallero et al., 2012). In this study the correlation test was performed a confidence level of 95% (p of 0.05).

3.3.3. Factor analysis

Factor analysis is used to transform a set of variables into factors, which successively extract the maximal part of the variance in the data set (Wackernagel, 1995). Several authors explain the scale problem when using parametric factor analysis on an ordinal data set and suggest using alternative procedures. Using Pearson's correlations in factor analysis with ordinal data almost always produces misleading results. When performing factor analysis on an ordinal data set, the polychoric correlation should be used instead of the Pearson's correlation (Muthén and Kaplan, 1985; Gilley and Uhlig, 1993; Basto and Pereira, 2012), as it was done in this study.

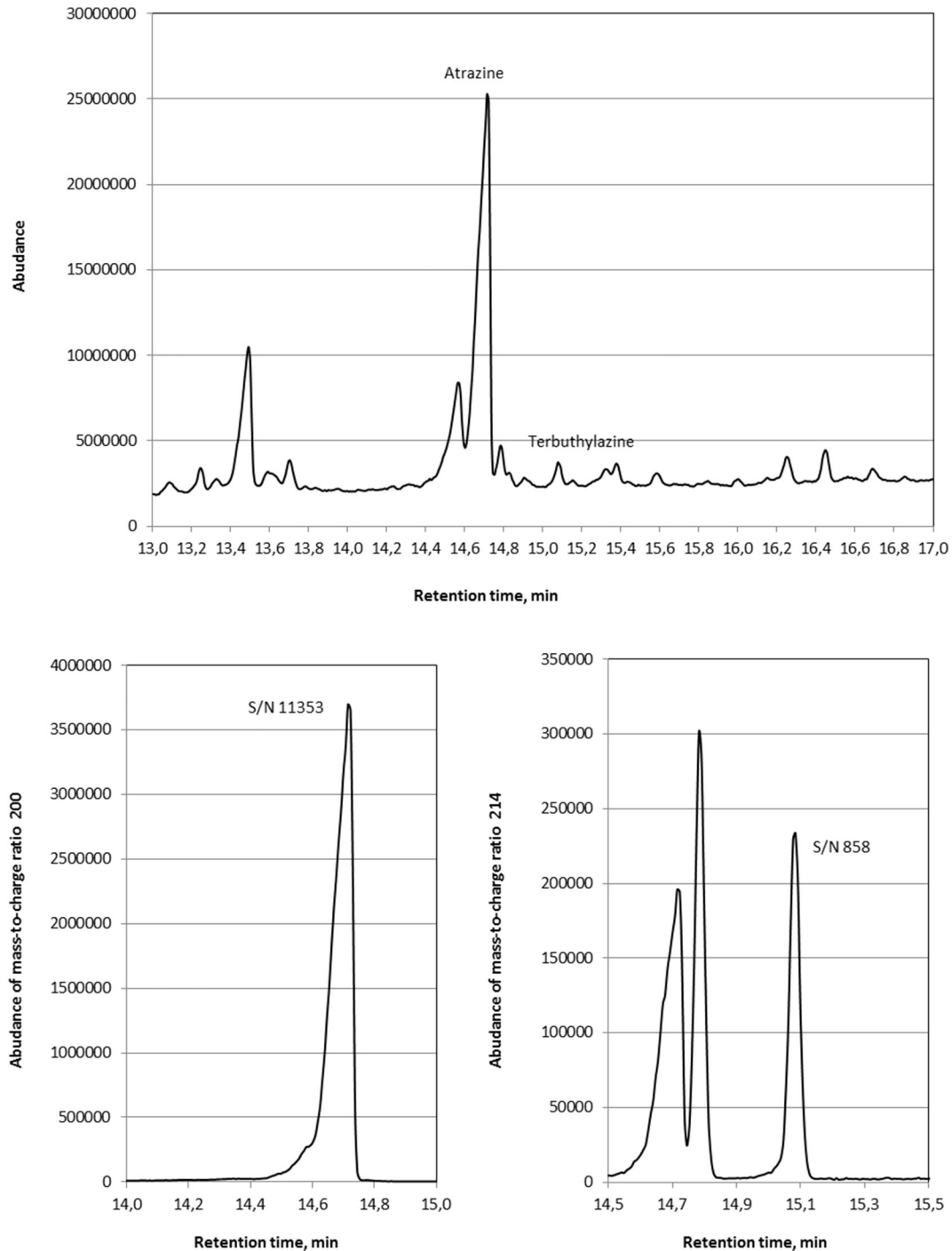


Fig. 3. Typical GC-MS total ion chromatogram with retention times and abundances for sum of mass-to-charge ratio (m/z) from 30 to 600 of extract from passive sampler. Below are extracted m/z of characteristic mass fragments for two detected pesticides. Sampling point IEILD-2 (exposure 15.9.2010–8.3.2011) with stable, low concentrations of atrazine and terbuthylazine (sampling date 20.9.2010: atrazine 0.060 $\mu\text{g/L}$ and terbuthylazine 0.0018 $\mu\text{g/L}$; sampling date 8.3.2011: atrazine 0.057 $\mu\text{g/L}$ and terbuthylazine 0.0018 $\mu\text{g/L}$). Below are extracted mass fragments m/z 200 of atrazine (at 14.7 min) and m/z 214 of terbuthylazine (at 15.1 min). Values of S/N presents signal to noise ratio.

A factor is a weighted combination of variables that is defined in such a way that the variance attached to it is maximized. The variance attached to a factor is described by the factor's eigenvalue. An eigenvalue indicates a measure of the significance of the factor: factors with the highest eigenvalues are the most significant. Eigenvalues of 1.0 or higher are considered significant (Kim and Mueller, 1978). The output of factor analysis is a list of significant factors, each of them grouping several variables – in our case, studied pollutants. Once the factors have been determined, factor scores can be calculated for each observation by a matrix multiplication of the factor score coefficient with standardized data. Factor scores determine which factor influenced the

variation in the hydrochemistry of the aquifer at the point where the sample was taken (Dalton and Upchurch, 1978). If the factor score at a given location is higher than 1, this indicates a significant control of the source represented by the factor to the hydrochemistry. A negative factor score (< -1) on the other hand indicates little or no contribution of the factor to the hydrochemistry (Prasanna et al., 2010).

3.3.4. Hierarchical cluster analysis

Hierarchical cluster analysis is one of a series of multivariate methods which find groups of the data. Hierarchical clustering first joins the most similar observations, and then successively the next

ones. The levels of similarity at which observations are grouped are used to construct dendrogram. A low distance shows that the two objects are similar, while a large distance indicates dissimilarity (Suvedha et al., 2009). In this study the hierarchical cluster analysis has been used for verifying the results obtained by factor analysis, made on the same data set as used for factor analysis. Therefore, for similarity measure between organic pollutants the polychoric correlation and weighted pair-group method were used.

