

## Research article

## Control of organic contaminants in groundwater by passive sampling and multivariate statistical analysis

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## ABSTRACT

Organic contaminants in groundwater are among the most challenging chemical compound contaminants today, particularly when it comes to understanding their occurrence, origin, and relations in groundwater, as well as the transport processes, fate, and environmental impacts involved. This paper presents the use of active carbon fibre (AFC) passive sampling and multivariate statistical processing of the results to predict the possible occurrence of organic compounds (OCs) in groundwater and to determine the origin of various anthropogenic activity. This study aims to deepen our knowledge on the control of OCs in groundwater by introducing a multi-analytical and multi-elemental holistic approach, using the Dravsko polje aquifer, the largest intergranular aquifer in Slovenia, as an example. The occurrence of OCs in groundwater was determined by means of ACFs and compared against the characteristics of the recharge area and the type of compounds detected. We combined hierarchical cluster analysis (HCA) and principal component analysis (PCA) to identify the relationship between different OCs in groundwater. The relationships between their occurrence, environmental setting and type of compound were determined using multiple linear regression (MLR). From the total of 343 organic compounds detected using passive sampling, 47 were included in further statistical analysis. MLR shows that the environmental setting is one of the most important factors affecting the different types of pollutants in groundwater. MLR models were calculated for different sources of pollution (agricultural, urban, and industrial) based on the environmental setting, land use, agglomeration, infrastructure networks, and hydrogeological characteristics of the aquifer. By means of HCA and PCA, we identified the relationships between different OCs in groundwater. As expected, the strongest correlations were found between primary compounds and their degradation products (e.g. atrazine and desethylatrazine) and compounds of similar use (e.g. atrazine and propazine, also desethylatrazine and propazine, atrazine and simazine). Some of them were also found to have a similar molecular structure (e.g. palmitic and stearic acid, 5-methoxygramine and 5-methoxytryptamine). The use of the same substances in different environments (agricultural/urban) makes them markers of both (different) origins. Therefore, it is particularly important to determine the combination of markers of different origin using multivariate statistical methods, especially in the case of mixed land use. This study identifies the main factors influencing the distribution of groundwater OCs and thus contributes to a more comprehensive understanding of the vulnerability of shallow groundwater to surface-derived contamination in similar environments.

## 1. Introduction

Groundwater is the largest source of drinking water in the world; and chronic toxicity resulting from low concentrations of organic compounds (OCs) in groundwater is an issue of growing concern and importance (Bunting et al., 2021). Along with other pollutants, organic compounds have been recognised as an important contributing factor to the global environmental pollution (Lapworth et al., 2012; Stuart et al., 2012). The number of OCs in groundwater increases substantially with

several million metabolites and degradation products of parent compounds. This group includes personal care products, pharmaceutical residues, pesticides, veterinary products, food additives, nanomaterials, and industrial compounds (Lapworth et al., 2015; Sorensen et al., 2015; Manamsa et al., 2016; Koroša et al., 2016; Mali et al., 2017). In addition to traditional organic pollutants (e.g. pesticides, aromatics, and halogenated solvents), research attention has recently come to focus on the detection of pharmaceuticals and other persistent chemicals in the environment (Lapworth et al., 2018a; Pinasseau et al., 2019a; Kiefer

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et al., 2019; Bunting et al., 2021; Richards et al., 2021).

As a growing number of contaminants are included in regulation schemes (Water Framework Directive WFD (2000/60/EC); GWWL (Voluntary Groundwater Watch List) (CIS Working Group Groundwater, 2019), it is important to understand their occurrence, movement, fate, and impact. Furthermore, we need to understand what data is available that could help improve our understanding of OCs in groundwater. Questions regarding their effect, toxicity, movement in the subsurface and unsaturated zones (UZ) make the process of regulating their use more challenging. The presence of contaminants of increasing concern in groundwater is closely associated with human activity, and many such contaminants have been detected at concentrations higher than expected. The occurrence and persistence of individual compounds in the environment depend on their respective physical-chemical properties, organic matter content (soil and unsaturated zone), total loading, redox conditions, and groundwater residence time (Lapworth et al., 2018a; Koroša et al., 2020).

Lapworth et al. (2018b) highlight significant shortcomings in water policy and emphasise the need for a coordinated approach across the EU to assess the contaminants of emerging concern, especially in the groundwater environment. Collaboration in the form of collecting evidence on OCs will help inform and drive policy on this topic and help develop a EU-wide regulatory framework for groundwater (Lapworth et al., 2018b). The European Commission's Groundwater Directive (2006/118/EC) sets out to "prevent and limit the input to groundwater of many contaminants of emerging concern." However, there are currently no formal regulations in place to control these contaminants and no obligation to monitor or report on them. In 2014, an amendment to Annex II of Directive 2006/118/EC stated that no new groundwater quality standards could be set for any pollutants due to insufficient information.

The monitoring programmes for groundwater that do exist are still largely based on the collection of spot samples. This approach provides a snapshot of contamination at a particular point in time and may therefore not be truly representative of the appertaining environmental conditions over time. More than a decade ago, passive sampling was introduced as an attractive alternative to the sampling of natural waters (Vrana et al., 2005; Alvarez et al., 2004; Vermeirssen et al., 2009; Van Metre et al., 2017; Charriau et al., 2016; Lissalde et al., 2016). In 2012, ISO 56637-23 was published as the first standard for passive sampling of surface waters, followed in 2014 by ASTM D7929-14 on passive sampling of groundwater. Compared to traditional sampling methods, passive sampling is less sensitive to accidental extreme variations in concentrations of organic pollutants in natural waters and allows for a simultaneous detection of a wide range of contaminants. A passive sampler can cover a long sampling period and integrate pollutant concentrations over time. Compared to conventional monitoring, the use of passive samplers can substantially reduce analytical costs; however, the validation procedure still remains a challenge (Vrana et al., 2014; Mali et al., 2017; Pinasseau et al., 2019b).

OCs in groundwater are traditionally categorised according to their use (Manamsa et al., 2016) rather than occurrence, transport, or impact on the environment. However, it is sometimes extremely difficult to assign certain compounds to a particular group, as they may belong to more than one category. The occurrence of OCs in groundwater is poorly characterised and understanding their temporal and spatial variation remains a priority. Many studies from around the world (Jerrett et al., 2010; Terzer et al., 2013; Li et al., 2016; Rostami et al., 2019) show that the spatial distribution of pollutants in groundwater is inferred through the use of general interpolation methods.

To prevent OCs from entering the groundwater, it is important to define their origin. A number of studies have been conducted to determine whether the concentration of OCs in groundwater can be associated to nearby land use (Lapworth et al., 2015; Li et al., 2021) and whether groundwater contamination originates from natural or anthropogenic sources. To define the source of contamination, several

factors need to be analysed simultaneously, including land use, hydrogeological conditions, and the occurrence and properties of individual OCs. When hydrogeochemical interpretation is combined with data on the geological and hydrogeological setting, multivariate statistical methods can contribute to a better understanding of groundwater flow in complex aquifer systems and the pollution they contain (Farnham et al., 2003; Stetzenbach et al., 2001). This paper presents the use of multivariate statistical methods on the results of ACF passive sampling to predict the potential occurrence of OCs in groundwater and to determine the origin of different types of anthropogenic activity. Multivariate statistical analysis has been successfully applied in a number of hydrogeochemical studies. It has been widely used in the assessment of hydrochemical datasets and has become a useful tool in the investigation of the main mechanisms affecting groundwater chemistry (Cloutier et al., 2008; Helstrup et al., 2007; Monjerezi et al., 2011). All the hydrogeochemical studies mentioned above demonstrate that multivariate statistical analysis is highly effective in classifying groundwater and identifying the most important mechanisms influencing groundwater chemistry. We combined hierarchical cluster analysis (HCA) and principal component analysis (PCA) to identify the relationship between different OCs in groundwater. The relationships between their occurrence, environmental setting, and chemical characteristics were determined using multiple linear regression (MLR). The aims of this study are: (1) to investigate the presence of organic pollutants in groundwater; (2) to define their anthropogenic origin; (3) to understand the links between OCs in groundwater; and (4) to evaluate the relationship between their occurrence in groundwater and the environmental conditions in the aquifer.

