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

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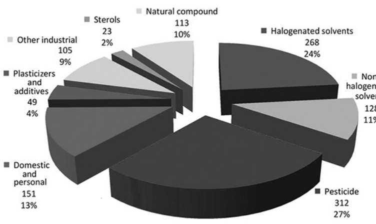
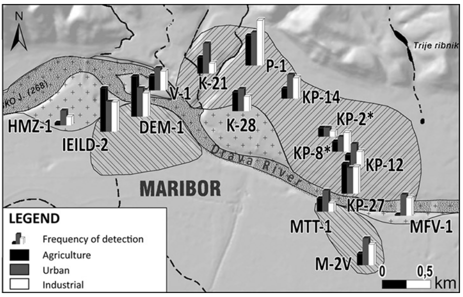
HIGHLIGHTS

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

GRAPHICAL ABSTRACT





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ABSTRACT

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

1. Introduction

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

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

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

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

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

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

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

2. Site description

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

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

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

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

3. Materials and methods

3.1. Sampling design

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

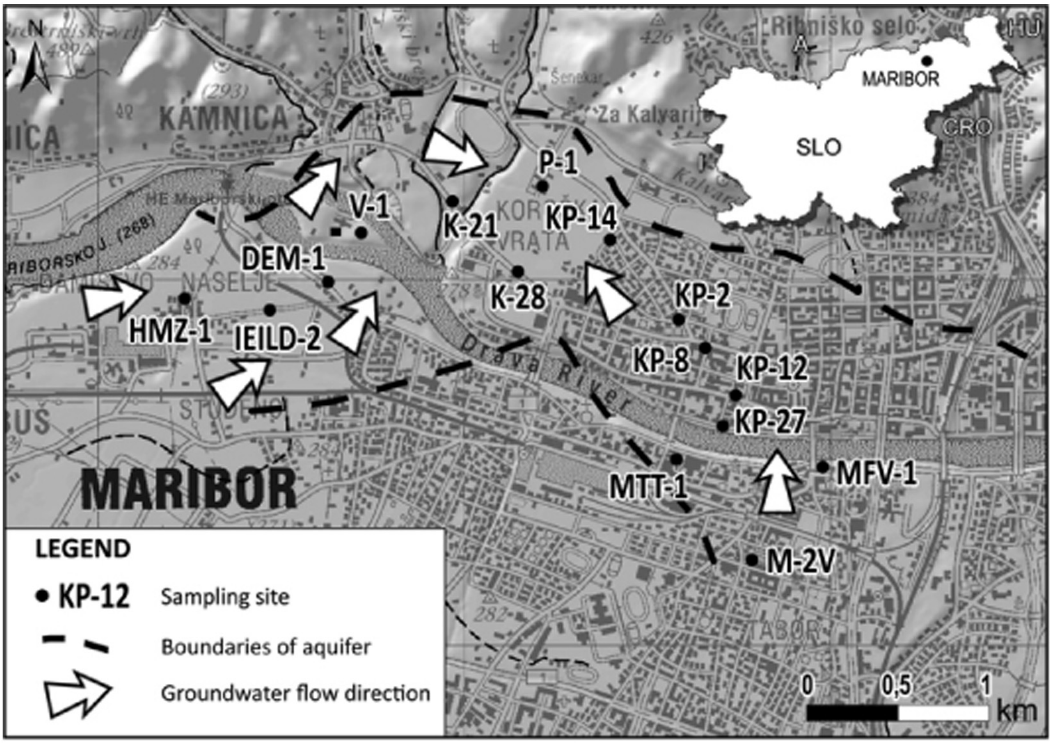

Fig. 1. Study area and sampling sites.

increased levels of pollutant substances were expected. Locations of the sampling points are shown in Fig. 1.

For the purposes of determining the MOs in groundwater using a passive sampler, two long-term sampling campaigns (approx. 6 months) at each sampling location covered a period of roughly one year in order to integrate the pollutant concentration over time. The first is a Summer series (from May to September 2010) with 423 mm of total precipitation, and the second the Winter series (from October 2010 to March 2011) with 313 mm of total precipitation, measured at the climatological station Maribor – Tabor (SEA, 2013). In total, 15 locations were sampled over the entire study area. Passive sampling devices were installed into all observation wells, 2 m above the aquifer base (from bottom of the well, respectively) in the saturated zone where contact with groundwater was constant. In both campaigns a total of 28 samples were collected. Due to damaged samplers at the sample locations KP-8, KP-2, only one sampling campaign was performed.

3.2. Passive samplers

The preparation of passive samplers and chemical analyses was conducted by the accredited laboratory of the Ljubljana Water Works and Sewerage in Slovenia, according to ISO 5667-23:2011 standards for sampling, and EPA 625 modified for chemical analysis. Quantitative analysis of selected compounds was performed according to the EPA 525.2 method. Total organic carbon content was between 0.1 and 5.0 mg/L. By the comparison of the results from different time of exposure, there were no noticeable interferences from macromolecular organics.

In this study, passive sampling devices with granular activated carbon from Merck (1.5 mm, extra pure, food-grade quality) were applied. Active carbon was cleaned by heating to 300 °C in clean environment. Afterwards, active carbon was reactivated by a water steam and inserted in ultrapure water for transport on the sampling site. Approximately 3 g of the activated carbon was inserted into the passive sampler comprised of 1-mm mesh pouches fixed to 1-mm thick wire, all made of stainless steel. The passive sampling devices were installed in screened borehole sections. The preparation of activated carbon prior to installation in the passive sampler is described in detail in a previous study (Cerar and Mali, 2016).

3.3. Analytical methods

Preparation of the passive sampler for chemical analysis as well as the actual analysis procedure are described in detail in a previous study (Cerar and Mali, 2016). The adsorbed material on the passive sampler was 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 the ISO/IEC 17025 standard (accreditation certificate LP-023). For the interpretation of chromatograms the AMDIS (**A**utomated **M**ass spectral **D**econvolution and **I**dentification **S**ystem) 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). GC–MS chromatograms were interpreted by estimating peak intensities on a scale of 1 to 5 and with remark of tentative or confirmed identification according to ASTM D 4128 – 01 standard. Estimated peak intensity is connected with certainty of identification and provides a starting point for the quantitative monitoring of compounds (EURACHEM/CITAC, 2003).

In addition to the qualitative monitoring with passive samplers, spot samples for quantitative analysis of different organic compounds were taken (Koroša et al., 2016). Based on these results, the parallels between detection limits for the analysis of spot samples were determined; similarly the detection limit of individual compounds with passive sampling was evaluated (Table 1). Limit of detection was assessed by intensity of response from standard solution (1/10 of concentration was detectable in the worst case) and achieved area for detected analyte. 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. A good correlation between the results of quantitative monitoring data and the results of

Table 1
Estimation of detection limits of the compounds.