4. Results

4.1. Selection of compounds

In total, 161 organic compounds were identified in the first, and 166 in the second sampling season (Mali and Auersperger, 2013, 2014). Of all identified compounds the 12 most frequently observed in groundwater at the studied sampling points were selected for more detailed analysis: caffeine, carbamazepine, atrazine, desethyl-atrazine, terbuthylazine, desethyl-terbuthylazine, metolachlor, simazine, 2,4-dimethyl-2H-benzotriazol, gibberellin A9, trichloroethene and tetrachloroethene (Table 1).

Depending on the nature of the substances, the selected organic compounds were divided into several groups. The first group includes pharmaceuticals and compounds in personal care products that represent an explicitly urban influence on groundwater pollution. Pharmaceuticals (carbamazepine, caffeine) accumulated in the samplers are mainly indicators of domestic sewage and indirectly, of urban areas as they enter the environment with human and animal excrement (Poynton and Vulpe, 2009), while 2,4-dimethyl-2H-benzotriazole most probably originates in the form of corrosion inhibitors, antifreezes, UV filters or biocides (Kloepfer et al., 2004). Caffeine is a good indicator of 'fresh' contamination as it decomposes quickly and remains in groundwater only for a short time, while carbamazepine is very stable and remains for a long time (Seiler et al., 1999). Pharmaceuticals, urban, and industrial pollutants reach groundwater by leaching from the sewage system, effluents from wastewater treatment plants, leaching from municipal landfills, storage tanks and other effluents in the soil (e.g. septic tanks) (Stuart et al., 2012). Interaction between surface water and groundwater is also important for groundwater pollution. Most municipal and industrial effluents are, after cleaning, discharged into surface water, which is then infiltrated into the groundwater (Hamscher and Hartung, 2008).

The second group comprises pesticides, which are largely indicators of the presence of agriculture. Pesticides indicate contamination by agriculture as well as other applications in the city (weed control). These pesticides are herbicides and are used for the control of pests, weeds and plant diseases. Pesticides often enter the environment through their application in agriculture; they reach the unsaturated zone from agricultural areas and come via groundwater to the consumer of drinking water. They occur in two forms, as primary compounds as well as their degradation products. They are quite stable in nature, since they can remain in water for several months (Lapworth and Gooddy, 2006). The use of atrazine in agriculture was banned in 2003, and was largely replaced by terbuthylazine (Heri et al., 2008). Atrazine represents a major problem, as it still occurs in the water (Ambrožič et al., 2008), from old burdens or unauthorized use of old stocks.

The third group comprises the volatile aliphatic halogenated hydrocarbons, which are indicative of industrial and urban contamination sources (Vogel and McCarty, 1985). The main sources are old industrial pollution loads and active industrial effluents (Ritter et al., 2002).

4.2. Basic statistics

4.2.1. Descriptive statistics

The descriptive statistics of recorded intensities of selected pollutants are presented in Table 2. Their median values of 54 observations range from 0 to 3. Low median values (0 and 1) are found in pharmaceuticals and personal care product compounds. Median values of pesticides are higher, ranging between 1 and 2. The highest median values are observed in volatile aliphatic halogenated hydrocarbons, 2 and 3.

4.2.2. Kruskal-Wallis test of ranks

Results of the Kruskal-Wallis test are listed in Table 3. The results revealed significant differences between sampling campaigns for carbamazepine, caffeine, 2,4-dimethyl-2H-benzotriazol and desethylterbuthylazine, at the 99% confidence level ($\alpha = 0.01$). Other constituents within this group do not show statistically significant differences at a 95% confidence level ($\alpha = 0.05$).

Among 16 sampling points, statistically significant differences at 99% confidence level ($\alpha = 0.01$) were found for 2,4-dimethyl-2H-benzotriazol, atrazine, desethyl-atrazine, metolachlor, simazine, gibberellin A9 and trichloroethene, and at 95% confidence level ($\alpha = 0.05$) for terbuthylazine, desethyl-terbuthylazine and tetrachloroethene. Other

Table 1

List of selected organic compounds detected in groundwater at the Vrbanški plateau aquifer, their sources and residence time in water.

CAS no.	Substance	Source	Residence time in water (days)
#1912-24-9	Atrazine	Herbicide	206–710 ^a
#6190-65-4	Desethylatrazine	Degradation product of herbicide atrazine	
#5915-41-3	Terbuthylazine	Herbicide	263–366 ^b
#30125-63-4	Desethylterbuthylazine	Degradation product of herbicide terbuthylazine	
#51218-45-2	Metolachlor	Herbicide	>200 in highly acidic water, 97 in highly alkaline waters ^c
#122-34-9	Simazine	Herbicide	330 ^d
#427-77-0	Gibberellin A9	Natural fungicide	
#58-08-2	Caffeine	Urban waste waters	1–12 ^e
#298-46-4	Carbamazepine	Drug	328 ^f
#16584-00-2	2,4-Dimethyl-2H-benzotriazole	Degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors	
#127-18-4	Tetrachloroethene	Dry cleaning, degreasing, industrial solvent	150–200 ^g
#79-01-6	Trichloroethene	Dry cleaning, degreasing, industrial solvent	1653 ^h

CAS no. is a unique numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance (CAS, 2016).

^a Schwab et al. (2006).

^b Navarro et al. (2004).

^c Kumar et al. (2013).

^d Spurlock et al. (2006).

^e Zoeteman et al. (1980) and Buerge et al. (2003).

^f Löffler et al. (2005).

^g Nelson (1997).

^h GSI Environmental (n.d.).

Table 2

Descriptive statistics of considered pollutants in the groundwater of the Vrbanški plateau aquifer, expressed as intensity and ranked on a scale of 0 to 5.

	Valid N	Median	Min	Max	10 Perc.	90 Perc.
<i>Pharmaceuticals, compounds in personal care products</i>						
Carbamazepine	54	0	0	4	0	2
Caffeine	54	1	0	3	0	1
2,4-Dimethyl-2H-benzotriazol	54	1	0	5	0	3
<i>Pesticides</i>						
Atrazine	54	2	0	5	0	4
Desethyl-atrazine	54	1	0	4	0	3
Terbuthylazine	54	1	0	2	0	1
Desethyl-terbuthylazine	54	1	0	2	0	2
Metolachlor	54	1	0	5	0	3
Simazine	54	1	0	3	0	2
Gibberellin A9	54	1	0	3	0	2
<i>Volatile aliphatic halogenated hydrocarbons</i>						
Tetrachloroethene	54	3	0	5	2	5
Trichloroethene	54	2	0	5	2	5

Min – minimum; Max – maximum; 10 Perc. – 10th percentile; 90 Perc. – 90th percentile.

chemicals within this group do not show statistically significant differences at the 95% confidence level ($\alpha = 0.05$).

