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**Analysis of phenolic compounds in the dissolved and suspended phases of Lake Balaton water by gas chromatography-tandem mass spectrometry**

T. Faludi<sup>a</sup>, Cs. Balogh<sup>b</sup>, Z. Serfőző<sup>b</sup>, I. Molnár-Perl<sup>a,\*</sup>

<sup>a</sup>*Institute of Chemistry, Department of Analytical Chemistry, L. Eötvös University, H-1518, Budapest 112, P.O. Box 32, Hungary;* <sup>b</sup>*Balaton Limnological Institute, Centre for Ecological Research of the Hungarian Academy of Sciences, H-8237, Tihany, Hungary;* \* *corresponding author; e-mail: perlne@chem.elte.hu; telephone: +36 1 372 26 16*

**Abstract**

As a novel approach to characterize the phenolic pollutants of Lake Balaton (western Hungary) ~~pollutants~~, 26 endocrine disrupting phenols (chlorophenols, nitrophenols, alkylphenols, triclosan, bisphenol-A) were quantified in dissolved and suspended particulate

matter (SPM) phases, alike. Sample collection was performed in the western and eastern basins, at twenty sites in April and October 2014.

Solid-phase and ultrasound-assisted extractions to withdraw target phenols from dissolved and suspended phases were employed. Compounds were derivatized with hexamethyldisilazane and trifluoroacetic acid for their quantification as trimethylsilyl derivatives by gas chromatography-tandem mass spectrometry. In Lake Balaton's dissolved phase 2-chlorophenol (103-164 ng/L), 4-chlorophenol (407-888 ng/L), 2,4-dichlorophenol (20.2-72.0 ng/L), 2,4,6-trichlorophenol (10.4-38.1 ng/L), 2-nitrophenol (31.0-66.5 ng/L), 4-nitrophenol (31.5-94.1 ng/L) and bisphenol-A (20.6-112 ng/L), while in its SPM 4-chlorophenol (<LOQ-1274 µg/kg, dry matter), 4-nitrophenol (423-714 µg/kg), 4-nonylphenol isomers (1500-2910 µg/kg) and bisphenol-A (250-587 µg/kg) were determined. Since phenolics appear partially or exclusively in the SPM the analysis of both phases proved to be of primary importance.

**Keywords:** phenolics; Lake Balaton; dissolved/suspended pollutants; GC-MS-MS

## 1. Introduction

One of the most important global environmental issues of our day is the ubiquitous presence of toxic organic compounds in the aquatic environment. Among the pollutants of particular concern are phenolic substances due to their potential endocrine disrupting properties in organisms like certain invertebrates (Prasain et al., 2012) and mammals (Wu et al., 2011), possibly even at low concentration levels (Rochester, 2013). By interfering with the human hormone system (Takayanagi et al., 2006), they can cause adverse health effects such as infertility (Chen et al., 2013) and birth defects (Philippat et al., 2012). The toxicity of

these substances to some freshwater algae (Aruoja et al., 2011) and fish (Holcombe et al., 1984) has also been reported.

Phenolic compounds are used extensively in various application areas around the globe. Cresols, chlorophenols and nitrophenols are important intermediates in the production of pesticides, preservatives and dyes (Pera-Titus et al., 2004; Harrison et al., 2005; Sanders et al., 2009). Long-chain alkylphenols (such as nonylphenol isomers) are employed in the synthesis route of alkylphenol ethoxylates, applied as industrial detergents (Cespedes et al., 2008). Triclosan is an important additive of many consumer products due to its antimicrobial properties (Ren et al., 2014), while bisphenol-A is an essential substance in the manufacturing of several resins and polymers (Asimakopoulos et al., 2012).

Surface waters can be exposed to anthropogenic phenolic substances either directly through municipal and industrial wastewater effluents (Zhong et al., 2012), agricultural runoff water discharges (Zgoła-Grześkowiak et al., 2009) and precipitation (Schummer et al., 2009) or indirectly through the biodegradation of certain detergents, pesticides, dyes and pharmaceutical drugs (Li et al., 2013). Due to the relatively high hydrophobicity (usually expressed with the octanol-water partitioning coefficient,  $K_{ow}$ ) of several phenolic compounds, such as 4-nonylphenol ( $\log K_{ow} = 4.48$ ), 4-octylphenol (4.12) and pentachlorophenol (5.01), a part of the total phenolic content of surface waters is expected to be retained by the SPM and sediment (Patrolecco et al., 2006; Petrovic et al., 2002).