Analyte	CAS no.	Average concentration in two spot samples, ng/L	*m*/*z*	Area, standard solution 200 μg/L	Area, sample	Limit of detection, ng/L
Desethylatrazine	6190-65-4	77.1	172	125,687	25,104,003	0.039
Desethylatrazine	6190-65-4	62.9	172	125,687	469,035	1.690
Desethylatrazine	6190-65-4	102.3	172	125,687	817,223	1.570
Desethylatrazine	6190-65-4	61.5	172	125,687	583,792	1.320
Desethylatrazine	6190-65-4	88.1	172	125,687	2,104,969	0.530
Atrazine	1912-24-9	78.5	200	123,449	52,778,653	0.018
Atrazine	1912-24-9	49.1	200	123,449	942,432	0.640
Atrazine	1912-24-9	216.4	200	123,449	4,963,796	0.540
Atrazine	1912-24-9	67.4	200	123,449	1,302,997	0.640
Atrazine	1912-24-9	121.7	200	123,449	6,664,972	0.230
Caffeine	58-08-2	54.5	194	198,393	87,367,802	0.012
Caffeine	58-08-2	11.7	194	198,393	108,749	2.130
Caffeine	58-08-2	4.6	194	198,393	200,427	0.460
Caffeine	58-08-2	5.6	194	198,393	145,195	0.770
Caffeine	58-08-2	4.2	194	198,393	391,475	0.210
Carbamazepine	298-46-4	10.2	193	102,995	9,806,214	0.011
Carbamazepine	298-46-4	60.2	193	102,995	22,635,055	0.027
Carbamazepine	298-46-4	16.9	193	102,995	193,078	0.900
Carbamazepine	298-46-4	25.3	193	102,995	1,586,824	0.160

m/*z* – mass-to-charge ratio.

qualitative monitoring data from passive sampling was observed (Auersperger et al., 2015).

3.4. Quality assurance and quality control

MOs are often found in personal care products and medicines, therefore rigorous quality control (QC) of sampling needs to be conducted both in the field and in the laboratory. Sampling personnel should avoid using products containing compounds of interest to prevent secondary contamination of samples at sampling (e.g. using cosmetics, drinking coffee and consuming other products containing compounds of interest).

In each series of passive samples, regular blank tests and control samples spiked with MOs 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 the individual sample report (Table 2). 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 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 QC. Regular spiked QC samples were analysed with each chromatographic run, including blanks of spring water used for calibration.

3.5. Categorization of MO compounds

For individual compounds each group was categorized according to type, typical use and likely source. Eight groups of MOs were determined based on type of source: Halogenated solvents, Non-halogenated solvents, Pesticides, Domestic and personal, Plasticisers and additives, Other industrial, Sterols and Natural compounds. Compounds and their degradation products that could be attributed to several different groups were classified into their most likely groups. The "Domestic and personal" category includes lifestyle, personal care products (PCP), household, pharmaceutical and food additive compounds (Manamsa et al., 2016).

Further, an evaluation of three different groups of pollutants according to their origin (urban, agricultural and industrial pollution) was performed, and a potential source, significant in our study area, was defined for each compound. Most of the pesticides were

Table 2
Compounds typical for secondary contamination (Auersperger et al., 2012).

Compound	CAS no.	t_r, min	Fragments *m*/*z*	Source
Benzene	71-43-2	2.7	78/51	Gasoline, burning
Trichloroethene	79-01-6	3.3	130, 95	Industrial solvent
Toluene	108-88-3	4.1	91/65	Gasoline, burning
Tetrachloroethene	127-18-4	4.6	166/131, 94	Industrial solvent
1,4-Diclorobenzene	106-46-7	6.5	146/111, 75	Impurity in DCM
Acetophenone	98-86-2	6.9	77, 105, 120	Cosmetic
2-Phenyl-2-propanol	617-94-7	7.1	43, 77, 121	Cosmetic
Naphthalene	91-20-3	8.4	128, 129, 127	Oil, burning
Diethylphthalate	84-66-2	12.1	149, 177, 150	Plastic
Galoxolide	1222-05-5	16	243/258, 195	Cosmetic
i-Propyl myristate	110-27-0	16.3	228, 211, 102	Cosmetic
Di-i-butyl phthalate	84-69-5	17.4	223, 149, 57	Plastic
Di-*n*-butyl phthalate	84-74-2	19.3	223, 149	Plastic
i-Propyl palmitate	42-91-6	21.1	256, 239, 102	Cosmetic
Di-(2-ethylhexyl)-phthalate	117-81-7	33.4	149, 167, 279	Plastic
Squalene	7683-64-9	42	69, 81, 137	Natural compound
Cholesterol	57-88-5	49	386/368, 275	Natural compound

classified as agriculture, due to their use in the control of pests, weeds and plant diseases as well as for other applications in the city (weed control) (Lapworth and Gooddy, 2006). The exception was a pesticide with the tentative identification of Gibberellin A9, which because its source is unknown, was linked to urban activity of some kind. The compounds in the groups Domestic and personal, Other industrial, and Sterols and Natural compounds were classified as urban use, as they are most significant for groundwater contamination by virtue of their leaching from the sewage system, and from municipal landfills, as effluents from wastewater treatment plants (Stuart et al., 2012, 2014). The groups of Halogenated solvents, Non-halogenated solvents, and Plasticisers and additives were categorized as industrial use, all of which are indicative of older industrial pollution loads and active industrial effluents (Ritter et al., 2002).

3.6. Land use classification of sampling sites

Characteristics of the recharge area were studied for each sampling site in terms of the hydrogeological characteristics of the aquifer, as expressed as groundwater flow velocity and groundwater direction. Groundwater flow was calculated according to Darcy (1856). Based on calculated groundwater flow velocities, the distance from the outer recharge area border and sampling location was determined with a length of 3 months (1155 m) as the outer border of the recharge area. Sampling locations are piezometers, where groundwater wasn't constantly pumped from the object, so the recharge area was limited to a 30° angle (Rules on determining water bodies of groundwater, 2005; Prestor et al., 2006). Land-use classification was carried out using the CORINE land use data set for Europe (EEA, 2006) for each sampling site (agriculture, urban, industrial and forest). Data processing and calculations were performed using Statistica software (Stat Soft Inc., 2012) and spatial distribution was performed using ArcMap (ESRI Inc., 2004).

4. Results and discussion

4.1. Detection of MO compounds

In total, 103 MOs were identified in the first (summer), and 144 in the second (winter) sampling campaigns. Of all the compounds identified, 53 that were observed in both campaigns in the groundwater at the study area were selected for more detailed analysis (Table 3). Among the eight defined groups (Section 3.5.), most of the compounds have been classified as Pesticides (19), followed by a group of Halogenated solvents with 9 compounds, Other industrial, and Domestic and personal, both with 5 compounds, Plasticizers and additives and Natural compounds with 4 detected compounds. In the Sterols group only two compounds were identified.

4.2. Frequency and intensity of MOs detections using passive sampler

Fig. 2 shows an overview of the most commonly detected compounds in groundwater and the intensity of the selected compounds. A total of 605 identifications of MOs were detected in groundwater across all sampling sites. The most frequently detected compounds belong to the group of Pesticides (196) at 32%, followed by Halogenated solvents, Domestic and personal, Other industrial MOs, and Non-halogenated solvents. Less than 10% of all the detections achieve the determination of Natural compounds, the Plasticizers and additives, and the Sterols.