## 2. Site description

The present study was conducted in the Dravsko polje aquifer (Fig. 1), which is located in north-eastern Slovenia and is part of the Drava Basin groundwater body. It is one of the most important sources of drinking water in Slovenia. The study area covers 293 km<sup>2</sup> (Fig. 1). It is a Quaternary unconfined granular aquifer of high permeability, above which there are no low-permeability layers that could protect it against potential pollution. As a result, the aquifer is vulnerable to surface-derived contaminants. Based on previous research, the hydraulic conductivity of the gravel is estimated to be 5·10<sup>-4</sup> to 6·10<sup>-3</sup> m/s (Urbanc et al., 2014), with an average aquifer thickness of 20 m (Urbanc et al., 2014). The effective porosity of the aquifer is estimated to be 0.25, with a minimum of 0.15 based on the volumetric weight of the naturally moist material (Žlebnik, 1982). The average thickness of the UZ is estimated to be 8.35 m (Urbanc et al., 2014; Mali and Koroša, 2015) and the average thickness of the saturated zone (SZ) is 12.05 m (Urbanc et al., 2014). The general direction of groundwater flow is from west to east. Water from the aquifer is pumped at four water supply stations. The aquifer is recharged from the Drava River, from infiltration of precipitation, and from small streams in the surrounding Pohorje hills. The area has a moderate continental climate with a mean annual temperature of 8–12 °C and a typical continental precipitation regime. The mean annual rainfall is between 1200 and 1300 mm. Due to diverse land use and activities, the Dravsko polje aquifer is affected by agriculture, the urban environment and industrial activities. The area is largely agricultural (44%), followed by forested land (20%) and urban (populated) areas, which represent sources of both urban and industrial pollution (19%), while the rest of the area consists of meadows.

## 3. Materials and methods

### 3.1. Sampling design

First, an assessment of the representative nature of the sampling sites was performed based on the ISO standard "Guidelines for Groundwater Sampling" (ISO 5667-18: 2001), which provides for the sampling of

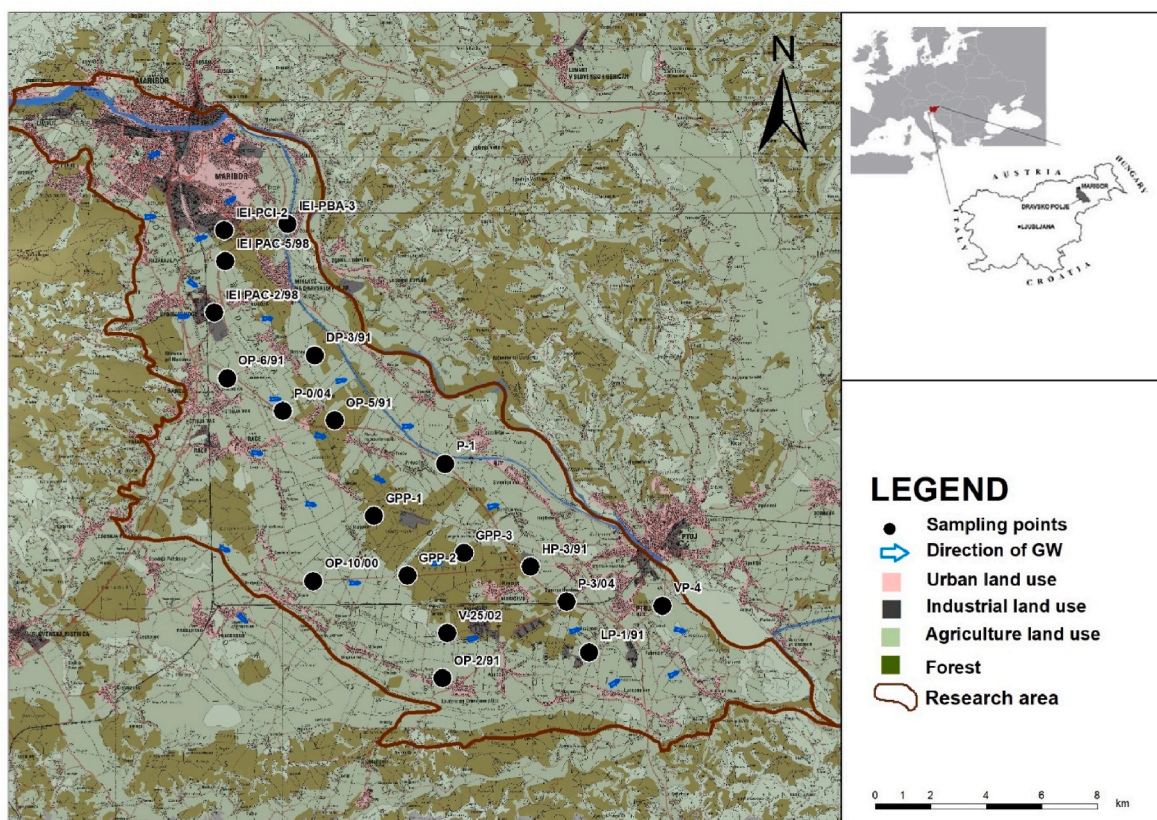


Fig. 1. Location of the Dravsko polje aquifer, map of the measuring points, land use, and groundwater flow direction.

groundwater in the UZ and in the SZ. For each sampling site, we reviewed the geographical location, data on the lithological profile, water flow direction, hydraulic permeability of the aquifer, aquifer depth, borehole construction data (drilling method, borehole material or well protection, depth and height of the filter, borehole volume) and protection and maintenance information of the sampling site.

The selected sampling sites covered the entire aquifer area of Dravsko polje. Sampling points were determined with a focus on regions with different types of intensive land use, and on specific geological and hydrogeological characteristics. Sampling was conducted from April 2013 to April 2015 during three campaigns over two different hydrogeological seasons: in summer, from April to October, and in winter, from October to April. OCs in groundwater were determined using the

passive sampling method with active carbon fibres. Passive sampling devices were installed into boreholes in the middle of the saturated zone (SZ) in filter areas to ensure groundwater flow into the borehole. Sampling was performed at 19 sampling sites. A total of 57 samples were collected over three campaigns; the locations are shown in Fig. 1.

### 3.2. Passive sampling

The preparation of passive samplers and chemical analyses were performed at the accredited laboratory of JP Vodovod-Kanalizacija d.o.o. in Slovenia, according to ISO 5667-23:2011 standards for sampling, and EPA 625 modified for chemical analysis. For passive sampling devices (Fig. 2), Zorflex® FM10 active carbon fibres (ACFs) from the

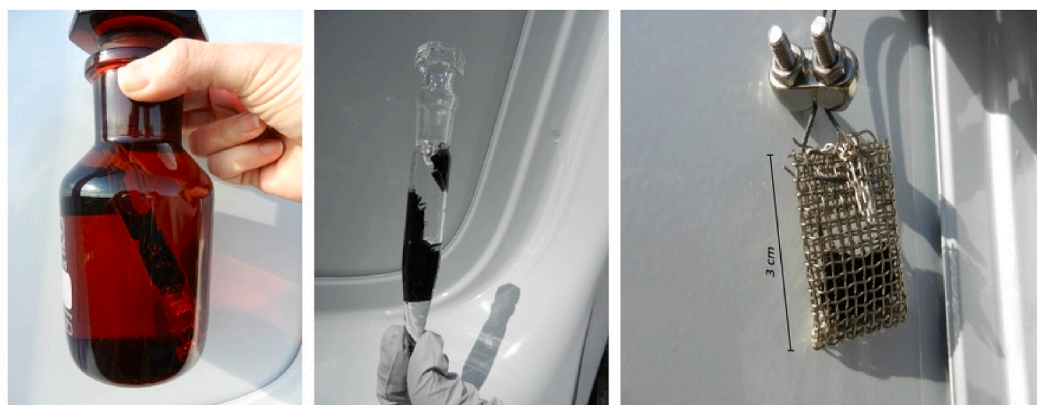


Fig. 2. Weighing bottles filled with UPW for the transport of passive samplers and stainless steel casing with ACFs (From left to right: brown weighing bottle filled with UPW for transport; sealed test tube with ACF; stainless steel meshes with ACF). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Calgon Carbon Corporation (Pittsburgh, USA) were used. ACFs were used as a strong and reliable adsorbent (Tadda et al., 2016). Properties of ACF can be also found in Li et al. (2014), Das et al. (2015), Karaer and Kaya (2016), Pingree et al. (2016), Wu et al. (2017), Shen et al. (2018). Before installation (3 cm<sup>2</sup> each), the ACFs were heated for 3 h at 300 °C in clean air derived from IQAir air purifiers. The ACFs were transferred to the test tubes using tweezers and were not allowed to cool. Before cooling, a few drops of ultrapure water (UPW) were added to generate steam. After that, the test tubes were filled with UPW and sealed. The sealed test tubes were put into a flask with UPW and active carbon on the bottom of the flask and then transported to the installation point. At the installation point, the stainless steel meshes were equipped with ACFs just before installation (Fig. 2). Stainless steel mesh was used for the passive sampler casing and was installed in a sufficiently deep borehole on a stainless steel wire.