Due to their toxicity and widespread presence in the aquatic environment, several phenols have been designated as priority pollutants by the EPA (USA CFR 40/423, Appendix A) and the European Union. Since the current version of the European Water Framework Directive (EWFD 2013/39/EU) defines environmental quality standards (EQSs) for the water sample as a whole, methods applied for surface water measurements shall include the analysis

of both the dissolved and - during some analytical procedures often discarded - suspended phases.

The presence of phenolic compounds in inland surface waters is relatively well documented, although most of the research undertaken in the field so far corresponds to the analysis of the dissolved phases of rivers. Various quantity of phenols have been detected ~~generally~~ within the 0.6 ng/L-29 µg/L concentration range in the Danube (on average 5-30 ng/L, Loos et al., 2010; 1.6-155 ng/L, Faludi et al., 2015) and Tisza rivers (20 ng/L-22 µg/L, Kovács et al., 2011), in Hungary, in several Chinese rivers (10 ng/L-29 µg/L, Gao et al., 2008; on average 24-362 ng/L, Wang et al., 2009) and in certain lakes in Finland (30-110 ng/L, Paasivirta et al., 1985) and in China (on average 0.6-464 ng/L, Zhong et al., 2010). Nonyl- and octylphenols have been identified within the 0.5-1000 ng/L concentration range (whole water) in the dissolved and suspended phases of the rivers Tiber, in Italy (130-580 ng/L, Patrolecco et al., 2006), Ter, in Spain (100-390 ng/L, Cespedes et al., 2008), Elbe, in Germany (0.9-52 ng/L, Heemken et al., 2001), Daliao, in China (0.5-777 ng/L, Li et al., 2013), Loudias, in Greece (13-277 ng/L in the dissolved phase, 0.05-2 µg/g in the SPM, Arditoglou and Voutsas, 2008) and two rivers flowing into Tokyo Bay (10-1000 ng/L in the dissolved phase, on average 0.33-3.5 µg/g in the SPM, Isobe et al., 2001).

Lake Balaton (a rift lake situated in western Hungary) with its approximately 600 km<sup>2</sup> water surface is the largest lake of Central Europe. With an average depth of 3.4 meters, it is considered a shallow lake, and as a result turbulence initiated by the northwestern winds prevalent in the area can facilitate the thorough mixing of its water layers and the rapid resuspension of its sediment. Another consequence of its shallowness (and moderate continental climate) is that the water temperature of the lake on calm summer days can rise to as high as 29-30 °C. The size of Lake Balaton's catchment area is 5200 km<sup>2</sup>, which is drained predominantly by River Zala flowing into the lake at its southwestern end, while several

considerably smaller streams make up the rest of the lake's inflow. The only outflow is the Sió canal situated at the southern bank of the eastern basin. Among factors which possibly influence Lake Balaton's ecosystem are various agricultural, industrial, and municipal activities in the surroundings of the lake. Recreational use (especially during summer) might cause additional environmental stress (Nguyen et al., 2005a; Nguyen et al., 2005b).

Efforts have been made over the past few decades towards the assessment of water quality in and around the lake, primarily focusing on inorganic pollutants. Researchers have carried out the speciation of elements in sediment (Hlavay and Polyák, 1998; Weisz et al., 2000; Nguyen et al., 2005a) and measured the distribution of heavy metals between water phases (Nguyen et al., 2005b). In contrast, only limited data is available regarding the organic pollutants of the lake: PAHs in sediment (Kiss et al., 1997) and selected pesticides in water (Maloschik et al., 2007) have been quantified, but several important toxic contaminant classes, such as phenols, haven't been investigated yet have yet to be investigated.