Significant differences were also found at four different locations for atrazine, desethyl-atrazine, terbuthylazine, metolachlor, simazine, gibberellin A9 and tetrachloroethene at 99% confidence level ($\alpha = 0.01$), and at 95% confidence level ($\alpha = 0.05$) for carbamazepine and desethyl-terbuthylazine. Other chemicals within this group do not show statistically significant differences at the 95% confidence level ($\alpha = 0.05$).

No statistically significant differences were found between three different sampling depths in the aquifer for all chemical parameters at the 95% confidence level ($\alpha = 0.05$) considered here.

4.2.3. Mann-Whitney U test

Results of the nonparametric Mann-Whitney U test for selected organic pollutants in groundwater between different groups of location are listed in Table 4. Mann-Whitney U test was done only to find differences between different groups of location for each pollutant in groundwater. The results between sampling campaigns are presented with Kruskal-Wallis test, since only two sampling campaign have been studied at the 95% confidence level ($\alpha = 0.05$). For finding differences

between three different sampling depths in the aquifer, Mann-Whitney U test has not been done, since no statistically significant differences were found for all chemical parameters based on Kruskal-Wallis test.

In general, the results show significant differences between Limbuš area and all other groups of locations for all selected organic pollutants except caffeine and 2,4-dimethyl-2H-benzotriazol at the 95% confidence level ($\alpha = 0.05$). Significant differences between Maribor City/Drava River and Tabor/Drava River areas are mainly found for pesticides which present old burdens (atrazine and desethyl-atrazine) and pesticides in use. Other organic pollutants within these groups of location do not show statistically significant differences at a 95% confidence level ($\alpha = 0.05$).

4.2.4. Polychoric correlation

Polychoric correlations for data are listed in Table 5 and show strength of linear relationship between two variables marked at a significance level of $\alpha = 0.05$. In this study we assumed for interpretation that a coefficient of between 0.4 and 0.7 indicates moderate correlation, while coefficients between 0.7 and 1.0 indicate a strong correlation between variables.

Strong correlations ($r \geq 0.7$) are observed within the group of pesticides comprising terbuthylazine, desethyl-terbuthylazine, metolachlor, simazine and gibberellin A9. The volatile aliphatic halogenated hydrocarbon trichloroethene is also in strong correlation with all of the above-mentioned pesticides except desethyl-terbuthylazine. Strong correlations are also observed between trichloroethene and tetrachloroethene, carbamazepine and 2,4-dimethyl-2H-benzotriazol, and between atrazine and its degradation product desethyl-atrazine.

Moderate correlations ($0.4 \leq r < 0.7$) are found within the group of pharmaceuticals and compounds in personal care products: carbamazepine, caffeine and 2,4-dimethyl-2H-benzotriazol. Both carbamazepine and 2,4-dimethyl-2H-benzotriazol are in moderate correlation with pesticides and tetrachloroethene, while caffeine does not show a good correlation with any other parameter ($r \leq 0.4$). Also atrazine and desethyl-atrazine correlate closely with each pesticide and with both volatile aliphatic halogenated hydrocarbons. Moderate correlation is also observed between tetrachloroethene and each pesticide.

Weak correlations ($r \leq 0.4$) were found between trichloroethene and the group of pharmaceuticals and with the compounds in personal care products. Particularly interesting is the weak correlation between

Table 3

Results of the Kruskal-Wallis test for selected organic pollutants in the groundwater passive samples at the Vrbanški plateau aquifer between various studied levels (total $n = 54$, $df =$ degrees of freedom; F = critical value; Sig. = significance level).

	Sampling campaign (df = 1)		Sampling point (df = 15)		Location (df = 3)		Depth of sampling (df = 2)	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.
<i>Pharmaceuticals, compounds in personal care products</i>								
Carbamazepine	17.67**	0.000	20.49	0.154	11.22*	0.011	1.00	0.605
Caffeine	10.53**	0.001	22.00	0.108	3.74	0.291	0.11	0.945
2,4-Dimethyl-2H-benzotriazol	9.35**	0.002	32.76**	0.005	6.02	0.111	0.56	0.757
<i>Pesticides</i>								
Atrazine	1.01	0.314	41.46**	0.000	22.21**	0.000	3.16	0.206
Desethyl-atrazine	1.63	0.201	38.91**	0.001	20.52**	0.000	5.13	0.077
Terbuthylazine	2.27	0.132	25.78*	0.040	12.44**	0.006	2.05	0.359
Desethyl-terbuthylazine	10.27**	0.001	25.04*	0.050	8.95*	0.030	1.74	0.419
Metolachlor	0.01	0.928	41.12**	0.000	21.11**	0.000	0.61	0.738
Simazine	0.41	0.524	40.78**	0.000	15.90**	0.001	0.24	0.888
Gibberellin A9	0.16	0.690	43.23**	0.000	18.62**	0.000	2.64	0.267
<i>Volatile aliphatic halogenated hydrocarbons</i>								
Tetrachloroethene	1.28	0.258	30.33*	0.011	11.43**	0.010	0.80	0.670
Trichloroethene	0.21	0.251	37.01**	0.001	6.74	0.081	0.92	0.631

* Significance level of 0.05.

** Significance level of 0.01.

Table 4
Results of the Mann-Whitney *U* test for selected organic pollutants in the groundwater passive samples at the Vrbanški plateau aquifer between different locations (total $n = 54$). The significant differences at 95% confidence level ($\alpha = 0.05$) are marked as grey fields.

	Lim./City	Lim./Tab.	Lim./Drava	City/Tab.	City/Drava	Tab./Drava
Carbamazepine						
Caffeine						
2,4-Dimethyl-2H-benzotriazol						
Atrazine						
Desethyl-atrazine						
Metolachlor						
Simazine						
Terbutylazine						
Desethyl-terbutylazine						
Gibberellin A9						
Trichloroethene						
Tetrachloroethene						

Lim. – Limbuš area; City – Maribor City area; Tab. – Tabor area; Drava – near the Drava River.

simazine and atrazine, and between simazine and desethyl-atrazine, as they belong to the same group of pesticides and are no longer in use.

4.3. Factor analysis

Factor analysis was used to explore the type of contamination in groundwater. Because of the ordinal character of the data set, factor analysis was carried out using polychoric correlation.

