



Organic micropollutants in water and sediment from Lake Mälaren, Sweden



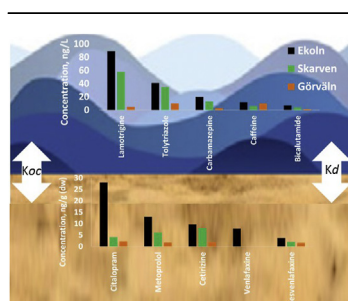
Oksana Golovko^{*}, Anna-Lena Rehr, Stephan Köhler, Lutz Ahrens

Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), SE-75007, Uppsala, Sweden

HIGHLIGHTS

- Occurrence and distribution of OMPs in water and sediment were studied.
- The partitioning of contaminants between lake compartments was estimated.
- The environmental risks of OMPs were assessed based on the RQ values.
- The sorption to sediment plays a minor role in removal of most of OMPs analyzed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 January 2020

Received in revised form

22 May 2020

Accepted 1 June 2020

Available online 6 June 2020

Handling Editor: Klaus Kümmerer

Keywords:

Pharmaceuticals

Aquatic environment

Lake

Target analysis

Sediments

ABSTRACT

The occurrence and distribution of 111 organic micropollutants (OMPs) were evaluated in water and sediment samples from Lake Mälaren, Sweden, using a liquid chromatography-tandem mass spectrometry method. The partitioning of contaminants between lake compartments was estimated using solid water distribution coefficients (K_d) and organic carbon-water partitioning coefficients (K_{OC}). In total, 30 and 24 OMPs were detected in lake water and sediment, respectively. Concentrations ranged from low ng/L to 89 ng/L (lamotrigine) in lake water and from low ng/g dry weight (dw) to 28 ng/g dw (citalopram) in sediment. Carbamazepine, lamotrigine, caffeine, and tolyltriazole were the dominant compounds in Lake Mälaren samples (both water and sediment). Seventeen OMPs were detected in both water and sediment samples, including carbamazepine, DEET, tolyltriazole, bicalutamide, caffeine, lamotrigine, and cetirizine. Log K_d values varied between 0.84 for lamotrigine and 4.4 for citalopram, while log K_{OC} values varied between 2.1 for lamotrigine and 5.9 for citalopram. These results indicate that sorption to sediment plays a minor role in removal of all OMPs analyzed in the aqueous phase except for citalopram and cetirizine, which showed high sorption potential. The environmental risks of OMPs were assessed based on the RQ values. The worst-case scenario for environmental risk assessment was conducted using the maximum measured environment concentration. For most of the target OMPs, including tolyltriazole, bicalutamide, fexofenadine, oxazepam, cetirizine, and diclofenac, the RQ values were below 0.01, indicating low or no risk to lake ecosystems.

© 2020 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Organic micropollutants (OMPs) such as pharmaceuticals, personal care products, pesticides, stimulants, and artificial sweeteners have been identified as emerging contaminants due to the

^{*} Corresponding author.

E-mail address: oksana.golovko@slu.se (O. Golovko).

possible threats to ecological environments (Liu and Wong, 2013; Petrie et al., 2015). Municipal, industrial, and on-site wastewater treatment facilities are considered major sources of OMPs in aquatic environments (Söregård et al., 2019; Gago-Ferrero et al., 2017). Conventional wastewater treatment facilities have low removal efficiencies for OMPs, which are present globally in groundwater and surface water, including drinking water reservoirs (Petrie et al., 2015; Yang et al., 2017; Patel et al., 2019). Typical concentrations of OMPs in surface water range from ng/L to µg/L (Petrie et al., 2015). Some OMPs, such as pharmaceuticals, have been observed to be pseudo-persistent due to continuous release into aquatic systems via effluent discharges (Brooks et al., 2006). After release to aquatic environments, they can distribute in the different environmental compartments and enter aquatic ecosystems.