~~As the available data on Balaton Lake's phenolic pollutants is still, for the being were not available, we assume that further data of these compounds in this freshwater environment might help to identify possible pollution sources and processes typical of inland surface waters and assist legislators in the improvement of environmental quality standards.~~

Our goal was to determine the distribution of 26 different phenolic compounds between the dissolved and suspended phases of Lake Balaton water samples by gas chromatography-tandem mass spectrometry, based on our previous experiences both in this field (Faludi et al., 2013, 2015) and also in others (Sebők et al., 2008, 2009; Andrási et al., 2011a, 2011b, 2013).

## **2. Materials and methods**

### **2.1. Materials**

All reagents were of analytical grade. Pyridine, sodium hydroxide, and concentrated hydrochloric acid were purchased from Reanal (Budapest, Hungary). Hexane, methanol, ethyl acetate, hexamethyldisilazane (HMDS), trifluoroacetic acid (TFA), and reference chlorophenols (CPs) like 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 3,5-dichlorophenol (3,5-diCP), 2,5-dichlorophenol (2,5-diCP), 2,6-dichlorophenol (2,6-diCP), 2,4-dichlorophenol (2,4-diCP), 2,3-dichlorophenol (2,3-diCP), 3,4-dichlorophenol (3,4-diCP), 2,4,6-trichlorophenol (2,4,6-triCP), 2,4,5-trichlorophenol (2,4,5-triCP), 2,3,4-trichlorophenol (2,3,4-triCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-tetraCP) and pentachlorophenol (pentaCP), methylphenols (MPs) like 2-methylphenol (2-MP), 4-methylphenol (4-MP) and 2,4-dimethylphenol (2,4-diMP), nitrophenols (NPs) like 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and other phenolic substances like 4-chloro-3-methylphenol (4-Cl-3-MP), 4-chloro-3,5-dimethylphenol (4-Cl-3,5-diMP), 4-n-octylphenol (4-n-OP), 4-n-nonylphenol (4-n-nonP), 4-nonylphenol isomeric mixture (4-nonP mixture), triclosan (TCN) and bisphenol-A (BPA) were all acquired from Sigma-Aldrich (St. Louis, MO, USA). Solid-phase extraction (SPE) cartridges (Supel-Select HLB, 6 cm<sup>3</sup>) were also obtained from Sigma- Aldrich. Glass microfiber filters (GF/A 125 mm, Ø, Cat No 1820-125) from Whatman (Maidstone, UK). Ultrasonic extractions were performed on the Bandelin Sonorex (RK 52 H) apparatus (Bandelin electronic, Berlin, Germany).

## 2.2. Sample collection

In order to achieve the largest coverage area ~~coverage~~ possible while ~~at the same time~~ also limiting the number of samples taken ~~to a reasonable level~~, a composite sampling method was ~~chosen~~ selected for this study. Composite sampling is a procedure during which carefully selected individual samples are physically mixed, and only the resulting composite sample

(representing the original samples) is analyzed, thereby reducing analysis costs while maintaining the integrity of the sampling process (Patil, 2006). This approach is especially advantageous in environmental monitoring studies where large spatial and/or temporal coverage is required (Jálová et al., 2013; Domínguez-Morueco et al., 2014).

The sampling sites of the individual samples of this survey were chosen to ensure that the resulting composite samples will provide the most accurate representation of Balaton water quality possible. In order to achieve this goal, littoral zones and open water areas near all important inflows (characterized with either by their considerable flow rate or their proximity to a known pollution source) were sampled.

Lake Balaton water ~~and sediment~~ samples were obtained by column ~~and mud~~ samplers at ~~5–5~~ 5 sites in the open water and 5 sites in the littoral zone near to the ~~frequented~~ important inflows of the western (Keszthely, Szigliget basin) and eastern (Siófok basin) basins of the lake ~~Lake Balaton~~ in early April and early October of 2014. Twenty sampling sites were selected altogether for this survey, 10 for each basin, as shown in Fig. 1. Two and a half L lake water from each sampling site was mixed to obtain a 25 L composite water sample for each basin.