A total of 54 observations and 12 variables were used for the analysis. The Varimax rotation technique was used to calculate factor loadings. Four factors were extracted due to the high percentage (13.3%) of total variance explained by the fourth factor, although only three factors have eigenvalues higher than 1. Four factors that define the 12 variable dataset account for 88.8% of the total data variation (Table 6). Factor F-1 explains the greatest amount of the total variance (36.7%) and 7.18 of the eigenvalues. This factor has high loadings of pesticides (terbutylazine, desethyl-terbutylazine, metolachlor, simazine and gibberellin A9). Also trichloroethene exhibits a high factor F-1 loading. The second factor F-2 accounts for 20.5% of the total variance and 1.4 of the eigenvalues and represents atrazine and its degradation product desethyl-atrazine. The third factor F-3 accounts for 18.3% of the total variance and 1.04 of the eigenvalue, and represents caffeine, carbamazepine and 2,4-dimethyl-2H-benzotriazol. Trichloroethene and tetrachloroethene are explained by the fourth factor F-4, which accounts for 13.3% of the total variance and 0.64 of the eigenvalue.

4.4. Hierarchical cluster analysis

Fig. 4 shows the results of hierarchical cluster analysis (HCA) presented as a dendrogram. A total of 54 observations and 12 variables were used for the analysis. Four major groups of pollutants were clustered, which correspond to the factors (Table 6), respectively. The similarity of the HCA to the factor analysis confirms the interpretations made using the factor analysis.

4.5. Seasonal variations of factors

The contribution of each factor at every sampling point (factor scores) was calculated for both sampling campaigns in order to examine the differences between sampling campaigns. Box-whisker plots show the distribution of factor scores in the two sampling campaigns for each factor (Fig. 5a–d). Like the Kruskal-Wallis test (Table 3), the box-whisker plots of factor scores also indicate the differences between two sampling campaigns. The results of the Kruskal-Wallis test revealed significant differences between two sampling campaigns and between sampling points for individual chemicals, while box-whisker plots of factor scores show differences between sampling campaigns for individual factors.

Fig. 5 shows that the median for F-1 scores in the first sampling campaign (summer period) is almost the same or lower than the median for the second sampling campaign (winter period), while median values for F-2 and F-3 are higher in the first period than in the second. On the contrary, F-4 shows higher score values in the first summer period compared to the second winter period.

4.6. Characteristics of sampling points

The natural and anthropogenic characteristics of pollution of each sampling point recharge area were assessed with respect to their factor scores. Based on previous isotopic studies of groundwater and hydrogeological conditions (Mali et al., 1995, 2003), a certain grouping of sampling points was observed (Table 7, Fig. 1). Group 1 (I) represents sampling points that are situated on the right bank of the Drava River and have no hydraulic connection with its waters. Groundwater at these sampling points is recharged by local infiltration of precipitation, and by inflows from surrounding hills. Group 2 (II) represents sampling points that are in hydraulic connection with the Drava River. The sampling points in group 3 (III) represent mixed waters recharged by the Drava River, the infiltration of precipitation, and by inflows from surrounding hills. Sampling points K-27, K-14, and P-1 are particularly interesting in this group with respect to their locations and hydrogeological conditions. Site K-27 is located along the Drava River, but its recharge area also extends below the river to the right bank. The next one, K-14, is located in the Maribor City and could be contaminated due to leakage of meteoric water from the roads, as was noted during the sampling. Since the piezometer P-1 is located near the pumping station, the groundwater is recharged from both sides (SW and SE) as part of the depression zone.

The average values of the summer and winter factor scores were calculated for each sampling point. Scatterplots (Fig. 6a–c) show very clear differences between factor scores of F-1 for each sampling point, which represents the influence of agricultural activity on groundwater chemistry, and the other three factors which represent the influence of old/past agricultural burdens (F-2), urban activities (F-3) and industrial impact (F-4). From the scatterplots it is evident that the widest range of factor scores is associated with factor F-2. The grouping of sampling points (Table 7) based on factor scores of F-1 is also clearly expressed in Fig. 6a–c, where values below -0.5 represent the sampling points of group II, and values above 0.75 the sampling points of group I. Values between -0.5 and 0.75 are typical of sampling points in group III. Two subgroups of sampling points could be isolated within group III with respect to their location and hydrogeological conditions. The first subgroup (IIIa) represents sampling points (V-1, HMZ-1 and KP-14) which are in hydraulic connection with the Drava River or meteoric water, while the second subgroup (IIIb) represents sampling points (KP-12, K-21, KP-2 and KP-8) located in the centre of the Maribor City.

Table 5
Results of the polychoric correlation between organic pollutants in the groundwater of the Vrbanski plateau aquifer ($n = 54$). Strong correlations are marked in bold and moderate correlations in italics at the 95% confidence level ($\alpha = 0.05$).

	Carbamazepine	Caffeine	2,4-Dimethyl-2H-benzotriazol	Atrazine	Desethyl-atrazine	Terbutylazine	Desethyl-terbutylazine	Metolachlor	Simazine	Gibberellin A9	Tetrachloroethene	Trichloroethene
Carbamazepine	1.00											
Caffeine	0.55	1.00										
2,4-Dimethyl-2H-benzotriazol	0.70	0.51	1.00									
Atrazine	0.55	0.04	0.44	1.00								
Desethyl-atrazine	0.46	-0.06	0.53	0.81	1.00							
Terbutylazine	0.48	0.25	0.62	0.50	0.64	1.00						
Desethyl-terbutylazine	0.68	0.32	0.68	0.57	0.61	0.87	1.00					
Metolachlor	0.62	0.21	0.65	0.52	0.63	0.86	0.87	1.00				
Simazine	0.46	0.23	0.48	0.34	0.37	0.77	0.77	0.78	1.00			
Gibberellin A9	0.62	0.36	0.67	0.55	0.65	0.86	0.89	0.90	0.75	1.00		
Tetrachloroethene	0.44	0.33	0.41	0.40	0.38	0.59	0.45	0.67	0.59	0.52	1.00	
Trichloroethene	0.18	0.00	0.36	0.55	0.53	0.76	0.62	0.72	0.71	0.71	0.74	1.00

Table 6

Results of factor analysis of 12 considered pollutants in groundwater in the Vrbanski plateau aquifer.

	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
Carbamazepine	0.32	0.43	0.75	0.03	0.85
Caffeine	0.08	-0.18	0.90	0.17	0.89
2,4-Dimethyl-2H-benzotriazol	0.47	0.37	0.64	0.02	0.76
Atrazine	0.20	0.90	0.12	0.23	0.90
Desethyl-atrazine	0.38	0.86	0.02	0.10	0.91
Terbutylazine	0.83	0.30	0.17	0.27	0.89
Desethyl-terbutylazine	0.84	0.35	0.32	0.05	0.79
Metolachlor	0.80	0.34	0.23	0.30	0.90
Simazine	0.84	0.03	0.15	0.34	0.84
Gibberellin A9	0.81	0.35	0.31	0.18	0.90
Tetrachloroethene	0.31	0.17	0.27	0.87	0.95
Trichloroethene	0.62	0.29	-0.16	0.66	0.93
Eigenvalue	7.18	1.40	1.04	0.64	
% of total variance	36.7	20.5	18.3	13.3	
Cumulative	36.7	57.2	75.5	88.8	

Bold values: loadings >0.6.