Analyses by individual compound are shown in Fig. 3. The most frequently detected were tetrachloroethene and trichloroethene, which belong to the group of the Halogenated solvents. Within the group of Pesticides atrazine and its metabolite desethylatrazine were also frequently detected, followed by metolachlor, gibberellin A9, terbuthylazine and desethylterbuthylazine. In the Domestic and personal compounds group erythritol and benzaldehyde were detected with considerable frequency. The typical sewage markers, caffeine and carbamazepine, have been ranked lower. Also 2,4-dimetil-2H-benzotriazole and 2-methyl-2H-benzotriazole from the group of Other industrial, and 2-ethyl-3-methylmaleimide, which belongs to the Natural compounds group, were detected relatively frequently.

4.3. Analysis of MOs based on typical use

As described in Section 3.5, the selected MOs were divided into three groups according to their intended use (agriculture, urban, industrial). Analysis of the compounds indicated uniform distribution of the compounds in all three groups. The Agriculture and Industrial groups with 18 in each, and the Urban group with 17 detected compounds.

Fig. 4 shows that the most frequently detected compounds in all sampling sites belong to the urban group (232), while the industrial compounds (194) and the agriculture (179) are less frequent.

Within the distribution of the frequency of the individual compounds with respect to their use (Fig. 3), a high incidence of industrial compounds, e.g. tetrachloroethene and trichloroethene, was observed. Among the MOs of agricultural origin the most frequent are the pesticides (atrazine and its degradation product desethylatrazine, and metolachlor). Atrazine has been forbidden since 2003 (Ambrožič et al., 2008; Heri et al., 2008). Of the 20 most frequently detected compounds, the urban compounds are the most represented, as expected, since the study area comprises the city.

4.4. Analysis of MOs based on seasonal variation

In order to investigate seasonal changes in the presence of MOs in groundwater, results from the summer and winter periods were split. In the summer series, a total of 253 compounds were identified, while in the winter series a higher number (352) were detected. Fig. 5 shows the frequency of identifications of each group of compounds in both sampling series. The numbers are higher for the winter sampling series for all groups, except for the Pesticides group. Regardless, however, the frequency of pesticides in both series is far higher than for any other group. This indicates the dominant presence of pesticides among MO pollutants in groundwater. The Halogenated solvents as well as Domestic and personal compounds see relatively greater frequency in winter, followed by the Non-halogenated solvents group. Other industrial, Natural compounds, Plasticizers and additives, and Sterols groups were detected in small amounts. A detailed overview of the detection frequency in percentage between sampling series by group, shows that the frequency of Pesticides and Halogenated solvents falls in the winter series.

Analysis identification was also performed for individual compounds for the two sampling series. In the summer series (Fig. 6), tetrachloroethene and trichloroethane are most frequent, followed by erythritol and atrazine, metolachlor, desethylterbuthylazine, terbuthylazine and desethylatrazine, while pharmaceuticals are detected only occasionally. In the winter series (Fig. 7), erythritol, 1,4-dioxane, and benzaldehyde are most often determined compounds, while trichloroethene and tetrachloroethene are only ranked fourth or fifth in terms of frequency. Carbamazepine and caffeine are detected at a far higher rate in the winter series compared to the summer series.

Results for the Pesticides group show frequent detections of atrazine, metolachlor and desethylatrazine in both series, and terbuthylazine, desethylterbuthylazine and propazine in the summer series. Although atrazine has been prohibited since 2003, together with its metabolite desethylatrazine, it is still found very frequently in the groundwater. A drop in the frequency of identification in the winter series is observed in all mentioned pesticides. In contrast, the metolachlor degradation

Table 3
List of selected MO compounds detected in groundwater, their grouping, source and typical use.

Code	CAS no.	t_R (min)[a]	Substance	Source	Group	Use
1	36038-53-6	8.0	1,1,4,4-Tetrachlorobutadiene (t.i.)	Industrial chemical	Halogenated solvents	I
2	87-61-6	8.7	1,2,3-Trichlorobenzene (t.i.)	Degreasing, pigments, chemical intermediates	Halogenated solvents	I
3	120-82-1	8.4	1,2,4-Trichlorobenzene (t.i.)	Insecticide, degreasing, pigments, chemical intermediates	Halogenated solvents	I
4	766-39-2	6.9	3,4-Dimethyl-2,5-furandione (t.i.)	Chemical intermediates	Halogenated solvents	I
5	593-71-5	4.1	Chloroiodomethane (t.i.)	Natural compound	Halogenated solvents	I
6	87-68-3	8.7	Hexachloro-1,3-butadiene (t.i.)	Solvent, coolants	Halogenated solvents	I
7	127-18-4	4.6	Tetrachloroethene (c.i.)	Dry cleaning, degreasing, industrial solvent	Halogenated solvents	I
8	75-25-2	5.4	Tribromomethane (t.i.)	Solvent, chemical intermediates	Halogenated solvents	I
9	79-01-6	3.9	Trichloroethene (t.i.)	Dry cleaning, degreasing, industrial solvent	Halogenated solvents	I
10	123-91-1	3.9	1,4-Dioxane (t.i.)	Oxygenate, solvent, stabilizer in halogenated solvents	Non-halogenated solvents	I
11	100-41-4	5.1	Ethylbenzene (t.i.)	Petroleum products, chemical intermediates, synthesis of styrene	Non-halogenated solvents	I
12	108-38-3 and 106-42-3	5.2	m- + p-xylene (t.i.)	Petroleum products, chemical intermediates	Non-halogenated solvents	I
13	95-47-6	5.4	*o*-Xylene (t.i.)	Petroleum products, chemical intermediates	Non-halogenated solvents	I
14	108-88-3	4.0	Toluene (t.i.)	Petroleum products, chemical intermediates, solvent, denaturant	Non-halogenated solvents	I
15	1912-24-9	14.2	Atrazine (c.i.)	Herbicide	Pesticide	A
16	98-10-2	11.8	Benzenesulfonamide (t.i.)	Degradation product of herbicide bensulide	Pesticide	A
17	314-40-9	17.7	Bromacil (t.i.)	Herbicide	Pesticide	A
18	–	25.0	Compound with major fragments *m/z* 162, 282 (t.i.)	Degradation product of herbicide metolachlor	Pesticide	A
19	6190-65-4	13.0	Desethylatrazine (c.i.)	Degradation product of herbicide atrazine	Pesticide	A
20	30125-63-4	13.2	Desethylterbuthylazine (c.i.)	Degradation product of herbicide terbuthylazine	Pesticide	A
21	110488-70-5	43.0	Dimethomorph (t.i.)	Fungicide	Pesticide	A
22	330-54-1 or 330-55-2 or as 102-36-3	9.7	Diurone or linurone (c.i.)	Herbicides linuron and diuron was detected after thermal decomposition in injector port as 3,4-dichlorophenyl isocyanate	Pesticide	A
23	60168-88-9	32.0	Fenarimol (t.i.)	Fungicide	Pesticide	A
24	120068-37-3	20.2	Fipronil (t.i.)	Insecticide	Pesticide	A
25	427-77-0	20.9	Gibberellin A9 (t.i.)	Natural fungicide	Pesticide	U
26	57837-19-1	17.0	Metalaxyl (t.i.)	Herbicide	Pesticide	A
27	51218-45-2	17.9	Metolachlor (c.i.)	Herbicide	Pesticide	A
28	23103-98-2	15.9	Pirimicarb (t.i.)	Insecticide	Pesticide	A
29	7287-19-6	16.9	Prometryn (c.i.)	Herbicide	Pesticide	A
30	139-40-2	14.3	Propazine (c.i.)	Herbicide	Pesticide	A
31	26259-45-0	15.3	Secbumeton (t.i.)	Herbicide	Pesticide	A
32	122-34-9	14.1	Simazine (c.i.)	Herbicide	Pesticide	A
33	5915-41-3	14.6	Terbuthylazine (c.i.)	Herbicide	Pesticide	A
34	80-56-8	5.8	Alpha-pinene (t.i.)	Insecticide, cosmetic, solvent, plasticizers	Domestic and personal	U
35	100-52-7	6.1	Benzaldehyde (t.i.)	Chemical intermediates, solvent, bee repellents	Domestic and personal	U
36	58-08-2	15.7	Caffeine (c.i.)	Urbane waste waters	Domestic and personal	U
37	298-46-4	26.0	Carbamazepine (c.i.)	Drug	Domestic and personal	U
38	149-32-6	7.9	Erythritol (t.i.)	Artificial sweeteners	Domestic and personal	U
39	119-47-1	27.7	2,2′-Methylenebis(4-methyl-6-*t*-butylphenol) (t.i.)	Antioxidant, stabilizer for polymers	Plasticisers and additives	I
40	3622-84-2	14.8	*N*-Butylbenzenesulfonamide (t.i.)	Plasticizer, metabolite of chlorobenzenes	Plasticisers and additives	I
41	78-40-0	7.7	Triethylphosphate (t.i.)	Plasticizer	Plasticisers and additives	I
42	115-96-8	14.3	Tris(2-chloroethyl) phosphate (t.i.)	Flame retardant	Plasticisers and additives	I
43	120-83-2	7.0	2,4-Dichlorophenol (t.i.)	Biocide, chemical intermediates	Other industrial	U
44	SERNO12256	9.4	2.4-Dimetil-2H-benzotriazol (t.i.)	Degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors	Other industrial	U
45	16584-00-2	8.6	2-Methyl-2H-benzotriazole (c.i.)	Degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors	Other industrial	U
46	626-43-7	9.0	3,5-Dichloroaniline (t.i.)	Chemical intermediates	Other industrial	U
47	95-16-9	8.9	Benzothiazole (t.i.)	Rubber additive, antimicrobial agents, flavors	Other industrial	U
48	2300-06-3	32.7	6β-Methylpregn-4-ene-3,20-dione (t.i.)	Steroid	Sterols	U
49	80-97-7	42.2	Cholesterol (t.i.)	Steroid, manure, septic tanks, sewage intrusion	Sterols	U
50	20189-42-8	8.9	2-Ethyl-3-methylmaleimide (t.i.)	Natural compound	Natural compound	U
51	624-92-0	4.2	Dimethyl disulfide (t.i.)	Natural compound, petroleum products	Natural compound	U
52	3658-80-8	6.2	Dimethyl trisulfide (t.i.)	Natural compound, petroleum products	Natural compound	U
53	10544-50-0	19.9	Sulphur S8 (t.i.)	Petroleum products, decomposition of tyres, reduction of sulphate	Natural compound	U