## **2.3. Sample preparation**

### **2.3.1. Solid-phase extraction (SPE) of the dissolved phase**

Water samples were filtered through glass microfiber filters. The filtrates were acidified with concentrated hydrochloric acid to pH 3 before subjected to solid-phase extraction. SPE procedures were performed on the Visiprep DL Vacuum Manifold for 12 samples (Cat No. 57044) acquired from Supelco (Bellefonte, PA, USA) with a flow rate of 4–5 mL/min. SPE cartridges were conditioned with 5 mL hexane, 5 mL ethyl acetate, 10 mL

methanol and 10 mL distilled water prior to extraction. After the extraction procedure, cartridges were dried by vacuum. Elutions were carried out with a 4 mL solvent mixture (hexane/ethyl acetate/methanol, mixed in 1/1/2 v/v ratios). The 4 mL eluent was collected into a vial containing 250  $\mu$ L methanol with sodium hydroxide ( $5 \times 10^{-3}$  M). The eluent (further on: extract) was evaporated to dryness by means of a rotary evaporator {Büchi Rotavapor R-200 and Büchi Vacuum pump V-700, both from Büchi (Flawil, Switzerland)} at 30–40 °C. Blank tests (reagent and SPE blanks) were carried out with each sample series.

### **2.3.2. Ultrasonic extraction of suspended particulate matter**

Glass microfiber filter papers (containing the SPM) were dried overnight at ambient temperature until constant weight, then the papers were cut into  $5 \times 5$  mm pieces and were put in glass beakers (150 mL). Extractions were made with a solvent mixture of hexane/ethyl acetate/methanol, applying the same solvent ratios as used for the SPE process (1/1/2, v/v ratio). At first, 40 mL of solvent mixture (if necessary, more, in order to cover the paper pulp completely) was added to the glass beakers and sonicated in an ultrasonic bath for 20 min. This step was repeated two times with 20 mL (or more) solvent mixture. The supernatant extract portions were filtered through glass micro-fiber paper after each extraction step and then they were unified into a single stock solution. Aliquots (taken with analytical precision) from this unified extract were basified with 250  $\mu$ L methanol containing sodium hydroxide ( $5 \times 10^{-3}$  M), and then evaporated to dryness with a rotary evaporator at 30–40 °C. Blank tests (reagents and glass filter paper blanks) were carried out with each sample series.

### **2.3.3. Derivatization of standard solutions and sample extracts**



Reference compounds weighed with analytical precision were dissolved in methanol (20–25 mg/25mL) and these stock solutions were further diluted into standard solutions (10×, 100×, 1000×). Aliquots from these standard solutions were basified with 250 µL methanol containing sodium hydroxide ( $5 \times 10^{-3}$  M), and then evaporated to dryness. The residues of standard solutions and of sample extracts were derivatized at 70 °C for 30 min with a reaction mixture of 125 µL pyridine, 225 µL HMDS and 25 µL TFA. The solutions were diluted with HMDS (5×) before GC–MS analysis. The target compounds were quantified as their trimethylsilyl derivatives.

#### 2.4. GC-MS-MS analysis

All measurements were carried out with a Varian 240 GC–MS/MS system (Varian, Walnut Creek, CA, USA), equipped with a Varian CP-8400 autosampler, and with a septum-equipped programmable temperature vaporizer (PTV) injector. The injection volume was 1 µL in all cases. The column used was a product of SGE (Victoria, Australia; SGE forte BPX-5 capillary: 30 m × 0.25 mm;  $df = 0.25$  µm). Helium (99.9999% purity) was used as a carrier gas, with the column flow rate fixed at 1 mL/min. The temperature of the transfer line, ion trap and vacuum manifold was 300 °C, 210 °C and 80 °C, respectively.

The optimized temperature programs, different for the PTV injector (a) and for the column oven (b), were the following:

(a) injections were made at 50 °C, held at 50 °C for 0.5 min, then heated up to 250 °C (200 °C/min), with a 3 min hold at 250 °C,

(b) column temperature program started at 50 °C, held for 1 min, then heated up to 140 °C by 10 °C/min, held for 2 min, then heated up to 210 °C by 20 °C/min, then up to 280 °C by 40 °C/min and held at 280 °C for 1 min (total program runtime: 18.25 min).