After 6 months of exposure of the passive sampling devices, the ACFs were immediately transferred to the laboratory. The UPW from the weighing bottles was removed and the ACFs were dried in an oven at 100 °C for 1 h. 3 ml of extraction solvent (dichloromethane with 5% MeOH) containing the internal standards caffeine-D9, phenol-D5, estrone-D4 and cholesterol-D4 was added to the weighing bottles for the elution of compounds, which was performed in an ultrasonic bath for 30 min. 2 ml of the remaining extraction solvent was collected into a syringe, filtered into a chromatographic vial, and concentrated to approx. 50 µl using nitrogen steam. As an alternative, derivatisation with a mixture of N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBASTFA) and 1% tert-butyldimethylsilyl chloride (t-BDMCS) was performed directly from the ACFs with the addition of 100 µl of a derivatisation reagent by reaction in an ultrasonic bath for 1 h, followed by the addition of 3 ml of the extraction solvent and elution of compounds in an ultrasonic bath for an additional 30 min. By derivatisation procedure polar analytes e.g. steroid hormones (e.g. estradiol and ethinylestradiol), pharmaceuticals (e.g. diclofenac), personal care products (e.g. triclosan and methyl triclosan) and polar pesticides and their degradation products (e.g. acidic herbicides), could be detected without additional manipulation with the samples.

### 3.3. Analytical methods

All samples were analysed using gas chromatography with mass spectrometry (GC-MS) (Agilent GC6900/QP5890, Agilent, Folsom, USA) using a Gerstel autosampler (Mülheim an der Ruhr, Germany) and a GC-MS Clarus 600 (Perkin Elmer, Waltham, USA), with a CIS autosampler (Switzerland). Chemstation and Agilent Deconvolution Reporting Software (DRS) with 5989–5076 EN retention times library (Agilent, Folsom, USA) and NIST 2008 spectral library and Turbomass software (Perkin Elmer, Waltham, USA) were used for the interpretation of chromatograms. The evaluation of the GC-MS chromatograms was conducted with the integration of the most abundant mass fragments from the compounds of interest discovered and a mass fragment m/z 203 of caffeine-D10 as a “internal standard”. Caffeine-D10 was chosen owing to its good mass spectrum definiteness and moderate polarity, which is similar to the average polarity values for the compounds of interest. The ratios between the areas for the compounds of interest and the internal standard were calculated. The results are given as the ratio of the area of signal to the area of internal standard (A/A<sub>is</sub>). The ratio allows for a comparison of the identifications of different groundwater samples; consequently, the spatial distribution of the compounds can also be determined and shown. Some of the compounds were determined with standards (confirmed), other were determined on tentative level according to ASTM D4128-01 database. The details of the analytical method are described in Auersperger et al. (2022).

### 3.4. Quality assurance and quality control

Since OCs are often present in personal care products and medicines,

rigorous quality control (QC) of sampling is required both on site and in the laboratory. To prevent secondary contamination of samples during sampling, sampling personnel should avoid using products containing compounds of interest (e.g. using cosmetics, drinking coffee, and consuming other products containing compounds of interest). For QC of the analytical method, the field and laboratory blank passive samplers were prepared, extracted, and analysed in parallel for each exposed sampler. Field blanks were tested by exposing the passive samplers to air at each installation point. The blanks were then analysed in the same way as the samples. The Laboratory Fortified Sample Matrix (according to the EPA 525.2 definition) was used to calibrate the overall procedure and QC. Regular spiked QC samples were analysed with each chromatographic run, including blanks of spring water used for calibration. Prior to validation, the analytical parameters (e.g. passive sample exposure time, drying procedure, and elution procedure) were optimised. Compounds identified in the blank tests were excluded from the report on individual samples. Active carbon for quality control procedures was stored in a laboratory in UPW for the entire duration of the installation and analysed at the same time as the collected passive samplers. During the analytical procedure, QC samples showed no diffusion of the material from the filter into the water before the UPW was removed from the vial.

### 3.5. Spatial analysis

The characteristics of the sampling site recharge area were studied in terms of their hydrogeological characteristics, expressed as groundwater flow velocity and groundwater direction. Groundwater flow was calculated according to Darcy (1856):

$$Q = -KA \frac{dh}{dL} = -KAi$$

where Q is the flow rate (m<sup>3</sup>/s) of the fluid flowing through the area A, and K is hydraulic conductivity. The flux of fluid through A is q = Q/A. dh is head difference, L is the distance between location h<sub>1</sub> and location h<sub>2</sub> and (h<sub>1</sub>-h<sub>2</sub>)/L (i) is hydraulic gradient.

The hydraulic conductivity (K) for each sample site and average  $n_e$  (0.15) was estimated based on previous pumping experiments and other studies (Urbanc et al., 2014). Based on the average hydraulic conductivity of all sampling points (3.5·10<sup>-3</sup> m/s) (Supplementary Data – Table S1), the average gradient (0.004) (Urbanc et al., 2014) and the average effective porosity, and the distance of the period of one year in the upstream direction of water flow was calculated. The potential recharge area for each measurement site was calculated based on an assumed annual variation in groundwater flow direction of 30° (Rules on determining water bodies of groundwater, 2005) and the one-year travel distance. The average recharge area measures 1.14 km<sup>2</sup>. Fig. 3 presents the shapes and directions of the recharge area. Supplementary Data – Table S1 lists the hydrogeological characteristics of the sampling sites.

We were able to identify the spatial conditions affecting each groundwater sampling site and thus determine their impact on groundwater. Land-use classification was performed using CORINE land cover (CLC) data for Europe (EEA, 2012) for the entire Dravsko polje and for each individual sampling site. We divided the proportions of each soil cover unit for the recharge area of each measurement site into four categories: agricultural land, forests, urban areas, and industrial areas, the rest being water areas (rivers, lakes, etc.). Urban areas include all settlement areas. Industrial plants, airports, quarries, and landfills were classified as industrial areas. The category of agricultural land includes arable land and all other agricultural land. The category of forests combines all types of deciduous, mixed, and coniferous forests as well as shrub forests. Intensive agriculture is mostly present in the southern part of the research area and less so in the northern part of the city of Maribor. The northern part is the most densely populated and therefore also

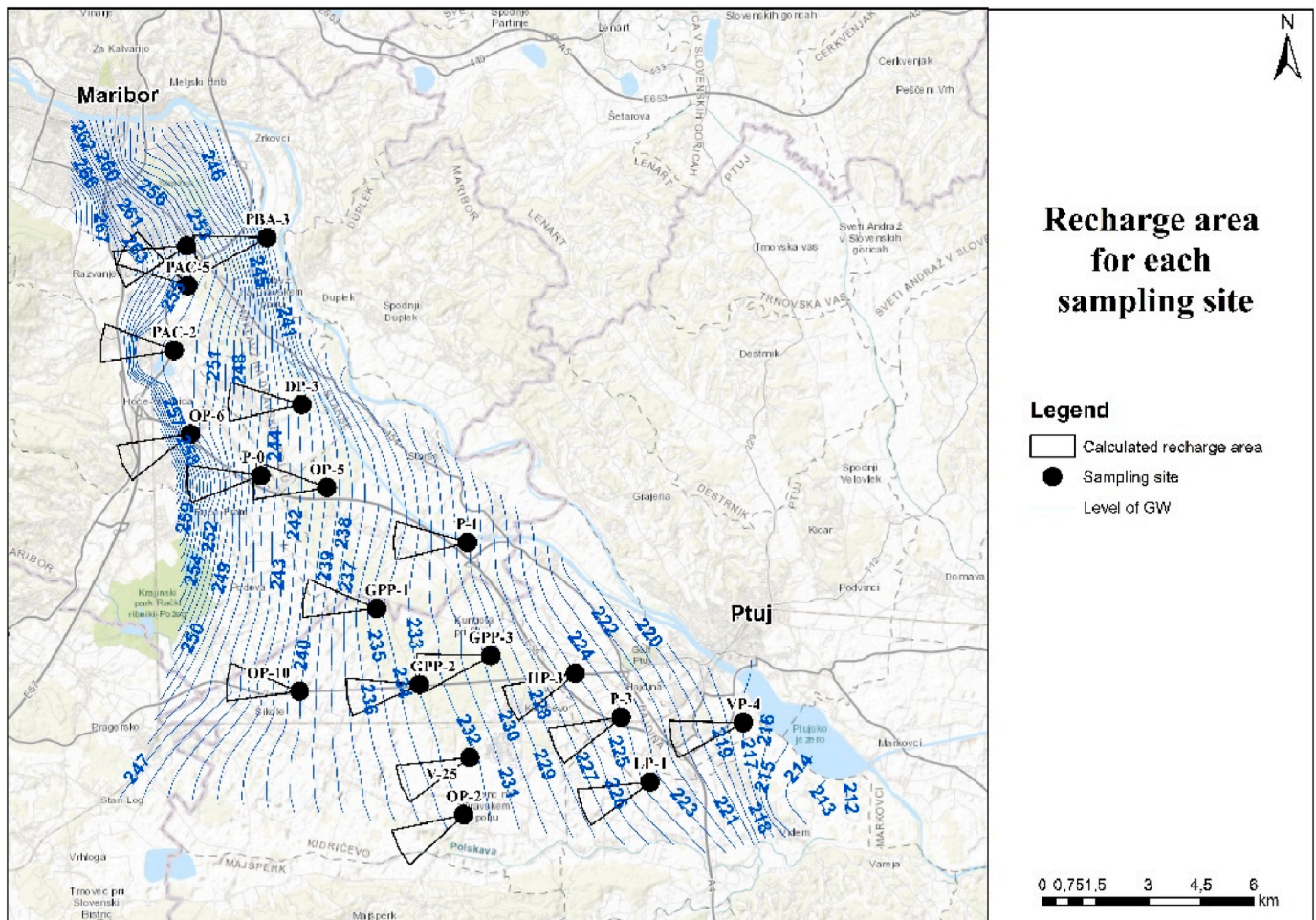


Fig. 3. Determined recharge areas for each sampling site.

has the highest proportion of built-up areas. Sewage systems, road and rail networks and the number of inhabitants were considered separately (Supplementary Data – Table S1). We also considered the presence of IED (Industry Emissions Directive) (European commission, 2010) stakeholders and illegal dumps in the recharge areas of the sampling sites. There are no such facilities in the areas under consideration.