I – industry, A – agriculture and U – urban; t_R – retention time of organic compound; t.i. – tentative identification; c.i. – confirmed identification.

[a] t_R – retention time of organic compound (Auersperger et al., 2005).

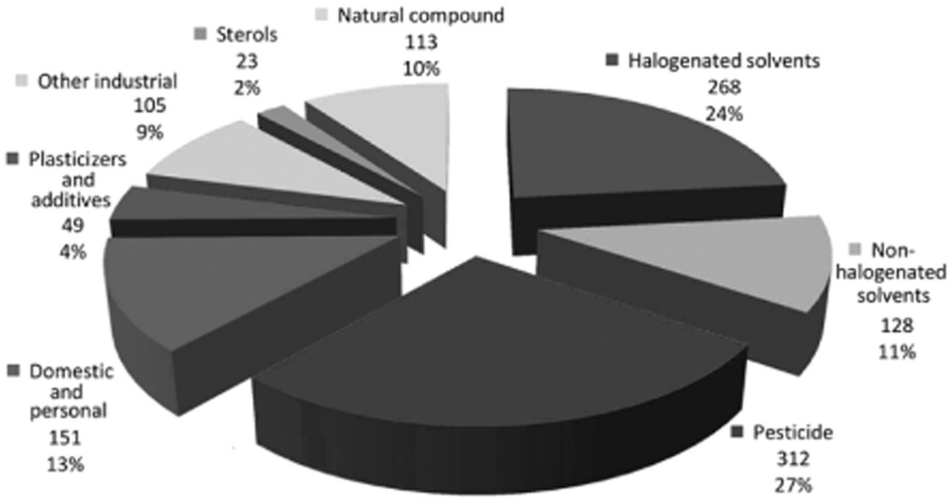

Fig. 2. Frequency of MO compound identification in groundwater with passive sampler.

product m/z 162.282, showed a marked increase in frequency of detections in the winter series. Giberllin A9, which was classified in the urban contaminants group, sees constant values with a slight increase in the winter series. Other pesticides do not show significant frequency changes between sampling series.

There is a larger difference between sampling series in the winter period for all Non-halogenated solvents. In the summer series, frequencies range from 1 to 5, while in the winter 7 to 14. In both series, the most frequently detected compound was 1,4-dioxane. In the summer series, toluene was detected once, while in the winter series it was detected in nine samples.

The frequency of identification of all compounds in the Domestic and personal group increased significantly in the winter series. The highest ascent is observed for benzaldehyde, followed by carbamazepine and caffeine. In the group of Other industrial compounds, 2-methyl-2H-benzotriazole and 2-methyl-2H-benzotriazole show a high rise in the rate of identification in the winter series. The same phenomenon can be observed for dimethyl-disulfide in the Natural compounds group. All these substances are markers of urban land use as source of groundwater contamination (Kloepfer et al., 2004; Stuart et al., 2014).

A comparison of detections for both sampling series based on the typical use of MOs is shown in Fig. 8. In the summer series, the frequencies of identifications are lower than in the winter series. In the summer series, indicators of agricultural pollution are more frequently detected, whereas those of urban and industrial pollution prevail in the winter series.