The ion-trap mass spectrometer was operated in the multiple reaction monitoring (MRM) acquisition mode during measurements. The optimized parameters (including the selected precursor and product ions) for all target compounds and the method validation data can be found in our previous publication (Faludi et al., 2015).

### **3. Results and discussion**

#### **3.1. Spatial and seasonal changes in the concentrations of phenolic pollutants**

Out of the 26 target compounds 8 were found in both basins of Lake Balaton in the dissolved and/or suspended phases regardless of sampling season: in total four chlorophenols (2-CP, 4-CP, 2,4-diCP, 2,4,6-triCP), two nitrophenols (2-NP, 4-NP), 4-nonylphenol isomers and bisphenol-A (Table 1). A comparison of the measured concentrations with available literature data on the phenolic pollutants of other inland surface waters can be found in Table 2.

Among Lake Balaton's quantified phenolic pollutants, chlorophenols were the most abundant, as they were accounted for on average 82 % of the total phenolic concentration measured. The concentrations of detected monochlorophenols (528-1052 ng/L, in total) are significantly higher compared to literature data available on inland surface waters, for example on Taihu lake and the Pearl river in China (on average 6 ng/L, Zhong et al., 2010; on average 252 ng/L, Wang et al., 2009) and on the river Danube (186 ng/L, Faludi et al., 2015), while the concentrations of 2,4-diCP (20-72 ng/L) and 2,4,6-triCP (10-38 ng/L) were comparable to what was measured during the above mentioned and other surveys summarized in Table 2. Of the two basins, the western proved to be more polluted with chlorophenols in both seasons (western: 862-1150 ng/L, eastern: 559-1050 ng/L, in total), although the concentration gap was small in autumn. The location of western basin sampling points WL3

and WO3 (Fig. 1) might explain this difference, as they are in close proximity to the inflow of river Zala, the biggest tributary of the lake. Concentration levels of all detected chlorophenols were higher in the autumn than in the spring (1050-1150 ng/L compared to 559-862 ng/L, sum of detected chlorophenols). This seasonal increase might be attributed to two factors: factors. One possible factor is the intensification of agricultural activity on the catchment area of the lake in late spring and summer (as mono- and dichlorinated phenols are important degradation products of popular phenoxyacetic herbicides; Czaplicka, 2004). One other possible factor is and the higher amount of municipal wastewater generated by the temporary population increase of coastal towns during the summer holiday season (because the disinfection of wastewater and tap water by chlorination generates chlorinated phenols; Ge et al., 2008).

The concentrations of detected nitrophenols were fairly consistent from basin to basin (eastern: 68-129 ng/L, western: 66-171 ng/L, 2-NP and 4-NP total), and were somewhat higher compared to the levels detected in recent years in River Danube (1-61 ng/L, Loos et al., 2010; Faludi et al., 2015; ~~Mei et al., 2015~~), but significantly lower than what was found in the polluted Taihu lake, in China (464 ng/L on average, Zhong et al., 2010). The measured decrease from spring to autumn (from 129-171 ng/L to 66-68 ng/L) might be explained with the acceleration of biodegradation processes in the summer. One possible source of nitrophenol pollution in the lake is rainwater: various nitrophenols (for example 4-nitrophenol, 2,4-dinitrophenol) have been detected in rainwater samples in Denmark (in the range of 92 ng/L-12 µg/L, (Asman et al., 2005)), in France (<LOD-140 ng/L, Schummer et al., 2009) and in Germany (median values 0,2-1,0 µg/L, Schüssler and Nitschke, 2001).

4-nonylphenol isomers were only determined in the SPM, in concentrations lower than the environmental quality standard (EQS) established by the EU for inland surface waters (an annual average of 300 ng/L for the sum of the dissolved and suspended phases, EWFD

2013/39/EU). Environmental levels expressed in ng/L (17-41) were generally below literature values (7-2400 ng/L), while concentrations expressed in µg/g for the suspended particulate matter (1.5-2.9) were in line with literature data (2-3.5 µg/g, Isobe et al., 2001; Arditoglou and Voutsas, 2008). No significant concentration difference was observed between the two basins, but a seasonal drop was registered from spring to autumn (from 37-41 ng/L to 17-20 ng/L), similarly to the case of nitrophenols. The same seasonal trend was observed by other research groups (Isobe et al., 2001; Li et al., 2004), and it is presumed to correlate with the lower degradation rate of nonylphenol ethoxylates (parent compounds of nonylphenol isomers) in the colder seasons compared to warmer ones.