We used the databases shown in Table 1. The input data were obtained mainly using ESRI software in vector format.

**Table 1**  
Databases (ESRI Shape) used for spatial analysis and geostatistical methods.

	Data set	Source/Literature
Land use	CORINE 2012	<a href="http://gis.arso.gov.si">http://gis.arso.gov.si</a>
Population density	Spatial units register (EHIS)	<a href="http://www.e-prostor.gov.si">http://www.e-prostor.gov.si</a>
Roads	Civil engineering facilities of economic public infrastructure (GJI)	<a href="http://egp.gu.gov.si/egp/">http://egp.gu.gov.si/egp/</a>
Railways	Civil engineering facilities of economic public infrastructure (GJI)	<a href="http://egp.gu.gov.si/egp/">http://egp.gu.gov.si/egp/</a>
Sewage system	Civil engineering facilities of economic public infrastructure (GJI)	<a href="http://egp.gu.gov.si/egp/">http://egp.gu.gov.si/egp/</a>
IED register	Emissions to water from industrial plants	<a href="http://gis.arso.gov.si">http://gis.arso.gov.si</a>
Wild dumps	Register of illegal dumps	<a href="http://register.oc.istimo.si">http://register.oc.istimo.si</a>

### 3.6. Data processing – statistical analysis

Data processing and calculations were performed using Statistica software (Stat Soft Inc., 2012) and spatial distribution was performed using ArcMap (ESRI Inc, 2004). Based on the results of the normality test (Davis, 2002), arithmetic mean (Am), median (Md), Kolmogorov-Smirnov (KS) and Shapiro-Wilk tests, it was found that the data were not normally distributed. For this reason, and due to the relatively small number of samples, non-parametric statistical tools were used.

The Spearman rank correlation coefficient was calculated to identify correlations between organic compounds (Helsel and Hirsch, 1992; Gauthier, 2001; Davis, 2002). Based on their high mutual correlations ( $\geq 0.7$ ) and statistical significance at  $p < 0.01$ , the compounds were divided into several groups. Absolute values of  $r$  between elements of 0.5–0.7 indicate a good correlation (red), while those of 0.7–1.0 indicate a strong correlation (bold and underlined).

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HCA and PCA were used to reveal the relationships between organic pollutants in groundwater. HCA classifies a set of variables so that they are as similar as possible to the mathematically grouped clusters, while the clusters are as different from one another as possible. The Pearson  $r$  distance with Ward’s method (Templ et al., 2008) was selected for the analysis of passive samplers. PCA was performed on the data from the contained measurement sites at one site and compared with the others, to produce average values for each compound at a given measurement site. For orthogonal rotation, the varimax method was used. In both HCA and PCA, a total of 2679 data inputs were used.

We determined the linear relationship between the dependent variable (OCs) and two or more independent spatial variables (e.g. land use, etc.) using MLR. The general form of the MLR model is as follows:

$$Y = \beta_0 + \beta_{1x_1} + \beta_{2x_2} + \dots + \beta_{ix_i} + \varepsilon$$

where Y is the predicted dependent variable,  $\beta_0$  to  $\beta_i$  are partial regression coefficients, and  $x_1$  to  $x_i$  are independent variables included in the model (Yan and Gang Su, 2009). The stepwise backward regression method was used (Montgomery et al., 2012). The measured values of organic compounds in groundwater were used as the dependent variable, while the spatial characteristics of the recharge areas that contained sampling points were used as independent variables. Linear correlations were performed between the variables, and multicollinearity between independent variables was tested using the Variance Inflation Factor (VIF). The VIF estimates how much the variance of each regression coefficient is inflated due to multicollinearity in the model. A VIF value of 1 means that there are no significant correlations between the independent variables, while a VIF value of 5 indicates a higher correlation between the variables, leading to less reliable regression results. The Durbin-Watson test (Marquín et al., 2003) was used to test for the presence of autocorrelation in the residuals.

## 4. Results and discussion

### 4.1. Detection of organic compounds using passive samplers

Of the total of 343 OCs detected (Fig. 4, Table S2 in Supplementary Data), 47 of those with the highest average values (more than 1 (A/Ais)) and maximum values (more than 11 (A/Ais)) were included in further statistical analysis (Table 2, Table S2 in Supplementary Data, Fig. 5). The largest proportion (29%) of all detected compounds were unknown compounds, 27% were urban compounds, including residues of medicines, 19% were pesticides, 7% were solvents, and 19% were other compounds, including industrial compounds. Some occur naturally in the environment, while some are the result of anthropogenic activities, and some remain unknown. Unknown (non-identified) compounds represented the largest share of detections in groundwater and may be of natural or anthropogenic origin. Although they may be present in low concentrations, we are still unable to identify these compounds or

determine whether they pose a risk to the environment. It is therefore important to determine their presence and impact on the environment, even at low concentrations.

The selected compounds were divided into groups according to their type of use and potential origin. Their use and origin by group are listed in Table 2 and Fig. 5. For individual compounds, each group was categorised by type, typical use, and likely source. Five groups of OCs were determined based on the type of source: Pesticides, Pharmaceuticals, Solvents, Urban Compounds, and Other Compounds. The compounds and their degradation products which could be assigned to several different groups were classified into their most likely groups. The Urban Compounds category includes lifestyle, personal care products (PCP), household, and food additive compounds (Manamsa et al., 2016).

Further, an evaluation of different groups of pollutants according to origin (urban, agricultural, and industrial pollution) was performed. Pesticides were classified as Agricultural Compounds due to their use in the control of pests, weeds, and plant diseases, as well as for other urban applications (weed control) (Lapworth and Goody, 2006). The compounds in the Pharmaceuticals, Urban Compounds and Other Compounds groups were classified as Urban Use Compounds, as they are most significant for groundwater contamination when leaking from sewage systems and from municipal landfills, and as effluents from wastewater treatment plants (Stuart et al., 2012). The groups Solvents and certain Urban Compounds were categorised as Industrial Use Compounds, all of which are indicative of older industrial pollution loads and active industrial effluents (Ritter et al., 2002).

Descriptive statistics of ratios (A/Ais) of the selected compounds detected with passive samplers are presented in Supplementary Data – Table S3. The average ratios (A/Ais) for the 47 selected OCs are shown in Fig. 5. The highest average values were detected for atrazine, tetrachloroethene, and desethylatrazine. Overall, most pesticides occur in higher proportions (A/Ais) than other compounds.