Differences in detection frequencies between the two sampling series could be explained by the different hydrogeological and climate conditions over the year, as well as differences in agricultural activities in the study area (Section 2). Despite of desorption processes, microbial and abiotic degradation as well as runoff into rivers, the greater leaching of contaminants is significant due to high permeable characteristics of the aquifer at study area. In the spring–summer period, when precipitation events are more abundant and intense (423 mm) than in autumn–winter period (313 mm), increased instances of pesticides of agricultural origin in the groundwater are observed, due to the increased application of such in the fields and leaching from the surface (Kreuger, 1998). Higher rainfall also caused greater leaching of old burdens, such as atrazine, which is still bound in the unsaturated zone. In contrast, the results show relatively higher values for metabolites of pesticides during the autumn–winter period, which is characteristic of lower precipitation levels and the presence of snow cover (Bloomfield et al., 2006). Also, the presence of organic compounds from urban and industrial pollution increases in this period. Usually, the sources of pollution are

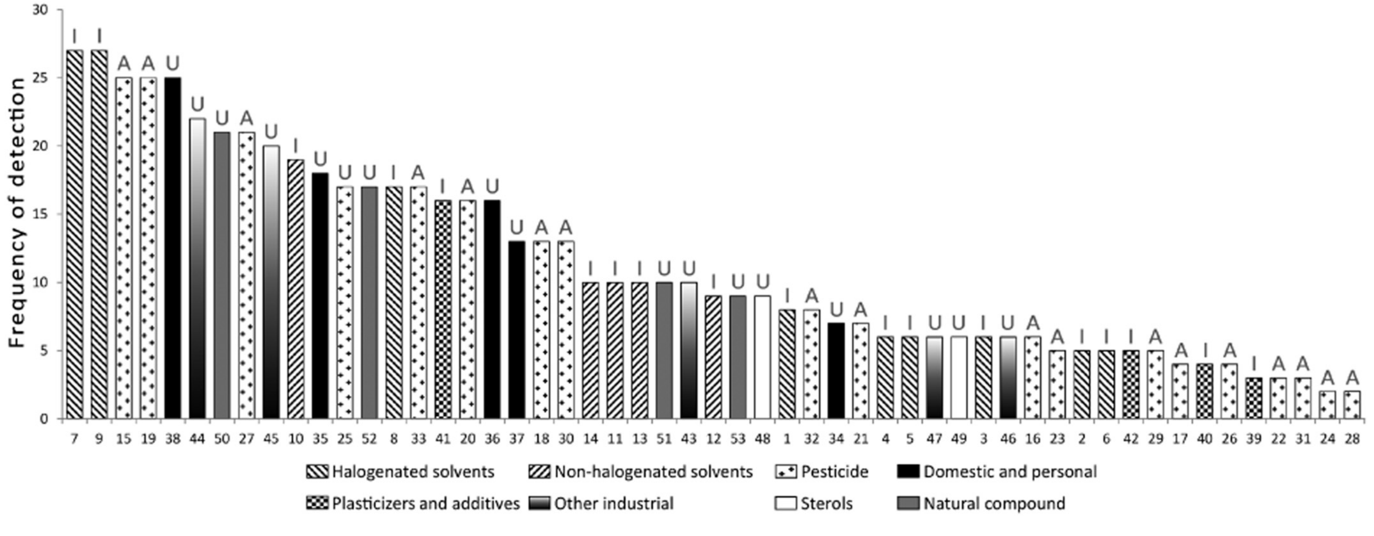

Fig. 3. Frequency of individual MO compounds in groundwater based on type of source (I – industry, A – agriculture and U – urban).

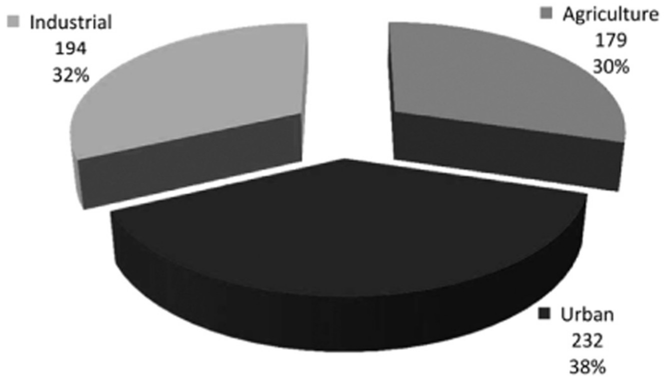

Fig. 4. Frequency of MO compounds in groundwater with passive sampler based on the groups agriculture, urban and industrial source.

sewage and discharges of waste-water. In our study area the industrial wastewater discharges are treated before disposal in public sewage system. The sewage system in the city has been renewed to a degree, yet there are parts where the network remains very old and where the leakage/losses are rather large. There are even areas with no regulated sewerage or have no organized sewage system whatsoever. We assume that losses from the sewage systems and emissions remain constant throughout the year. Thus, in the summer period, when groundwater levels are higher with more precipitation, compound concentrations of sewage origin undergo a faster rinsing and diluting process. In both series, high frequencies of trichloroethene and tetrachloroethene are identified. In the second period, relatively lower identification frequency for both compounds has been observed – just as with agricultural indicators. Both the values and dynamics of identification for these two compounds are explained by the possibility of old, buried industrial loads (Cerar and Mali, 2016). Leaching increases with the rainy season (Clara et al., 2004; Bloomfield et al., 2006), resulting in a higher incidence of these pollutants in groundwater. In the area where the aquifer is recharged by the Drava River (Section 4.5), the greater dilution of contaminants in groundwater is present. Since the discharges of Drava River are lower in the winter series (275 m^3/s) compared to summer series (320 m^3/s) (SEA, 2017), and consequently lower recharge of aquifer and lower groundwater table level, we assume that dilution in winter series is lower. In contrast, in the areas where the Drava River does not represent the recharge component of the aquifer, the dilution is dependent only on the amount and intensity of precipitation.

4.5. Spatial distribution of detected MOs

Pollution loads on individual sampling sites were assessed based on the results of frequency detection at each sampling site. Different groups of MO compounds were used to evaluate the pollution source. In general, pollution loads were estimated according to the sum of detection frequencies for 53 compounds in two sampling series (Fig. 9). The highest frequency values are observed on sampling sites P-1, DEM-1, IEILD-2 and K-27. As expected, sampling sites KP-2 and KP-8 exhibit lower frequencies values because only a single sampling was performed. Sampling sites HMZ-1 and MFV-1 exhibit the lowest MO frequency detection values in groundwater.

Analysis of frequency detections of MOs in groundwater at each sampling site based on compound groupings and typical use was interpreted on the basis of results from previous studies on groundwater dynamics (Mali et al., 2012; Koroša et al., 2016). Based on the natural and anthropogenic characteristics of each sampling site recharge area, sampling sites were classified and separated into three groups (Koroša et al., 2016):

(I) Group I represents sampling sites that are in direct hydraulic connection with the Drava River (HMZ-1, MFV-1, K-28).
(II) Group II represents sampling sites situated on the right bank of the Drava River, and are separated into two groups, depending

