



Survey on the micro-pollutants presence in surface water system of northern Serbia and environmental and health risk assessment



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ABSTRACT

This study demonstrates the occurrence of 940 organic micro-pollutants in surface water of four rivers, one irrigation canal system, and two lakes in Vojvodina Province, the northern part of Serbia, summing in total eighteen samples. The number of detected chemicals ranged from 22 to 84, with 127 micro-pollutants detected at least once, representing 13% of the studied substances. The targeted compounds include n-alkanes, sterols, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides polychlorinated biphenyls, pesticides, pharmaceutical active compounds, industrial chemicals, plasticizers, etc. Among the analysed compounds, sterols were the most dominant with maximum quantified concentrations. The substances which were quantified with frequency over 50% were two PAHs (2-methylnaphthalene, benzo(ghi)perylene), five sterols (cholesterol, cholestanol, stigmaterol, fucosterol, beta-sitosterol), three pharmaceuticals and personal care products (L-menthol, diethyltoluamide, caffeine), and ten household chemicals (4-tert-octylphenol, dimethyl phthalate, methyl palmitate, phenylethyl alcohol, 1-nonanol, alpha-terpineol, 2-phenoxy-ethanol, methyl myristate, acetophenone, and 2-ethyl-1-hexanol). The list of priority substances under the European Union Directive 2013/39/EU includes 49 priority substances (PSs) out of which 34 were analysed. Among these, eleven PSs were quantified, and only two compounds (fluoranthene and benzo (a) pyrene) exceeded EU Environmental Quality Standards targeted values. The obtained results were compared with the previously published data that dealt with the same targeted number of micro-pollutants in sediment samples. This revealed connections between the same sampling locations. Environmental risk assessment showed the existence of potential ecological risk as 72% of the obtained values for the ecological hazard index (HI) at investigated locations were higher than the targeted value ($HI > 1$). Estimated values for hazard quotient (HQ) and hazard index (HI) for non-carcinogenic risk were lower than the targeted value, indicating no non-carcinogenic risk through dermal contact and non-intentional ingestion of water. Estimated values for cancer risk were all below 1×10^{-6} , which is not considered to pose significant human health risk.

1. Introduction

In order to get a wider picture about contamination status, sources, human health and ecological risks of micro-pollutants presence in environmental matrices, many national and international institutions have been developing guidelines for selection of micro-pollutants that should be monitored since many chemicals are in daily use (more than 100,000) (Von der Ohe et al., 2011). Environmental Quality Standard Directive 2008/105/EC (EC, 2008), followed by amended Directive 2013/39/EU (EU, 2013) and Decision 2015/495/EU (EU, 2015) together with the Directive 2000/60/EC (Water Framework Directive, WFD) (EC, 2000) led to the establishment of a list of 66 organic pollutants with the wide range of chemical nature (49 priority substances

(PSs) from Directive 2013/39/EU (EU, 2013) and 17 contaminants of emerging concern (CECs) from the Watch List of Decision 2015/495/EU (EU, 2015).

Conversely, limited data on the occurrence of emerging compounds (ECs) in the freshwater environment is available, because of the difficulty and expenses involved in sampling and analysis since the majority of analytical protocols are focused on regulated compounds (Murray et al., 2010). Therefore, method development and validation of emerging compounds is a financial and technical challenge. The analytical techniques capable of identifying and quantifying many different chemical groups are becoming essential tools in prioritizing organic micro-contaminants. An automated identification and quantification system with gas chromatography–mass spectroscopy database (AIQS-DB

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GC–MS) method for identification and quantification of hundreds of semi-volatile organic compounds (SVOCs) in environmental and food samples in a single analytical run was developed by Kadokami et al. (2005).

There are many studies relating the human health risk of selected classes of persistent chemical compounds (PAHs, PCBs) in different matrices, i.e. water, sediment, soil, road dust (Yu et al., 2014; Škrbić et al., 2017a, 2017b; Tongo et al., 2017). However there is limited information dealing with the simultaneous health risk assessment for more than one chemical class (Tang et al., 2017). In order to overcome this gap, this study deals with human health risk estimation of several groups of SVOCs quantified in surface water using the US Environmental Protection Agency (USEPA) protocol for human health risk assessment (USEPA, 2004, 2011, 2017).

There are many European countries (40, including the Republic of Serbia) without a single surface water monitoring study on the presence of micro-pollutants in the period of 2012–2017 (Sousa et al., 2018). Although Directive 2013/39/EU (EU, 2013) and Decision 2015/495/EU (EU, 2015) have been issued to prevent the adverse effects of specific compounds, many other emerging organic compounds which have been frequently found, such as caffeine, naproxen, metolachlor, estriol, acetaminophen, ibuprofen, atenolol, bisphenol A, etc are not included in the mentioned regulatory documents. Therefore, monitoring campaigns of compounds most frequently found in elevated concentrations, which are not included in the current regulations, and their risk assessment should be performed in different countries, over different seasons, comprising relevant sampling points in a more concerted way (Sousa et al., 2018). As a result, the aims of this study were a) to obtain extensive data regarding presence of a wide range of SVOCs in the water systems of northern Serbia; b) to compare the data with the previously published data for similar water systems and previously published data on the determination of the same number of SVOCs in sediment samples from the same locations at the same period of sampling (Škrbić et al., 2018); c) to evaluate the environmental and human health risks; d) to identify areas of concern for further investigation, and e) to determine the possible sources of emission by applying multivariate statistical analysis.