In the Pesticides group (12), we find compounds and their transformation products that are commonly used or have been used in the past to control weeds (atrazine, simazine, propazine, terbutylazine, metolachlor). The Pharmaceuticals group (4) includes carbamazepine, triacetin, and two pharmaceutical intermediates (5-metoksigramine, 5-metoksitriptamine). The Solvents group includes 10 compounds. Fragrances, cosmetics, food additives, etc. are found in the group of Urban

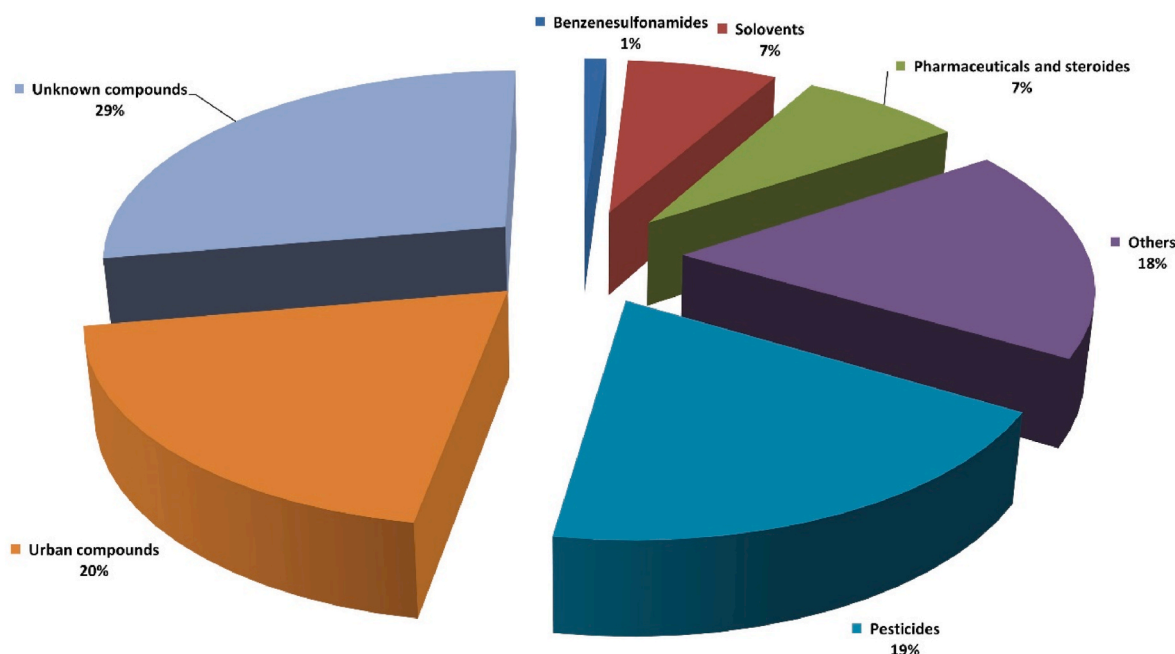


Fig. 4. Detected organic compounds in groundwater according to use.

**Table 2**  
Selected OCs (n = 47) according to the highest ratios (A/A<sub>is</sub>) and frequency of detection in groundwater.

Substance	CAS no.	Usage	Group	Source
2,2-dihydroxyacetophenone	1075-06-5	ti chemical intermediate	Other compounds	URBAN
2-Methylphenol	95-48-7	ti disinfection, solvent, chemical intermediate	Other compounds	INDUSTRIAL
Tetraethylene glycol dimethyl ether	143-24-8	ti Solvent	Solvents	INDUSTRIAL
1-(2-Methoxypropoxy)-2-propanol	13429-07-7	ti Solvent	Solvents	INDUSTRIAL
2-(2-methoxypropoxy)propan-1-ol	13588-28-8	ti Solvent	Solvents	INDUSTRIAL
2,4-dimethyl-2H-benzotriazole	–	ti degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors	Urban compounds	URBAN
2-butenylbenzene	1560-06-1	ti petroleum products	Other compounds	INDUSTRIAL
2-Hexanol	626-93-7	ti flavors, fragrances	Urban compounds	URBAN
2-methyl-2H-benzotriazole	16584-00-2	c. degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors	Urban compounds	URBAN
5-Methoxygramine	16620-52-3	ti Pharmaceutical Intermediates	Pharmaceuticals	URBAN
5-Methoxytryptamine	608-07-1	ti Pharmaceutical Intermediates	Pharmaceuticals	URBAN
Acetamide	60-35-5	ti solvent, a plasticizer, a chemical intermediate	Solvents	INDUSTRIAL
Atrazine	1912-24-9	ci Herbicide	Pesticides	AGRICULTURAL
Benzaldehyde	100-52-7	ti chemical intermediates, solvent, bee repellents	Solvents	URBAN
Benzylalcohol	100-51-6	ti cosmetics, chemicals intermediate	Urban compounds	URBAN
Butyl hexadecanoate	111-06-8	ti cosmetics, food additives	Urban compounds	URBAN
Carbamazepine	298-46-4	ci Drug	Pharmaceuticals	URBAN
Chloridazon methyl desphenyl	17254-80-7	ti degradation product of the herbicide	Pesticides	AGRICULTURAL
Desethylatrazine	6190-65-4	ci degradation product of herbicide atrazine	Pesticides	AGRICULTURAL
Desethylterbuthylazine	30125-63-4	ci degradation product of herbicide terbuthylazine	Pesticides	AGRICULTURAL
Diethyldiglycol	112-36-7	ti Solvent	Solvents	INDUSTRIAL
Dimethyl oxalate	553-90-2	ti degradation of halogenated pesticides	Pesticides	AGRICULTURAL
Dimethyl sulfoxide	67-68-5	ti solvent, chemical intermediate	Solvents	INDUSTRIAL
Dodecanal	112-54-9	ti Cosmetics	Urban compounds	URBAN
Dodecyl acetate	112-66-3	ti natural compound	Urban compounds	URBAN
Ethofumesate	26225-79-6	ti Herbicide	Pesticides	AGRICULTURAL
Indole	120-72-9	ti cosmetics, chemicals intermediate	Urban compounds	URBAN
Isobutyl stearate	646-13-9	ti cosmetics, food additives	Urban compounds	URBAN
Metalochlor	51218-45-2	ci Herbicide	Pesticides	AGRICULTURAL
Metalochlor-M m/z 162,282	–	ti degradation product of herbicide matalochlor	Pesticides	AGRICULTURAL
Methyl octanoate	111-11-5	ti chemical intermediate, fragrances, naravna spojina	Urban compounds	URBAN
Methyl palmitate	112-39-0	ti chemical intermediate	Urban compounds	URBAN
Nitrosomorpholine	59-89-2	ti solvent, chemical intermediate	Solvents	INDUSTRIAL
Palmitic acid	57-10-3	ti emulsions, polymer coatings, food	Urban compounds	URBAN
p-cymen-8-ol	1197-01-9	ti natural compound, digestion of the plant material, flavors	Urban compounds	URBAN
Phenol	108-95-2	ci disinfection and chemical intermediate	Other compounds	INDUSTRIAL
Propazine	139-40-2	ci herbicide	Pesticides	AGRICULTURAL
Simazine	122-34-9	ci herbicide	Pesticides	AGRICULTURAL
Stearic Acid	57-11-4	ti chemical intermediate, cosmetics, pharmaceuticals	Urban compounds	URBAN
Terbuthylazine	5915-41-3	ci herbicide	Pesticides	AGRICULTURAL
Tetrachloroethylene	127-18-4	ti dry cleaning, degreasing, industrial solvent	Solvents	INDUSTRIAL
Tetrahydro-8-hydroxy-4-oxoquinoline-2-carboxylic acid	4886-42-4	ti –	Other compounds	URBAN
Triacetin	102-76-1	ti solvent, Cosmetics, Pharmaceuticals	Pharmaceuticals	URBAN
Trichloroethylene	79-01-6	ti dry cleaning, degreasing, industrial solvent	Solvents	INDUSTRIAL
Tridecanal	10486-19-8	ti natural compound, cosmetics	Urban compounds	URBAN
Undecanal	112-44-7	ti cosmetics, natural compound	Other compounds	URBAN
Unknown comopund m/z 176, 252,	–	ti degradation product of herbicide	Pesticides	AGRICULTURAL

CAS no. - compound registration number; t.i. - tentative identification; c.i. - confirmed identification (determined using standards).