Italicized values: loadings $0.3 < x > 0.6$.

Transformation method: Varimax.

4.7. Seasonal variations at individual sampling points

On the basis of factor scores we also attempted to specify the characteristics of individual pollution sources at each sampling point during each sampling campaign. To this end the average values of factor scores of two sampling campaigns were calculated at each sampling point. The diagrams in Figs. 7–8 show the specific changes of factor scores between the two sampling campaigns. The arrow between sampling points indicates the direction of change from the summer to the winter period. The relations between factor scores of F-1 and F-2 for each sampling campaign and each sampling point are shown in Fig. 7. From Fig. 7 it is evident that values of F-2 are higher and those of F-1 lower in sampling points K-27, MFV-1, V-1 and HMZ-1 in the winter period. Sampling point P-1 also shows, to a smaller degree, increased values of F-2 and lower values of F-1 during the winter period. The group of sampling points IEILD-2, MTT-1, MV-2, and K-28 has increased F-1 values and decreased F-2 values.

Fig. 8 shows that F-3 values increase and F-4 values decrease in the winter period at all sampling points except HMZ-1, at which the value of F-4 becomes slightly elevated. In the group of sampling points MV-2, MTT-1, KP-14 and KP-12 a greater decrease of F-4 score values and an increase of F-3 score values are observed as at other sampling points.

5. Discussion

Sampling results show that the groundwater of the Vrbanski plateau aquifer is the most polluted with volatile halogenated aliphatic hydrocarbons, since the intensities are highest, while the intensities of pesticides and pharmaceutical compounds and personal care products are lower (see Table 2). The correlations between studied organic compounds (Table 5) could be explained by the use of these substances where human activities have a significant impact on groundwater quality. As expected, strong correlations are observed within the group of pesticides, since they belong to the group of herbicides. However, atrazine and desethyl-atrazine, which are also herbicides, form another individual group of pesticides. This could be explained as old burdens, since the application of atrazine on fields has been forbidden since 2003 (Ambrožič et al., 2008). Another interesting point is the moderate correlation of tetrachloroethene with pesticides and organic compounds typical of urban activities (carbamazepine, caffeine and 2,4-dimethyl-2H-benzotriazole), while the correlations between trichloroethene and pesticides are strong, but very poor with indicators of urban activities. Since both substances (trichloroethene,

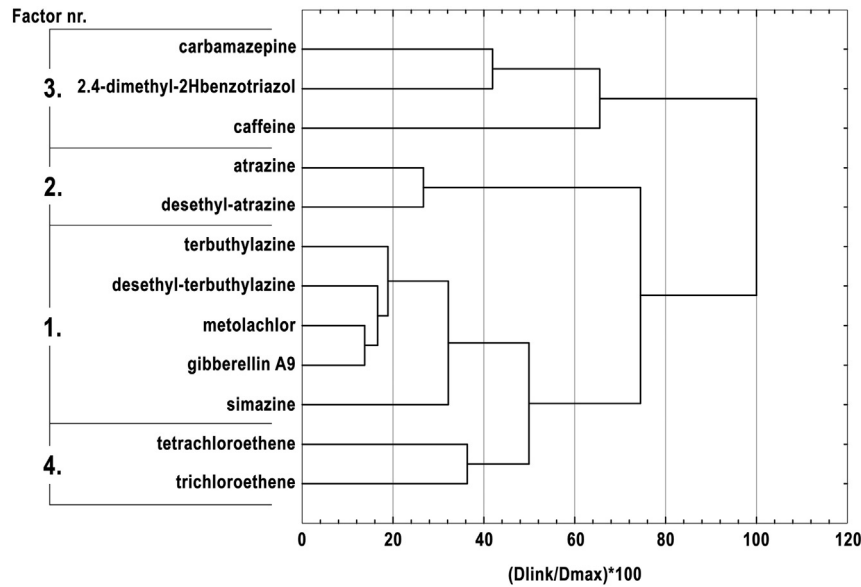


Fig. 4. Dendrogram of hierarchical cluster analysis classification between selected organic pollutants in groundwater in the Vrbanjski plateau aquifer. Four main groups were clustered, which correspond to the factors. Factor nr. – Factor number obtained by factor analysis.

tetrachloroethene) are typical indicators of industrial pollution (Vogel and McCarty, 1985), the various strengths of correlation may be explained in connection with land use. Based on the sampling results of pollutant intensities, trichloroethene occurs more often in agricultural areas, whereas the incidence of tetrachloroethene is more closely linked to the urban area. Correlations between pollutants are also confirmed by the results of factor analysis (Table 6) and hierarchical cluster analysis (Fig. 4), which extracts four groups from the sources mentioned above. Pesticides that originate from agricultural pollution are explained by factors F-1 and F-2. Factor F-2 mostly explains atrazine and desethyl-atrazine, and factor F-1 other pesticides that are currently in use. Both factors cumulatively explain 57.2% of the total variance. It can be concluded that contamination with pesticides is an essential problem of groundwater pollution in the area. Pesticides occur far more often as mixtures of multiple pesticide compounds than individually. They are likely used in intensive agriculture to control pests, weeds and plant diseases, as well as in urban environments where they are employed in city gardens, for weed control in parks and in areas with infrastructure such as railways (see Fig. 1) (Lapworth and Goody, 2006).

Irrespective of this, atrazine, with its high intensity and frequency (Mali and Auersperger, 2014) in groundwater still represents a major problem in the pesticide group. The loadings on factor F-3 generally indicate the pollution of groundwater from urban activities, such as leaching from sewage systems, effluents from wastewater treatment plants, and leaching from municipal landfills, cisterns and other effluents into the soil and further into the groundwater. Factor loadings show that caffeine is explained only by factor F-3, while carbamazepine and 2.4-dimethyl-2H-benzotriazole are also included with moderate loadings on factors F-1 and F-2. We could explain this connection by the influence of urban pollution from residential agglomerations in rural areas. Settlements on the outskirts of the Maribor City do not have a regulated sewage system. The absence of caffeine in groundwater is explained by its rapid decomposition (Zoeteman et al., 1980; Buerge et al., 2003) since being less persistent in groundwater than in surface water (Stuart et al., 2012). If caffeine is present in the groundwater, it is a sign of fresh contamination from an urban source (sewage). The other two, carbamazepine and 2.4-dimethyl-2H-benzotriazole, are more resistant to microbial degradation in the environment and are highly persistent in