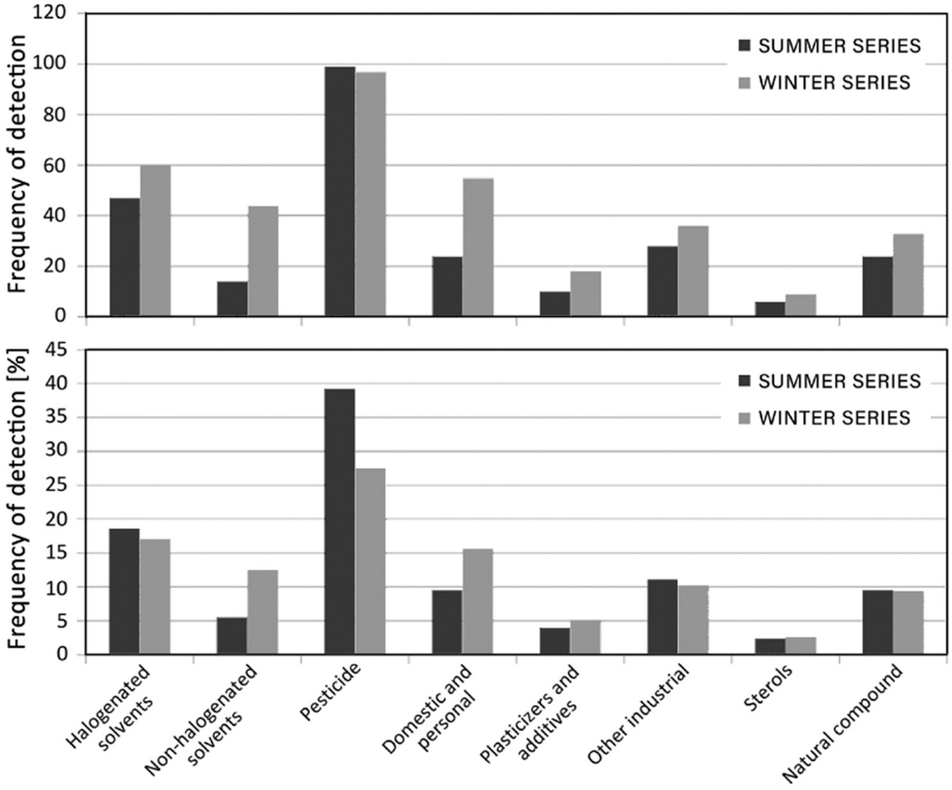

Fig. 5. Comparison of MO identification frequency for the summer and winter sampling series.

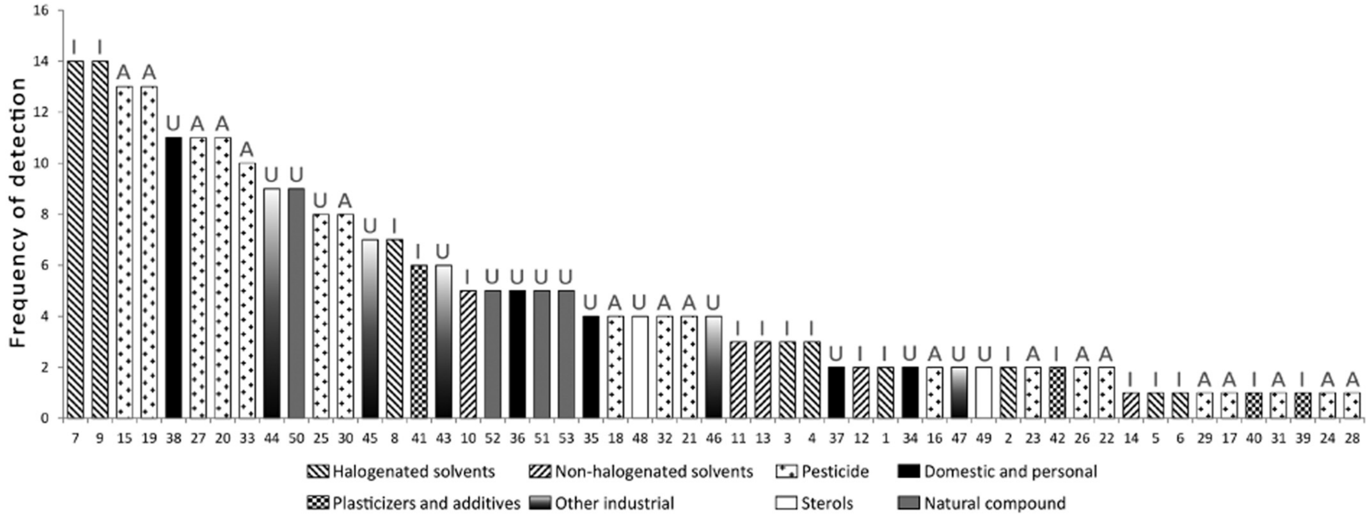

Fig. 6. Frequency of selected MO compound identification in groundwater–summer series (I – industry, A – agriculture and U – urban).

on location. They are recharged mostly by the local precipitation, and have no hydraulic connection with each other or with the Drava River.

(IIA) The Limbuš area (DEM-1, IEILD-2) is located in the western part of the study area, and according to the direction of groundwater flow, upstream from the pumping wells of Maribor Island.

(IIB) Area (MTT-1, MV-2) is located in the eastern part of the area, downstream from the pumping stations.

(III) Group III represents sampling sites with mixed waters recharged by the Drava River, the infiltration of precipitation, and by inflows from surrounding hills (KP-12, KP-8, K-27, KP-2, Well XIV, V-1, KP-14).

Table 4 shows the number of identifications for each group of compounds at each sampling site. Pesticides, which are most frequently identified, exhibit the most significant differences between sampling sites. The most polluted sampling site is piezometer P-1, located near the pumping station, where the groundwater is recharged from both sides (SW and SE) as part of the depression zone. High contamination levels could be the result of the old, historical contamination in the piezometer that cannot be cleaned due to the small diameter. Also, sampling sites IEILD-2 and DEM-1 show a very high risk of groundwater pollution mostly from pesticides, with both located in the Limbuš area, which lies directly in the hinterland of surrounding agricultural areas. Sampling site K-27 exhibits a relatively high rate of indicators of groundwater pollution, as it lies along the Drava River, but its recharge area also extends below the river to the industrial area on the right bank. Sampling sites HMZ-1 and MFV-1 show the least indication of groundwater pollution. Groundwater at both sites is largely recharged by the only mildly polluted Drava River. Other indicators of urban activities as well as the Industrial compounds do not exhibit significant differences between groups of sampling sites. This could be explained by the urban environment of the study area, where urban and industrial sources are both present.

4.6. Land use related to MO compounds

Table 5 presents classifications of land use by group of sampling site. Agriculture land prevails in recharge areas of group IIA sampling sites, while sampling sites in recharge areas from other groups see urban land dominate. As expected, the small proportion of forest in the