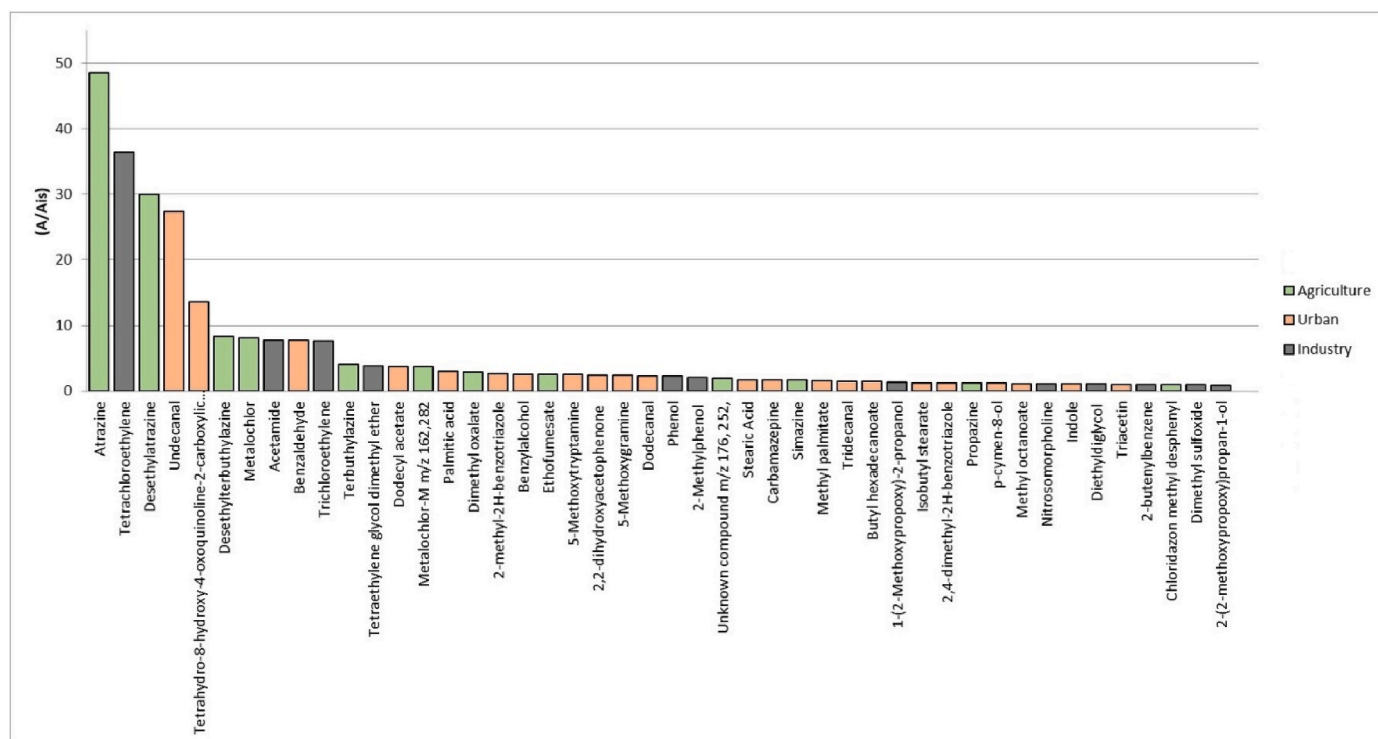


Fig. 5. Average ratios (A/A<sub>is</sub>) of 47 selected OCs by the passive sampling technique.

Compounds (15). There are 6 compounds in the Other Compounds group, most of which are related to disinfection and use as chemical intermediates (Table 2).

#### 4.2. Relationship between different organic compounds in groundwater

In addition to specific spatial environmental conditions, the occurrence of OCs in groundwater is also affected by the type of OCs and the use of different compounds for different purposes. Statistical analyses were performed to determine the relationships and correlations between organic compounds. Supplementary Data – Table S3 shows the summary statistics for 47 organic compounds detected in groundwater. The variables in the data set are not normally distributed. The Mean and Md values are different. This is also confirmed by the results of the KS and Shapiro-Wilk test (Supplementary Data - Table S4). In both cases – according to the Kolmogorov-Smirnov test and the Shapiro-Wilk test – the values of  $p$  are lower than 0.05.

As expected, the strongest correlations were found between primary compounds together with their degradation products and compounds of similar use. Some have similar molecular structures. Their presence therefore depends on their properties, which consequently affects their behaviour in the aquifer. Correlations were calculated using the nonparametric Spearman method (Supplementary Data - Table S5). Statistically significant Spearman's correlation coefficients ( $r_s$ ) ( $r_s > 0.50$ ) are indicated in red at 95%. Strong correlations ( $r_s > 0.70$ ) of the results of the passive sampler are reflected in several variables (bold and underlined). The highest correlation between all variables ( $r_s = 1.00$ ) was found between ethofumesate and 5-methoxygramine; high correlations were also observed between ethofumesate and 5-methoxytryptamine, as well as between 5-methoxygramine and 5-methoxytryptamine. The latter two can be attributed to the same source. Both are metabolites of dopamine (5-methoxygramine) and serotonin (5-methoxytryptamine), which are of human or animal origin, but can also be produced in plants (TOXNET, 2018). Given their very similar origin, their strong correlation is logical. These compounds are also strongly associated with the herbicide ethofumesate, which is used

to control weeds in beetroot crops (List of authorized plant protection products in the Republic of Slovenia, 2002).

In the Pesticides group (Supplementary Data - Table S5), the compounds indicate statistically dependent characteristics. Very strong correlations were observed between metolachlor and the unknown compound m/z 176, 252 ( $r_s = 0.94$ ), between atrazine and propazine ( $r_s = 0.92$ ), atrazine and desethylatrazine ( $r_s = 0.94$ ), desethylatrazine and propazine ( $r_s = 0.91$ ), and atrazine and simazine ( $r_s = 0.73$ ), etc. The weakest correlation between pesticides was found between simazine and metolachlor (Supplementary Data - Table S5). We attribute the high correlation to their similar use in agriculture. The high correlations were observed between palmitic acid and stearic acid ( $r_s = 0.93$ ), which results from their very similar structure and origin. Both are saturated fatty acids, and are most commonly present in our diets (Ruiz-Núñez et al., 2016). Positive correlations ( $0.7 > r_s > 0.5$ ) are also evident among other compounds (Supplementary Data - Table S5), which are linked to the factors and groups described in section 4.2.

A comparison of the HCA dendrogram (Supplementary Data – Fig. S1) with the results of PCA (Table 3) shows that HCA and PCA provide similar results. HCA results are divided into four groups. The first and second clusters merge at D/D<sub>max</sub> 44%, while the third and fourth clusters merge at D/D<sub>max</sub> 59%.

The compounds classified into the first two clusters (Supplementary Data – Fig. S1) are compounds used in agriculture and urban areas on a daily basis. In the third and fourth groups, we find compounds used in urban areas and in industry; there are no agricultural compounds in these groups. The first group consists mainly of compounds of urban origin and two pesticides, metolachlor and ethofumesate, which are still in use today. All other pesticides are in the second cluster – in the Agricultural cluster, which also includes old pesticides (atrazine, propazine, etc). The third group consists of compounds of mixed origin, both from urban and industrial areas. This group also includes chlorinated solvents. Chlorinated solvents are organic hydrocarbons that are commonly used in industrial production and are subsequently found in discontinuous aquifers as pools of residue (Li et al., 2018). Chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE),



**Table 3**  
Principal component analysis (PCA) results (weights marked red above 0,7).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
1-(2-Methoxypropoxy)-2-propanol	0,80	-0,29	-0,17	0,14	0,20
2-(2-methoxypropoxy)propan-1-ol	0,92	-0,12	-0,02	0,05	0,09
2,2-dihydroxyacetophenone	0,75	-0,02	-0,07	0,19	-0,53
2,4-dimethyl-2H-benzotriazole	-0,05	-0,10	0,93	0,18	0,03
2-butenylbenzene	0,72	0,23	-0,12	0,44	0,11
2-Hexanol	-0,29	0,22	-0,09	0,02	-0,72
2-methyl-2H-benzotriazole	0,48	-0,15	0,81	0,14	0,06
2-Methylphenol	0,85	0,01	0,07	0,18	-0,32
5-Methoxygramine	-0,14	0,18	-0,06	-0,94	0,08
5-Methoxytryptamine	-0,27	0,12	0,12	-0,86	0,08
Acetamide	0,08	0,37	-0,11	-0,21	-0,32
Atrazine	-0,06	0,88	0,19	-0,15	-0,19
Benzaldehyde	0,31	-0,17	-0,06	0,16	-0,79
Benzylalcohol	0,80	0,15	0,13	0,07	-0,09
Butyl hexadecanoate	-0,23	0,34	0,09	-0,51	0,19
Desethylatrazine	-0,05	0,80	0,15	-0,31	0,04
Desethylterbutylazine	0,03	0,13	0,91	-0,28	0,08
Diethyl diglycol	0,94	-0,16	0,01	-0,01	0,15
Dimethyl oxalate	-0,15	0,09	0,37	-0,55	0,07
Dimethyl sulfoxide	0,93	-0,15	-0,01	0,06	-0,04
Dodecyl acetate	0,05	-0,20	-0,12	-0,56	-0,40
Dodecanal	0,31	-0,05	-0,22	0,16	-0,57
Ethofumesate	-0,15	0,22	-0,04	-0,92	0,10
Phenol	0,08	0,04	0,02	0,18	-0,89
Isobutyl stearate	-0,01	0,64	0,16	-0,27	0,03
Indole	0,95	0,08	-0,01	0,13	0,15
Carbamazepine	-0,05	-0,09	0,92	0,00	-0,06
Methyl octanoate	0,13	-0,34	-0,23	-0,20	0,00
Methyl palmitate	-0,35	0,62	-0,13	0,17	-0,10
Chloridazon methyl desphenyl	-0,06	0,34	0,67	-0,10	0,24
Metalochlor	-0,16	0,09	0,04	-0,71	0,13
Metalochlor-M m/z 162,282	-0,07	0,48	0,46	-0,65	0,10
Unknown compound m/z 176,252,	-0,18	0,51	0,16	-0,78	0,09
Nitrosomorpholine	0,73	-0,25	0,18	0,26	-0,33
Palmitic acid	-0,09	0,91	-0,11	0,01	-0,04
p-cymen-8-ol	0,84	-0,01	0,04	0,24	-0,40
Propazine	0,06	0,89	0,04	-0,22	-0,04
Simazine	-0,20	0,26	0,83	-0,03	-0,05
Stearic Acid	-0,15	0,86	-0,04	-0,12	0,03
Terbutylazine	0,05	0,08	0,86	-0,34	0,02
Tetraethylene glycol dimethyl ether	0,57	0,01	0,45	0,36	0,36
Tetrahydro-8-hydroxy-4-oxoquinoline-2-carboxylic acid	-0,14	-0,08	-0,05	-0,84	0,14
Tetrachloroethene	0,02	-0,23	-0,11	-0,07	0,39
Triacetin	0,68	-0,19	-0,17	0,08	-0,32
Tridecanal	0,14	-0,38	-0,23	0,36	-0,40
Trichloroethene	0,52	-0,20	-0,08	0,44	0,47
Undecanal	0,53	-0,24	-0,13	0,07	-0,13