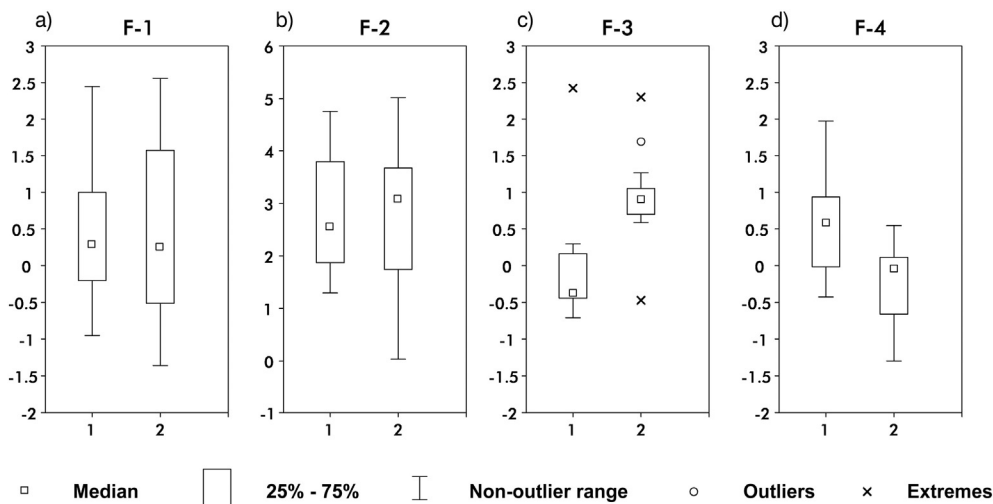


Fig. 5. (a–d) Box and whisker plots of the factor scores according to sampling campaigns for individual factors (1 summer ($n = 28$) and 2 winter ($n = 26$) campaigns).

Table 7
Grouping of sampling points based on their hydrogeological characteristics in groundwater at the Vrbanški plateau aquifer.

Group	Hydraulic connection with the Drava River	Sampling points
I	No hydraulic connection	M-V2, MTT-1, DEM-1, IEILD-2
II	In hydraulic connection	MFV-1, K-28
III	Mixed waters	K-27, P-1, HMZ-1, V-1, KP-14, KP-12, K-21, KP-2, KP-8

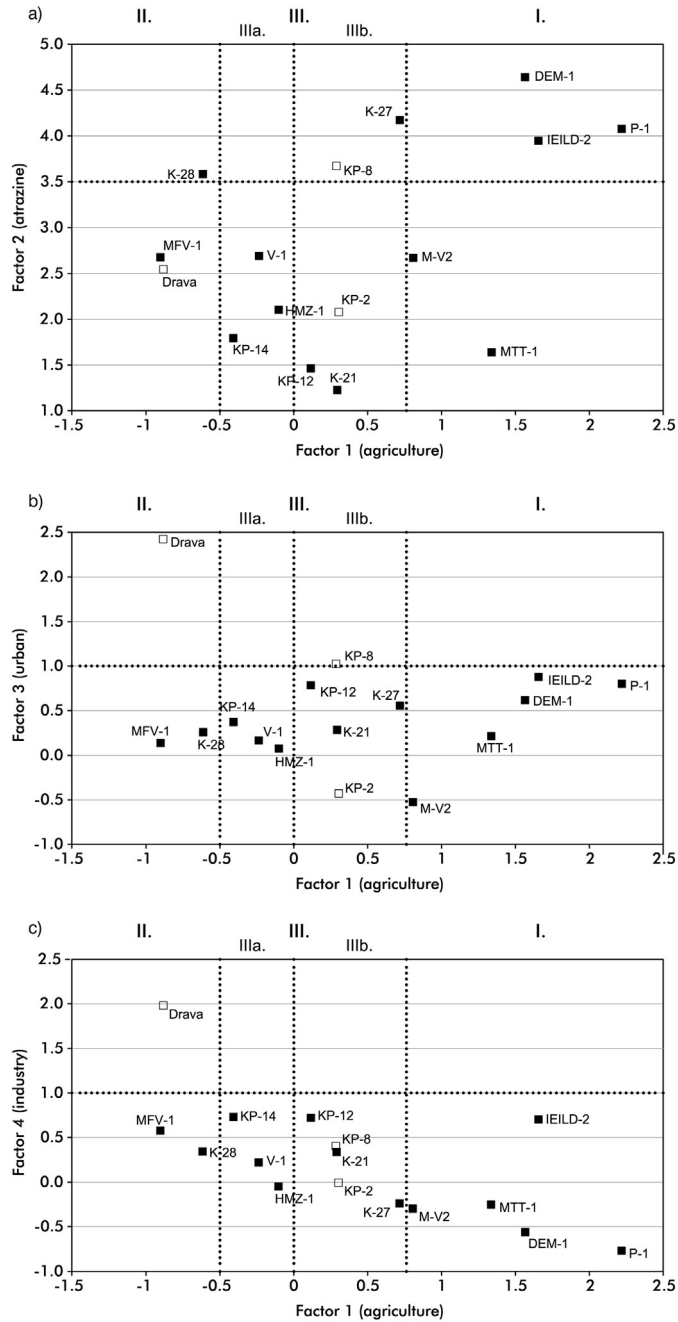


Fig. 6. (a–c) Bivariate plots of factors with the average factor scores at each sampling point. Groups of sampling points are marked by Roman numerals. Black squares are samples from both sampling campaigns, and white squares are samples from only one sampling campaign.

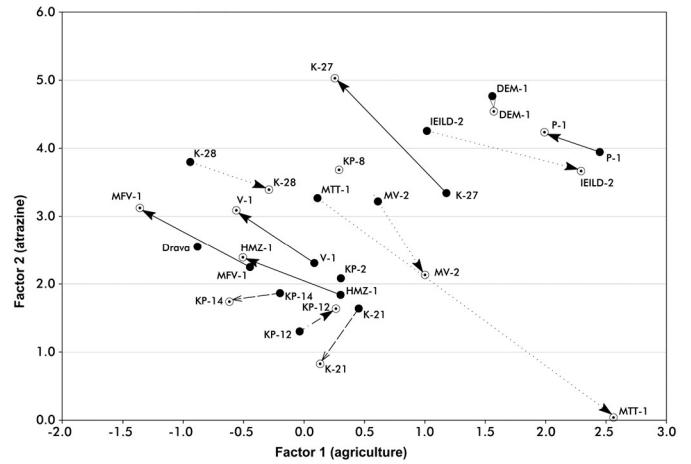


Fig. 7. Diagram of F-1 and F-2 factor scores according to sampling campaigns at each sampling point, with arrows pointing from the summer (black circles) to winter (empty circles with dot) situation.

groundwater (Fram and Belitz, 2011; Liu et al., 2013), as are the pesticides (Aelion and Mathur, 2001; Caracciolo et al., 2005), and may remain in groundwater for a long time.