2. Materials and methods

2.1. Sample collection

The total number of samples taken was 18, including several locations on The Danube, the River Tisza, the River Begej, the River Krivaja, Danube-Tisza-Danube irrigation canal and two lakes (Fig. 1). These locations were chosen to cover all surface water systems in northern Serbia. Description of the sampling locations and water system types are given in Table 1. For comparison purposes, the codes of sampling (S1–S10) of our previous study (Škrbić et al., 2018), which dealt with the determination of the same number of SVOCs in sediment samples taken from the same sampling locations at the same period (as water samples), are found in Table 1 along with the codes of sampling locations (RW1–RW18) reported in this study. The total number of sediment samples in the previous study was ten. Two additional locations, which were not included in the previous study, are the natural lake Tikvara and the artificial lake in Bođani. The lakes have been used for fishing and recreational activities, especially for swimming during summer.

Water samples (coded from 1 to 18, Table 1, Fig. 1) were taken from surface water (up to 1.0 m deep) using amber glass bottles, in September 2014. The samples were transferred into glass bottles (1 L) previously washed with detergent, purified water, acetone, hexane and also with the sampled water from the point of collection. The bottles containing water samples, with minimum air head-space, were kept in an ice box and transported to a laboratory. Water samples were stored in the dark at a temperature of 4 °C and extracted within two weeks after sampling.

2.2. Sample preparation and micro-pollutants determination

Before extraction, surface water samples were filtered through a Whatman GMF-150 glass fibre filter. The extraction of the micro-pollutants was based on liquid-liquid extraction using dichloromethane followed by re-constitution in hexane without any sample clean-up involved in sample preparation. Full list of the chemicals used and the description of the sample preparation method are given in the Section S1 of the Supplementary material. The surface water extracts were analysed by using gas chromatographic–mass spectrometric (GC–MS, QP-2010 Plus, Shimadzu, Kyoto, Japan) method. This method is capable of operating in both selected ion monitoring (SIM) and total ion monitoring (TIM) modes and in conjunction with a mass spectral database it is able to identify and quantify nearly 1000 SVOCs (Table S1). Additionally, gas chromatography–triple quadrupole mass spectrometry (GC–MS–MS, TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan) (selected reaction monitoring, SRM), which provides lower quantification limits, was employed for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), as OCPs and PCBs are generally presented in environmental matrices at lower concentration ranges in comparison to the other targeted compounds (Škrbić et al., 2018). For the substances which were quantified by multiple methods (GC–MS (TIM/SIM) and/or GC–MS–MS (SRM)) results obtained by GC–MS–MS (SRM) were preferentially used followed by the results of GC–MS (SIM) and GC–MS (TIM).

Data on the analytical quality control, internal standards, GC–MS–SIM/TIM and GC–MS–MS–SRM settings, method limits of detection (MDL) are given in Tables S1–S3 and in the Sections S2 and S3 of the Supplementary material.

The MDLs of PAHs, OCPs, sterols, and PCBs measured by SIM were 1, 2, 8–320, and 0.4–1.6 ng/L, respectively, while the MDL of OCPs and PCBs measured by SRM ranged from 0.1 to 0.4 ng/L. The MDL of the remaining compounds measured by TIM were between 5 and 500 ng/L (Duong et al., 2015). The accuracy and precision of the developed method for more than 200 model compounds, that represent semi-volatile organic compounds that can be measured with GC–MS–SIM/TIM and GC–MS–MS–SRM, were reported in the previously published studies (Kadokami et al., 1995; Jinya et al., 2011).

2.3. Statistical analysis

Descriptive statistical parameters such as mean, median, minimum, and maximum values were calculated to describe the micro-pollutants contents in all samples using Microsoft Excel 2007 (Microsoft Office). Principal component analysis (PCA) was used to clarify possible emission sources of groups of SVOCs that are structurally similar or have similar usage. The data are log-transformed before applying the statistical analysis to get more symmetric distribution (Škrbić and Đurišić-Mladenović, 2010). In the statistical analysis, when concentrations were below the MDL, a value of half of the MDL was used (Škrbić et al., 2005a; Škrbić and Đurišić-Mladenović, 2007; Montuori et al., 2016). Statistical analysis was carried out by using DEL 13.2 Statistica (Tulsa, Oklahoma, USA).

2.4. Ecological and human health risk assessment

Ecological risk of the micro-pollutants quantified in the study was evaluated by calculating risk quotients (RQs) of individual compounds relative to fish (one of three different representative trophic levels of the ecosystem, such as algae, *Daphnia magna*, and fish) as the representative of environmental living organisms (Ginebreda et al., 2010). The estimation was carried out based on EMEA guidelines (CHMP, 2006; Ginebreda et al., 2010; Chen et al., 2015); RQ was calculated as the ratio between Measured Environmental Concentration (MEC) and Predicted No-Effect Concentration (PNEC). If the value of RQ is higher than unity it is interpreted as environmental risk, while

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