chloroform, and 1,1,1-trichloroethane are used for a variety of commercial and industrial purposes, including dry cleaning, metal cleaning, degreasing, automotive aerosols, in the printing, paper, and textile industries, for paint removal and in the furniture industry (Doherty, 2000; Huang et al., 2014). Contamination of groundwater with chlorinated solvents is frequently observed in industrial areas as a result of improper handling or accidental leakage. They can also be released into the environment during production, storage, transport, and use (Bhatt et al., 2007). Industrial compounds in this group are chemically different from industrial compounds in the fourth group. The fourth and last group comprises compounds that include indole and 2-methyl-2H-benzotriazole, also used as anti-corrosion agents, in cosmetics, and as chemical intermediates. Looking at the results, we can see that clusters are separated according to the type and use of compounds.

PCA reveals similar relationships between different OCs in groundwater as HCA. The compounds were defined more precisely with the PCA based on five different factors. These factors are related to the similarities of the variables and describe 73.3% of the variance. These factors were selected based on eigenvalues with a value greater than 3. The results of the PCA are presented in Table 3. The strongest factor is 1 (F1), which accounts for 29.5% of the total variance. Factor two (F2) represents 15.5%, factor three (F3) represents 11.2%, factor four (F4) represents 9.5%, while the factor five (F5) represents the smallest

fraction (7.5%) of the total variance (Table 3). In F1, compounds belonging to the group of Solvents and General Use Compounds show the highest correlation. Spatially, this factor is most strongly represented at measurement points whose recharge areas are more populated, in the north, where the city of Maribor is located, and in the south of the aquifer, where there are individual settlements. Factor 2 connects pesticides and compounds of agricultural origin, which is most present in the southern part, where intensive agriculture is practised. The third factor (F3) connects the compounds of mixed origin (urban, industrial, agricultural) and is distributed throughout the entire area (Supplementary Data – Fig. S1), which can be divided into two parts. The first consists of compounds originating from the sewer network, that is, everyday urban activities, while the second consists of pesticides linked to urban use. Similar connections with carbamazepine, simazine, and terbuthylazine were detected in the Maribor area (Koroša et al., 2016). The fourth factor (F4) links pharmaceutical intermediates, which are also used in veterinary products and pesticides still in use today. The fifth factor (F5) links compounds whose origin is very difficult to determine.

Both PCA and HCA showed that substances and their degradation products of agricultural origin are most strongly interconnected. Also used in urban areas, pesticides have been used for weed control on highways, rail tracks and public or private amenities (Lapworth et al., 2006; Marot et al., 2008) and also in urban and industrial areas (Sorensen et al., 2007), so they also correlate well with typical substances of urban origin. This explanation is supported by the results of the MLR analysis from section 4.2. With MLR, urban pollution is defined in association with urban infrastructure (discharges, sewerage), as well as the management of green areas with various activities that involve the use of pesticides. The results of the analysis indicate that the same organic substances are used for different purposes and in different environments (Lapworth et al., 2018a; Richards et al., 2021; Khan et al., 2022). This fact makes it difficult to clearly distinguish between the different types of pollutants, explain their occurrence, and determine their origin. In the case of the aquifer in question, an area of mixed land use was considered on the surface of the aquifer and in the recharge area of each individual point. In order to define more precisely the connection between the occurrence of OCs and land use, it would be necessary to carry out analyses at sampling sites with very clearly defined land use in the recharge area.

#### 4.3. Relationship between the occurrence of organic compounds and environmental setting

Determining the relationships between the occurrence, environmental setting, and type of compound is a very complex process. Environmental settings are in constant interaction with each other. Different physicochemical conditions and various natural and anthropogenic processes trigger different chemical and physical changes, which also occur in the environmental media during the migration process into the groundwater. Therefore, a holistic approach is important and necessary to determine the origin and relationships between OCs in groundwater. The connections between the occurrence of OCs (as dependent variable) and environmental settings (independent variable) were made using MLR methods based on the independent variables presented in Table 4. These are the shares of agricultural, urban, industrial, and forest land use in the recharge area of the sampling site, as well as the population, length of roads, railways, and sewage systems in the recharge areas. The set of independent variables also includes aquifer properties (thickness of UZ and SZ and hydraulic conductivity) at the sampling site. The MLR calculations of the dependent variables included data from Table 2, depending on the source of pollution (agricultural, urban, or industrial). Table 4 presents the independent (environmental) variables included in the MLR analysis for each pollution source (Eq. (1), Eq. (2), Eq. (3)).

For agricultural pollutants, distribution models were created using the Box-Cox transformation. The regression equation of the agricultural

**Table 4**

Independent spatial variables used in MLR calculations and those included in the MLR equation for each source of pollution (agricultural, urban, industrial).

Independent variables used in MLR	MLR - significant variables		
	AGRICULTURAL	URBAN	INDUSTRIAL
Forest (%)		x	
Agriculture (%)	X	x	
Urban (%)		x	x
Industry (%)			
No. of population			
Roads (m)			x
Sewage (m)		x	
Railway (m)		x	x
Trans. coeff.(m/s)	X	x	x
UZ (m)	X		
SZ (m)	X		

pollutants model as calculated using the MLR is presented in Equation (1).

$$Y = 34,77 + 0,02 \times \text{agricultural land use} - 366,91 \times \text{hydraulic conductivity} - 0,15 \times \text{thickness of UZ} + 0,39 \times \text{thickness of SZ} + \epsilon \quad (1)$$

The results of the Durbin-Watson test ( $d = 2.4$ ) show that there is no first order linear autocorrelation in the calculated multiple linear regression model, as the value lies between the two critical values of 1.5 and 2.5. A scatter plot of the observed and predicted contaminants shows that almost all predicted values lie within the prediction level (75%) (Supplementary Material – Fig. S2, Fig. S3, Fig. S4).

For the MLR models for urban pollutants, we used the logarithmic transformation of the independent variable (Fig. 6). The regression equation of the urban pollutants model as calculated using the MLR is presented in Equation (2).

$$Y = 0,38 + 192,26 \times \text{hydraulic conductivity} - 2,4 \times 10^{-4} \times \text{railway} - 1,3 \times 10^{-4} \times \text{sewage systems} + 1,9 \times 10^{-4} \times \text{roads} - 3,0 \times 10^{-2} \times \text{urban land use} - 6,6 \times 10^{-3} \times \text{forest} - 6,6 \times 10^{-3} \times \text{agricultural land use} + \epsilon \quad (2)$$

The variables of the spatial model for urban pollutants are positively related to each other ( $R = 0.82$ ). The coefficient of determination ( $R^2$ ) explains 67% of the variability of the dependent variable. Six regression coefficients (b) which are statistically significant at the confidence level ( $p < 0.05$ ) are characteristic for the indication of urban pollutants in groundwater. Of the regression coefficients (b), seven coefficients are statistically significant at the confidence level ( $p < 0.05$ ). Other variables which could affect the spatial distribution of urban pollutants were excluded from the model.

A logarithmic transformation of the dependent variables was used in the MLR calculations for industrial pollutants (Fig. 6). The regression equation of the industrial pollutants model using the MLR is presented in Equation (3).

$$Y = -0,65 - 0,04 \times \text{urban land use} + 2,9 \times 10^{-4} \times \text{roads} - 2,8 \times 10^{-4} \times \text{railways} + 175,2 \times \text{hydraulic conductivity} + \epsilon \quad (3)$$

The independent variables included in the MLR calculations for each pollution environment indicate that the area in question is an area of highly mixed land use. In the case of diffuse agricultural pollution, the parameters of aquifer properties (UZ, SZ, hydraulic conductivity, etc.) proved to be more important for the assessment of this pollution. Urban pollution results from the point pollution from discharges and sewage systems, as well as the use of pesticides in parks, gardens, and for infrastructure maintenance. Industrial pollution is associated with areas of agglomerations and industrial zones and with transport infrastructure. Of the hydrogeological parameters, the permeability coefficient was identified as an important independent variable.