Characteristics of factor F-4 are attributed to industrial activities. These contaminants enter the surface water with effluents from the sewage system and from sources of industrial discharge, and are further transported into groundwater after mixing with surface water (Squillace and Moran, 2007). It is interesting that trichloroethene occurs with relative high factor loadings on two factors, F-1 and F-4, which can indicate the appearance of different types of contamination in the same area. Characteristically all four factors indicate the influence of human activities as one of the most important threats to groundwater chemical quality.

In general, results of the Kruskal-Wallis ranking test show significant differences (Sig. level 0.01 or 0.05) between two sampling campaigns for pharmaceuticals and compounds in personal care products (Table 3). We could conclude that seasonal conditions reflect the intensity of urban pollution in groundwater, while pesticides and volatile aliphatic halogenated hydrocarbons show significant differences between sampling points. The differences between sampling campaigns of each factor loading are visualized by Box-Whisker plots (Fig. 5), which show the distribution of factor scores at all sampling points. The scores of the first two factors show a wide range of values in both sampling campaigns, but their distribution range is wider in the second sampling campaign (Fig. 5a, b). The median of F-1 in the first sampling campaign

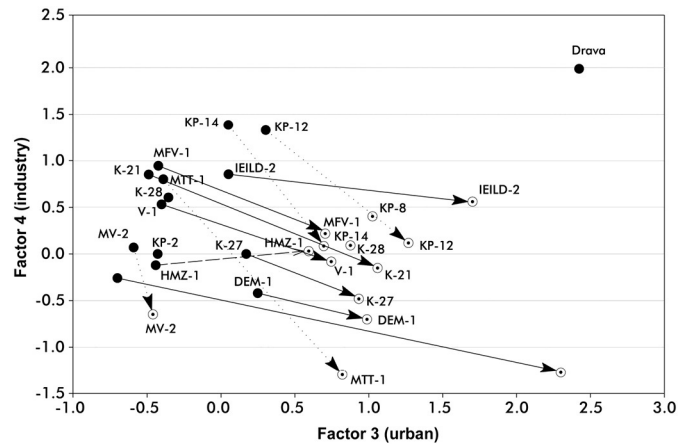


Fig. 8. Diagram of F-3 and F-4 the factor scores according to sampling campaigns at each sampling point, with arrows pointing from the summer (black circles) to winter (empty circles with dot) situation.

(summer period) is almost identical to or lower than the median in the second sampling campaign (winter period) due to changes in meteorological conditions over the year and differences in agricultural activities. Precipitation events during the summer period were more abundant (SEA, 2013), as was the application of pesticides higher (Kreuger, 1998). Depending on the amount of precipitation, volatilization of pesticides, uptake by plants, runoff into rivers and microbial and abiotic degradation, pesticide leaching is reflected in groundwater quality (Bloomfield et al., 2006). The winter period is characterized by lower precipitation volumes (SEA, 2013), the presence of snow cover, lower volatilization and higher moisture content of the unsaturated zone. Also the application of pesticides on agricultural land is negligible; therefore, leaching of pesticides into groundwater is smaller and concentrations of pesticides in groundwater decrease (Bloomfield et al., 2006). On the other hand, the median value of F-2 is lower in summer than in winter due to old burdens of the very persistent atrazine and desethyl-atrazine in the soil. Further, due to meteorological conditions in winter and a hydraulic connection with the Drava River, with reduced dilution and biodegradation, these higher concentrations in the groundwater are significant (Bloomfield et al., 2006). The highest variation between the sampling campaigns is reflected by scores of factor F-3.

Factor scores of F-3 are lower in the first sampling campaign than in the second one (Fig. 5c). We assume that sewer leakage is constant throughout the year, as well as input from this source into groundwater. But due to the lower precipitation volumes in winter, the dilution is smaller, leading to higher values of urban indicators in groundwater (Clara et al., 2004). On the other hand, factor F-4 shows higher factor score values in the first sampling campaign compared to the second winter period (Fig. 5d). Tetrachloroethene and trichloroethene, which are mainly associated with F-4, are very persistent pollutants of industrial origin in the oxic groundwaters of shallow aquifers (Squillace and Moran, 2007). The marginally higher median value in the summer period can be explained by increased leaching from industrial sources of groundwater pollution and discharges from industrial plants, due to greater precipitation volumes and further recharge of groundwater, hastening transport through the unsaturated zone and reducing the chance of degradation (Squillace and Moran, 2007). Similar characteristics of seasonal variations were also observed at individual sampling points described below.

Each group of sampling points could be described using a combination of the characteristics of the four factors employed here. Fig. 6a shows the plot of F-1 and F-2 factor scores for each sampling point. Scores of F-2 above 3.5 represent sampling points of very intensive gardening and agricultural activities in their recharge areas, while sampling points with values below 3.5 indicate less intensive activity. Also, two subgroups of sampling points with F-2 values above 3.5 can be isolated based on their location in the study area and human activities in recharge areas (Fig. 1). The first subgroup comprises points DEM-1 and IEILD-2 in the Limbuš area, which are characterized by high F-1 (>1.5) and F-2 (>3.5) values and by particularly intensive agricultural activity in the recharge area. Similar factor scores are also observed in point P-1 (group III). The second subgroup contains sampling points K-28, KP-8 and K-27, all of which are located in the centre of the Maribor City, and have intensive gardening in recharge areas. These sampling points belong to groups II and III. Based on concurrent quantitative monitoring data very similar pesticides concentrations were recorded at these sampling points (Koroša et al., 2016).

At sampling points DEM-1 and IEILD-2 also the impact of unregulated sewerage has been observed, with F-3 factor scores above 0.5 (Fig. 6b). Carbamazepine and caffeine concentrations in groundwater are the main detectable pollutants from urban sources at these sampling points (Koroša et al., 2016). Fig. 6c shows that the F-4 factor scores at IEILD-2 show the appreciable influence of industry on groundwater chemistry.

Sampling points MTT-1 and M-V2 have abandoned industrial objects as well as an industrial railway station in their recharge areas

(Fig. 1). At these sampling points lower F-3 (−0.5–0.5) and F-4 values (<0.5), and higher F-1 (>0.5) values are also observed owing to the presence of pesticides (Koroša et al., 2016) and trichloroethene (National laboratory of health, environment and food, unpublished data), as mentioned previously.

Group II sampling points have low factor scores of F-1 (<−0.5) and moderate F-2 (2.0–3.5) values (Fig. 6a). Factor scores of F-3 and F-4 are also low at sampling points MFV-1 and K-28 (Fig. 6b, c). As expected, the highest F-3 (2.5) values are observed in the Drava River site, due to all indicators of urban pollution, especially caffeine, and F-4 (2.0) values, possibly due to contamination with chlorinated solvents. These contaminants enter the surface water (Drava River) with effluents from the sewage system and industrial discharges, and are further transported into groundwater after mixing with surface water. Results coincide entirely with the results of data from quantitative monitoring (Koroša et al., 2016), where the highest concentrations of caffeine are present in the Drava River and where concentrations of pesticides at these points are insignificant.