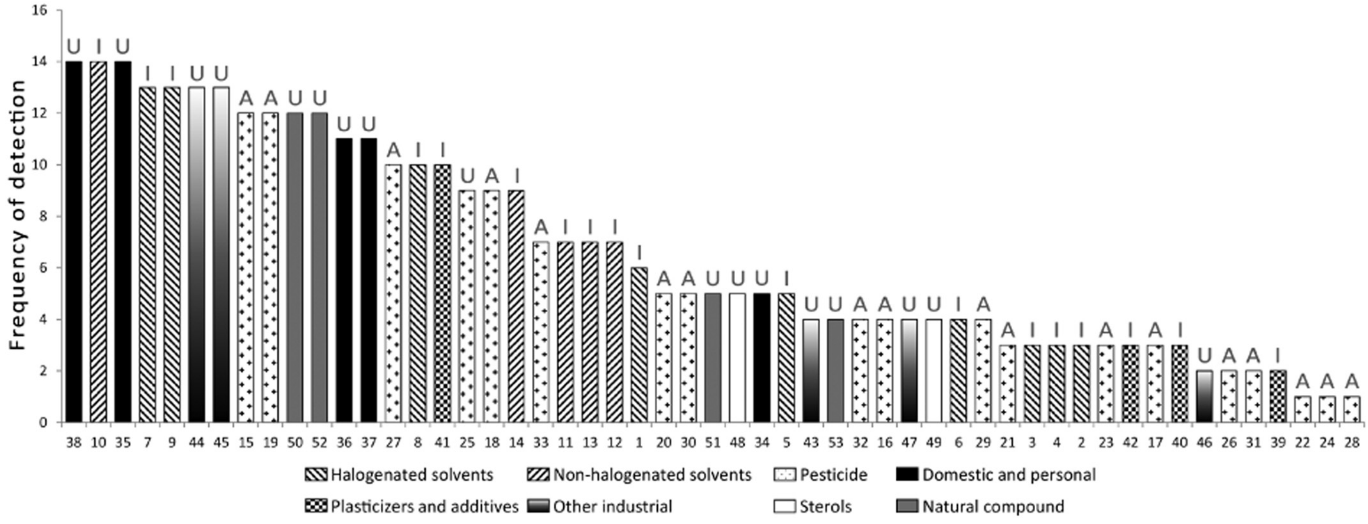

Fig. 7. Frequency of selected MO compound identification in groundwater– winter series (I – industry, A – agriculture and U – urban).

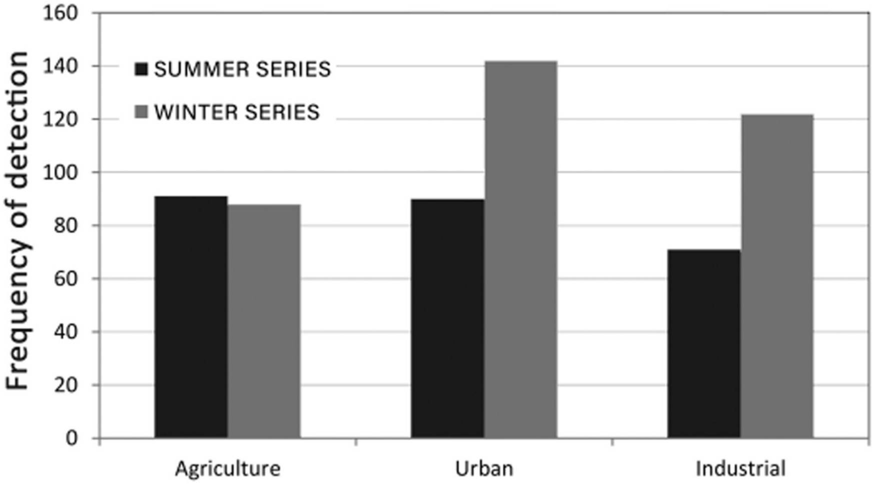

Fig. 8. Comparison of MO identifications in groundwater for sampling series in summer series and winter series based on type of use.

recharge areas of sampling sites is significant, owing to the location of the study area.

Mean frequency MO values by individual group of compounds in each group of sampling sites are presented in Table 6. Pesticides are most frequently detected in all groups of sampling sites; Halogenated solvents and Domestic and personal compounds are also detected with greater frequency. Group I represents the lowest mean MO frequency detection value (27.7), which indicates a greater influence from the recharge of surface water (Drava River), and consequently a greater dilution of pollutants in the groundwater. The most contaminated groundwater (100 detections) was observed in sampling sites from Group 2, which is largely recharged via the local infiltration of precipitation, and has no connection with Drava River and therefore exhibits lower dilutions of contaminants. Two subgroups (IIA and IIB) very clearly show the effect of land use (Table 7). The higher frequency of MOs in groundwater from sampling sites in Group IIA reflect the highest impact of intensive agricultural activity (28 detections), whereas sampling sites in Group IIB show the highest impact of urban sources i.e. largely unregulated sewage system (16 detections). Also, the area where sampling sites from Group IIB are located comprises a former industrial area, and includes a railway cargo depot and sports facilities (2,4-DHBT from the Other industrial group), which together with the use of pesticides to control weeds in urban areas, exert a significant impact on groundwater (8.5 detections). Group III consists of sampling sites located in the centre of the city, which are affected by contamination from various sources (agriculture, urban load and industry).

From the analysis of the spatial distribution of MOs in groundwater and land use classifications of the study area, it is evident that each sampling site is largely characterized by mixed land use, resulting in pollution of groundwater from various sources of various origins (Fig. 10). Koroša et al. (2016) also obtained similar results with their quantitative analysis of selected pesticides and pharmaceutical compounds based on classifications of land use.

Results of the analysis of detection frequency of MOs in groundwater show mixed land use in the study area; therefore, the dominant source of the pollution was difficult to specify. Differences in MO frequencies between groups of sampling sites may be the result of different recharge components and, to a lesser extent, land use.

5. Conclusions

The presence of MO contaminants in the groundwater could be determined using the passive sampling technique. A total of 103 MOs were identified in the groundwater of the study area – the Maribor City aquifer in the first (summer) sampling series – and a total of 144

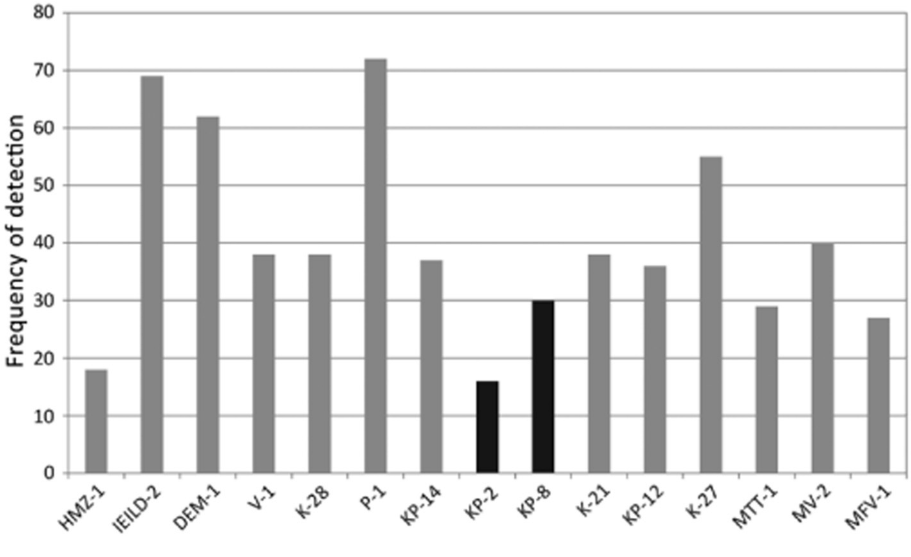

Fig. 9. The total frequency of selected MO compound identifications in groundwater at each sampling site. Sampling sites where only one sampling was performed are marked in black.

Table 4
Total frequencies of MO detections in groundwater in each group of compounds at each sampling site.