The main aim of this MLR method was to calculate the relationship between the occurrence of OCs in groundwater and the environmental

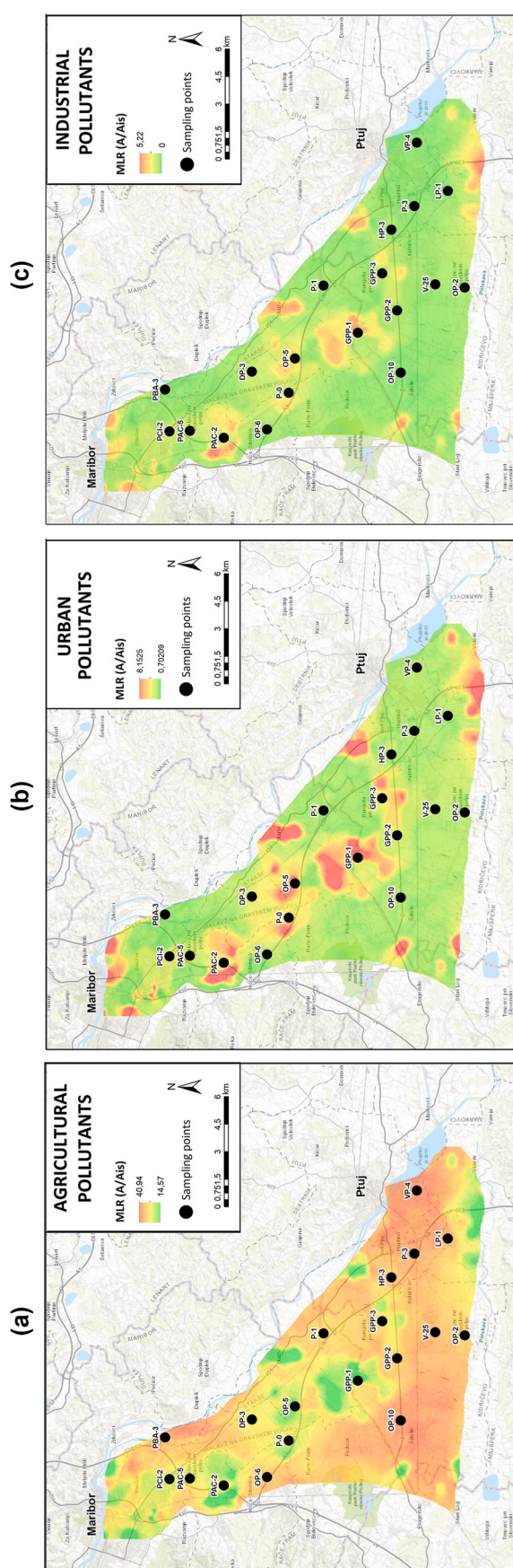


Fig. 6. Estimation of the presence of a) agricultural pollutants, b) urban pollutants and c) industrial pollutants in the groundwater of the Dravsko polje aquifer using the multiple linear regression method.

setting for each source of pollution in the aquifer. This type of approach allows for the creation of contamination prediction maps that can help determine the main source of pollution and assess the actual size of the affected area, as well as improve the interpretation of the data.

In some cases, individual pesticides can also be detected in forests and urban areas. Atrazine has historically been used both in agricultural and amenity area applications, and is also quite common in urban areas (Lapworth et al., 2015). In addition, some compounds registered as pesticides are also used as biocides (e.g. diuron). Pesticides are usually specific to a crop, which is why distinguishing between urban/agricultural/pasture settings alone may not be adequate. However, the detection of OCs in groundwater is not very clearly related to land use classes. In some cases, urban pollutants are also detected in natural areas (e.g. forests) and in agricultural lands. This conclusion may not be entirely surprising, as the area under investigation is an area of highly mixed land use.

According to Fig. 6a, higher values of agricultural pollutants can be expected in the southern part of the Dravsko polje aquifer, where the groundwater flow rate is lower and agriculture is much more intensive than in its northern part. In this area, the SZ is thicker, while the UZ is thinner. In the northern part of the city of Maribor, and in the central area, which is covered with forests, the highest A/Ais ratios of agricultural pollutants are not expected. Higher values of urban pollutants (Fig. 6b) can be expected in the middle part of the aquifer, in the vicinity of urban areas, which are characterised by sewerage infrastructure and septic tanks, where the sewerage network is not regulated. According to Fig. 6c, higher levels of industrial pollutants can also be expected in the southern part of the Dravsko polje and at the edges of the field, near settlements and various industrial plants. The occurrence of such pollutants is also affected by the thickness of the UZ and SZ.

## 5. Conclusions

This study provides an important baseline characterisation and information on the key controls on groundwater OC distribution. The study confirmed that specific environmental factors/conditions, human activities, and chemical characteristics of OCs affect their occurrence in groundwater. We used a broad screening approach to identify and characterise OCs in groundwater by means of ACF passive sampling.

- (1) The presence of OCs in groundwater was investigated by means of passive sampling. Over the course of the three-year research period, 343 organic compounds were identified by means of passive sampling. We determined their type of use and potential origin (29% is represented by unknown compounds, 27% by urban compounds (including residues of medicines), 19% by pesticides, 7% by solvents and 19% by other compounds, including industrial compounds).
- (2) The multivariate statistical models (MLR, PCA, HCA) have proven to be a useful tool for determining the relationships between the type of OCs, their occurrence in groundwater, and the hydrogeological and environmental conditions.
- (3) MLR shows that the environmental setting is one of the most important factors affecting different types of pollutants. In our case, the independent variables included in the MLR calculations indicate that the area under investigation was a highly mixed land-use area. The permeability coefficient was identified as the most important hydrogeological parameter among the independent variables.

-In the case of diffuse agricultural pollution, the parameters defining aquifer properties proved to be more important in the pollution assessment. The presence of agricultural pollutants in groundwater depends on agricultural land use in recharge areas, the hydraulic conductivity of the aquifer, and the thickness of the unsaturated and saturated zones.

- The presence of urban OCs depends on railway and sewage system networks, roads, urban and agricultural land use, forests, and hydraulic conductivity.
  - The presence of higher levels of industrial pollutants is expected in areas characterised by urban land use, roads, and railways; these levels are also affected by the hydraulic conductivity of the aquifer.
- (5) Based on MLR models, prediction maps for different types of pollution depending on land use can be created. This type of approach helps in the reconstruction of primary sources of contamination to assess the actual size of the affected area, and allows for better interpretation of the data. Moreover, the potential type of pollution and its origin can also be predicted.
  - (6) The study found that the connections between OCs in groundwater are affected by several factors. As expected, the strongest correlations are found between primary compounds and their degradation products (e.g. atrazine and desethylatrazine) and compounds of similar use (e.g. atrazine and propazine, also desethylatrazine and propazine, atrazine and simazine). Some have a similar molecular structure (e.g. palmitic and stearic acid, 5-methoxygramine and 5-methoxytryptamine). Their presence thus depends on their properties and consequently on their behaviour in the aquifer.
  - (7) Both factor and cluster analysis showed that substances and their degradation products of agricultural origin are most closely connected. As pesticides are also used in urban areas, they also correlate closely with typical substances of urban origin. This explanation is supported by the results of the MLR analysis. With the MLR, urban pollution is associated with urban infrastructure (discharges, sewerage) as well as the management of green areas characterised by various activities which involve the use of pesticides. The results of the analysis indicate that the same organic substances are used for different purposes and in different environments.

The method used in this study is based on a significant assumption. The method presented here only works with data on the presence/absence of OCs and this information may vary across the year. Therefore, the sampling time of passive sampler exposure may be critical in this regard. In order to obtain more accurate statistical models that could be used to assess the parameters influencing the occurrence of specific groups of pollutants in groundwater in general, also several additional analyses would have to be conducted. One such procedure would be the selection of sample sites characterised by a more homogeneous land use in the recharge areas. Better results could also be obtained with a denser sampling network, as well as by applying another, more complex predictive method (e.g., multiple polynomial regression, neural networks, etc.). Only the simultaneous investigation of as many OCs as possible could lead to a sufficient understanding of their presence in groundwater. In addition to conventional chemical analyses, passive sampling analyses are of great importance for studying the characteristics of OCs, their sources, their pathways, and the processes to which they are exposed in the environment, and finally for the successful management of their emissions in groundwater. In this sense, the presence/absence information is a less specific criterion for vulnerability than concentration. However, the passive sampling method has proven to be very useful for the preliminary determination of the presence of pollutants in groundwater. This study highlights the importance of using an integrated approach to determine the origin and relationships of OCs in groundwater.

## CRediT author statement

**Anja Koroša:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing-Original draft, Visualization, Writing - Review & Editing, Funding

acquisition.

**Nina Mali:** Conceptualization, Methodology, Resources, Writing-Reviewing and Editing, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.115440>.

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