Sampling points of group III (KP-14, KP-12, K-21, KP-2 and KP-8), with the presence of all pollutants considered herein, are located in the centre of the Maribor City and present the area with mixed recharge waters. The F-1 scores range between the other two groups of sampling points, while the values of other factors show similar scores (Fig. 6). We could conclude that the influence of urban and agricultural activities in this part of the research area is considerable, whereas the impact of industry does not affect the groundwater quality in terms of particularly high concentrations of pollutants. From Fig. 6 it is evident that the main influences on groundwater quality at K-27 are gardening, and pollution from some pesticides and trichloroethene in the recharge area, as indicated by the high F-1 and F-2 scores, and lower F-3 and F-4 scores. From the qualitative monitoring data with passive sampling also urban pollution is significant. The highest intensities in groundwater are found to be 2,4-dimethyl-2H-benzotriazole. The results of different factor values have been confirmed by comparing them with quantitative monitoring data (Koroša et al., 2016).

Based on the average values of factor scores also the characteristics of individual pollution sources at each sampling point during each sampling campaign were determined (Figs. 7 and 8). We assumed that the F-1 and F-2 scores (Fig. 7) at all sampling points would be lower in the winter period due to seasonal variations, as was previously presented. However, this is not entirely the case. Fig. 7 shows increased F-2 values and decreased F-1 values at sampling points P-1, K-27, MFV-1, V-1 and HMZ-1 in the winter period. On the other hand, the group of sampling points IEILD-2, MTT-1, MV-2, and K-28 indicates increased F-1 values and decreased F-2 values. Increased F-1 values could be explained by the higher concentration of trichloroethene, which is largely used in the recharge areas of these sampling points in combination with pesticides, which are also present in high concentrations in groundwater, largely owing to the presence of simazine, metolachlor and desethylterbuthylazine (Koroša et al., 2016).

Increased F-3 values and decreased F-4 values in the winter period at all sampling points except HMZ-1 (Fig. 8), could also be explained by characteristic seasonal variations in factors as already presented before. A greater drop in F-4 and a rise in F-3 score values compared to other sampling points is observed in the group of sampling points MV-2, MTT-1, KP-14 and KP-12. These could be explained by their specific locations, as MV-2 and MTT-1 are located directly in the area of an abandoned industrial production zone with a high likelihood of contamination from industrial sources, while KP-14 and KP-12 lie within the Maribor City area, where the influence of chlorinated solvents from roads is appreciable.

6. Conclusion

The aim of the presented study was to assess the applicability of merging passive sampler techniques with statistical methods to assess

groundwater quality, with a view to improving groundwater management. The objective of the research was to determine, using passive sampling techniques, whether contamination from anthropogenic sources currently occurs in groundwater from the gravel aquifer of the Vrbanški plateau, and to further determine the origin of these contaminants as well as the related seasonal variations, depending on the type of activity present, using multivariate statistical analysis.

In this study the 12 most common or frequently identified organic pollutants in the groundwater from the Vrbanški plateau aquifer were included in the statistical analysis. With regard to the origin of contamination, these pollutants can be divided into several groups: pesticides, pharmaceuticals and compounds found in personal care products, and volatile aliphatic halogenated hydrocarbons. Based on the approach of polychoric correlation, strong correlations were observed within the group of pesticides, and between volatile aliphatic halogenated hydrocarbons and pesticides. Moderate correlations were observed within the group of pharmaceuticals and compounds of personal care products as well as between tetrachloroethene and each of the pesticides. These associations between pollutants were also confirmed and detailed using factor analysis.

Results of the study, as summarized by statistical factor analysis and hierarchical cluster analysis, show that groundwater contains the 12 organic pollutants studied herein from four sources: pesticides from agriculture (F-1) and old agricultural burdens (F-2), pharmaceuticals and compounds in personal care products derived from urban activities (F-3), and volatile aliphatic halogenated hydrocarbons as indicators of industry (F-4). Based on similar results of both methods the interpretation made using factor analysis could be confirmed.

The results of factor analysis also revealed differences between the sampling campaigns performed in summer and winter at individual sampling points. The dynamics of individual pollutants in groundwater depends on the meteorological conditions related to each sampling campaign and the various human activities in recharge areas. The influence of pollution from agriculture is almost the same or a little higher in the summer period, while the impact of atrazine and desethyl-atrazine is lower in the summer period. The results for pollutants of urban origin are similar, with higher concentrations of organic compounds in the winter period, whereas the influence of industrial pollutants on groundwater pollution is lower in the winter.

Based on factor scores, the dynamics of groundwater and pollutants, and land use, differences at different sampling points within each sampling campaign could be observed. Groundwater at sampling points in group I (IEILD-2, DEM-1, MTT-1 and M-V2) is recharged mainly by local infiltration of precipitation and is mostly polluted with contaminants from agriculture, industrial sources, and less from urban sources. Groundwater at sampling points in group II (MFV-1 and K-28) is hydraulically connected with the surface water (Drava River), and contains less pollutants like atrazine and desethylatrazine – except at the Drava River, where it is more polluted with contaminants from urban and industrial sources. Sampling points in group III (K-27, P-1, HMZ-1, V-1, KP-14, KP-12, K-21, KP-2 and KP-8) are characterized by mixed waters and are affected by contamination from various sources (agriculture, urban and industry).

The passive sampling technique has proved to be a useful monitoring tool for assessing groundwater quality, due to possibility of studying of a wider range of chemical parameters over longer sampling periods and the elimination of extreme variations. Using this approach provides a more general indication of groundwater status than can be obtained using conventional techniques. Factor analysis has been found to be an effective tool with which to interpret the possible origin of groundwater pollution, even for results on the ordinal scale obtained through passive sampling. By interpreting the extracted factors, the origin of the substances in question can be related to various sources. The combination of both methods has proved to be a reliable approach, as the results of this research are supported by the data from the quantitative monitoring of pollutants in groundwater at the Vrbanški plateau

aquifer. This approach presents a cheaper and more effective monitoring design model than the commonly used quantitative techniques employed for the purposes of assessing groundwater quality.

The results obtained will serve as a basis for the further planning of groundwater quality monitoring designs, the exploration of aquifers for drinking water supply, and additionally for the planning of water resource protection measures. Further, quantitative results will also serve as the basis with which to improve hydrogeological conceptual models for aquifers by enabling more accurate simulations of groundwater dynamics and the migration of pollutants in aquifers, which in turn will also contribute to more effective management of groundwater resources. However, the future work should focus on improving of passive samplers and developing of analytical methods, which will obtain the actual concentrations of pollutants in groundwater, and will present a basis for better insight and understanding of groundwater quality status.

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