Bisphenol-A was also present in each basin in both seasons. Its measured concentrations (25-118 ng/L) were in the range of other surface waters (predominantly rivers) around the globe (Table 2), aside from the seemingly more polluted Elbe river in Germany and several Chinese rivers (concentrations as high as 776-3500 ng/L, Heemken et al., 2001; Huang et al., 2012). The western basin was found to be more polluted, possibly because western basin sampling points WL1 and WO1 were in the proximity of Burnót stream, which receives 109.000 m<sup>3</sup> cleaned industrial sewage annually from a mineral water bottling factory. A spring to autumn bisphenol-A concentration decrease (as in the cases of nitrophenols and nonylphenol isomers) was observed, as concentrations measured in April (53-118 ng/L) in both basins were higher than in October (25-26 ng/L).

Although the concentrations of phenolic compounds detected in Lake Balaton are below their respective environmental quality standards defined by the EU for inland surface waters and the available acute toxicity levels regarding certain freshwater organisms (in the mg/L range for algae and in the µg/L range for fish, Aruoja et al., 2011; Holcombe et al., 1984), due to the ability of these substances to bioaccumulate in a wide range of aquatic species including algae, certain invertebrates, and several species of fish (Ahel et al., 1993;

Mayer et al., 2007; Liu et al., 2011; Lee et al., 2015), the identified phenolic pollutants might still be detrimental to the health of the lake's ecosystem. To gain a better understanding of the possible effects of these substances to Lake Balaton's ecosystem, additional studies (for example tissue analysis of aquatic organisms and toxicological experiments) will have to be undertaken.

### **3.2. Distribution of phenols between the dissolved and suspended phases**

On average, a little less than 5 percent of the total measured phenolic content was bound to the suspended particulate matter of the samples. 2-CP, 2,4-diCP, 2-NP and 2,4,6-triCP were only detected in the dissolved phase, while 4-chlorophenol, 4-nitrophenol and bisphenol-A were partially and 4-nonylphenol isomers were exclusively retained by the SPM (Figs. 2a-d). These results are generally in line with prior expectations, given the relatively low hydrophobicity of bisphenol-A, nitrophenols, mono-, di- and trichlorophenols, and the higher hydrophobicity of 4-nonylphenol isomers. No significant basin-to-basin or season-to-season difference was observed in the distribution of a certain compound between water phases.

## **4. Conclusions**

The goal of this study was the analysis of phenolic endocrine disrupting compounds in Lake Balaton, contemplated in light of the negative environmental impact of these substances and the scarcity of available data on their concentration in larger lakes. The application of a composite sampling protocol ensured sufficiently large area coverage (spanning from the southwestern to the northeastern edges of the lake) for the accurate assessment of phenolic

pollution. Two sampling campaigns have been conducted (in the spring and autumn of 2014) to quantify possible seasonal fluctuations.

Our survey has confirmed, for the first time to our knowledge, the presence of 8 different phenolic pollutants in the dissolved and suspended phases of Lake Balaton water.

As certain compounds were found partially or exclusively adsorbed to the SPM, the results underline the importance of regarding the suspended particulate matter as an integral part of water samples in water quality evaluation studies and during the legislative process of defining environmental water quality standards.

## **Figure Captions**

### **Fig. 1**

Open water (O) and littoral zone (L) sampling sites of the spring and autumn sampling campaigns carried out in the western (W: WO1-WO5; WL1-WL5) and eastern (E: EO1-EO5; EL1-EL5) basins of Lake Balaton

### **Figs. 2a-d**

Distribution of substituted phenols between the dissolved and suspended phases of Lake Balaton water measured in the eastern (April: a, October: b) and in the western (April: c, October: d) basins, concentrations are presented in ng/L; error bars on the columns indicate the standard deviation of three parallel measurements; values in parentheses reveal partition percentages between the two phases

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