	HMZ-1	IEILD-2	DEM-1	V-1	K-28	P-1	KP-14	KP-2[a]	KP-8[a]	K-21	KP-12	K-27	MTT-1	MV-2	MFV-1	No. of identifications
Halogenated solvents	4	10	9	7	9	17	5	3	6	4	4	11	3	6	9	107
Non-halogenated solvents	2	5	5	5	1	9	6	1	5	2	5	6	2	4	1	59
Pesticide	3	31	29	11	14	22	7	6	8	12	9	22	11	10	1	196
Domestic and personal	4	8	7	5	5	8	6	1	4	7	7	4	4	5	4	79
Plasticizers and additives	0	5	2	1	0	4	3	0	2	1	2	1	1	4	2	28
Other industrial	2	6	5	3	5	7	5	3	2	4	3	5	4	6	4	64
Sterols	1	2	2	0	1	2	1	0	0	1	1	2	0	1	1	15
Natural compound	2	2	3	6	3	3	4	2	3	7	5	4	4	4	5	57
Frequency	18	69	62	38	38	72	37	16	30	38	36	55	29	40	27	605

[a] sampling sites where only a single sampling was performed.

in the second (winter) sampling series. The 53 most significant compounds were selected and classified into eight groups of MOs based on the type of their source: Halogenated solvents, Non-halogenated solvents, Pesticides, Domestic and personal, Plasticizers and additives, Other industrial, Sterols and Natural compounds. Three groups of compounds were determined based on type of use: agriculture, urban and industry.

A total of 605 identifications of MOs were observed in groundwater across all sampling sites. The most frequently detected compounds all belonged to the Pesticides group, followed by the Halogenated solvents group, and Domestic and personal groups. The most frequently detected micro-organics were tetrachloroethene and trichloroethene, which belong to the group of the Halogenated solvents. Atrazine and its metabolite desethyl-atrazine from the Pesticides group, and erythritol and benzaldehyde from the Domestic and personal group were also frequently detected. Caffeine and carbamazepine, which are typical sewage markers, ranked lower in frequency. The most frequently detected compounds among the groups based on type of use, belong to the urban group.

In our case, the differences in detection frequencies between the two sampling series could be mostly explained by the different hydrogeological and climate conditions over the year and by the different land use in the study area. In the summer series, the total frequencies of identification are lower than in the winter series. Indicators of agricultural pollution are more frequently detected in the summer series. In the winter series, which is characterized by less precipitation and the presence of snow cover, pollution from urban and industrial sources prevails, which is largely the result of constant leakage/losses from old, unregulated or the absence of sewage systems and of discharges from the many industrial plants and facilities over the course of the entire year.

Three groups of sampling sites were determined based on groundwater dynamics and the anthropogenic characteristics of the recharge areas. The significant differences between sampling sites that were observed could be largely attributed to the use of pesticides (agriculture). The lowest frequency values of all of the selected MOs were observed in Group I, where groundwater is hydraulically connected with the Drava River. The most contaminated groundwater was observed in the sampling sites from Group II, which are recharged mainly by the local infiltration of precipitation. This group was divided into two subgroups based on different land- use scenarios. The IIA group showed pollution of groundwater from intensive agricultural activity, while sampling sites from Group IIB reflect pollution from urban and industrial sources. Groundwater samples at the sampling sites from Group III exhibit contamination from various sources.

The results also indicate mixed land use of the various study areas, therefore the dominant source of pollution was often difficult to specify. Differences in MO frequencies between groups of sampling sites may be the result of different recharge components and, to a lesser extent, of land use.

Results show that pesticides still present a major problem for groundwater pollution in the area – even those pesticides that have been banned and not used since 2003 (atrazine).

Passive samplers based on activated carbon have been shown to be a useful tool to quantify micro-organic compounds in groundwater. Using such a sampling technique a wide range of previously unknown and unspecified compounds in groundwater could be determined. They should be further included and applied as part of a continuous quantitative monitoring regime. Further research will focus on validation techniques and the evaluation of uncertainty in measurement schemes in order to achieve semi-quantitative results.

Table 5
Classification of land use by sampling site group in groundwater catchment area.

	Agriculture (%)	Urban (%)	Industry (%)	Forest (%)
Group I	6	52	31	12
Group IIA	71	4	10	16
Group IIB	0	92	8	0
Group III	5	73	13	9

Table 6
Mean frequencies of MOs for individual groups of compounds by different groundwater recharge component groups.

	I	IIA	IIB	III
Halogenated solvents	7.3	9.5	4.5	8.1
Non-halogenated solvents	1.3	5.0	3.0	5.6
Pesticide	6.0	30.0	10.5	13.9
Domestic and personal	4.3	7.5	4.5	6.0
Plasticizers and additives	0.7	3.5	2.5	2.0
Other industrial	3.7	5.5	5.0	4.6
Sterols	1.0	2.0	0.5	1.0
Natural compound	3.3	2.5	4.0	4.9
Mean frequency	27.7	65.5	34.5	46.0

Acknowledgements

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Table 7
Mean frequencies of MOs for individual use groups by different groundwater recharge component groups.

	I	IIA	IIB	III
Agriculture	5.3	28.0	8.5	12.9
Urban	13.0	19.5	16.0	17.4
Industry	9.3	18,0	10.0	15.7
Mean frequency	27.7	65.5	34.5	46.0

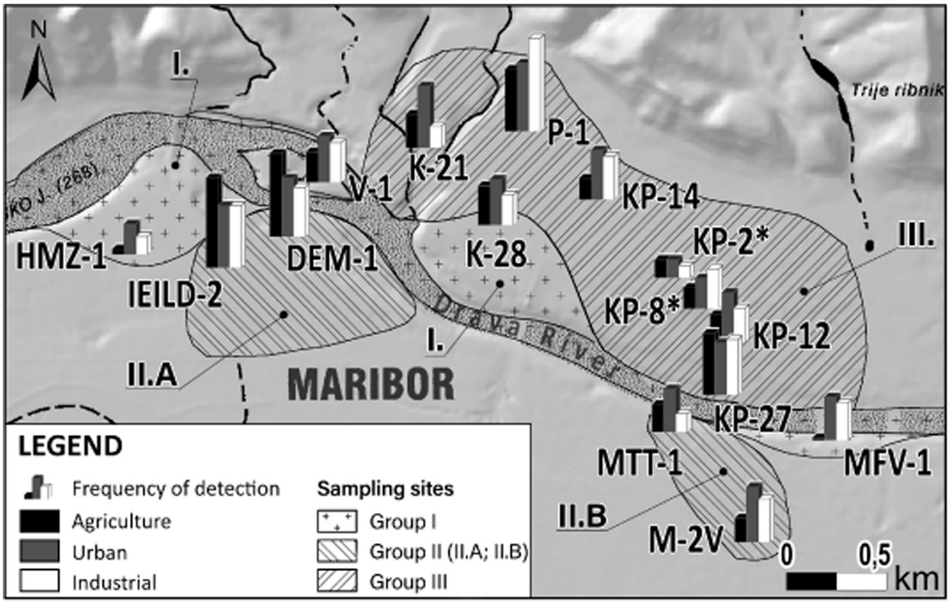

Fig. 10. Spatial distribution of detection frequency of MOs in groundwater based on type of use at each sampling site.

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