Sediment has been shown to be a major sink for OMPs with high octanol/water partition coefficient (K_{ow}), and thus high hydrophobicity (Gong et al., 2012). Hydrophobic chemicals bind easily to sediments and to suspended particulate material deposited in the water column (Zoppini et al., 2014). Re-suspended sediment can constitute an additional source of OMPs and can ultimately enhance OMP bioavailability in aquatic environments (Zoppini et al., 2014). Due to the process of accumulation and desorption of toxic pollutants in the sediment-water system, sediment supplies the bioavailable fraction of toxic compounds for not only benthic organisms but also for aquatic organisms (Petrie et al., 2015). Some studies have investigated the presence of OMPs in Swedish waters (Falås et al., 2012), but a systematic large-scale study of OMPs in water and sediment in aquatic environments doesn't exist. Thus, there is a knowledge gap on OMPs in water and sediment, impeding risk assessments and further regulatory action.

This study assessed the occurrence and distribution of 111 OMPs in water and sediment along a pollution gradient in Lake Mälaren, Sweden. Specific objectives were to i) investigate the occurrence and spatial distribution of these OMPs in water and sediment, ii) evaluate their sediment-water distribution, and iii) assess the environmental risk to the ecosystem. The overall aim was to improve future monitoring of OMPs and their potential risk assessment.

2. Material and methods

2.1. Selected target compounds and chemicals

The 111 OMPs evaluated in the study consisted of pharmaceuticals, industrial chemicals, personal care products, pesticides, parabens, vitamins, artificial sweeteners, stimulants, contrast medium, opioids, and isoflavones. Target compounds were selected based on information in the literature on their occurrence and ubiquity in aquatic environments (Petrie et al., 2015; Yang et al., 2017), and on their human use and consumption (Petrie et al., 2015; Patel et al., 2019). All analytical standards used for analysis were of high purity grade (>95%) and purchased from Sigma-Aldrich (Sweden). Isotopically labeled standards (IS) ($n = 26$) were obtained from Wellington Laboratories (Canada), Teknolab AB (Kungsbacka, Sweden), Sigma-Aldrich (Sweden), and Toronto Research Chemicals (Toronto, Canada). Detailed information about internal standards (ISs) and native standards can be found elsewhere (Rostvall et al., 2018).

Ultrapure water was generated by a Milli-Q Advantage Ultrapure Water purification system and filtered through a 0.22 µm Millipak Express membrane and LC-Pak polishing unit (Merk Millipore, Billerica, MA). Methanol, acetonitrile, ammonium acetate, formic acid, ammonia, and ethyl acetate of high analytical grade were acquired from Sigma-Aldrich (Sweden).

For solid phase extraction (SPE), empty polypropylene (PP) tubes and the sorbent materials Septra ZT (Strata-X), Septra ZT-WCX (Strata-X-CW), and ZT-WAX (Strata-X-AW) were purchased from Phenomenex (Torrance, USA). The sorbent material Isolute ENV+ and frits (20 µm, 6 mL) were obtained from Biotage (Ystrad Mynach, UK). The water samples were filtered using glass micro-fiber filters (grade GF/F, Whatman, thickness 0.42 mm, pore size 0.7 µm), and the sediment sample extracts were filtered using regenerated cellulose syringe filters (15 mm diameter and 0.2 µm pore size) (Millipore, Cork, Ireland).

2.2. Study site and sample collection

Sampling of lake water ($n = 7$) and sediment ($n = 3$) was conducted in November 2017 in three basins (Ekoln, Skarven, and Görväln), which are all connected and part of Lake Mälaren (Fig. S1 in Supporting Information (SI)). Detailed information about water sampling can be found elsewhere (Rehrl et al., 2020). Water samples were collected at three different depths (0.5 m, 15 m, 30 m) from Ekoln and Görväln, while only surface water samples (0.5 m) were collected from Skarven.

Water samples were taken as grab samples in 1L pre-rinsed PP bottles. The water samples were collected according to the international standard (ISO 5667-4) by using Ruttner water sampler. The samples were stored dark in a cooling room until further processing without any pretreatment steps (Fedorova et al., 2014). Sediment samples were collected from the top 2 cm at multiple sites at Ekoln, Skarven, and Görväln (detailed information about sediment sampling can be found in Sahlin et al. (2018)). The sediment samples were collected into pre-rinsed 0.25-L brown glass jars. The jars were sealed with Teflon-lined lids and transported on ice to the laboratory, where they were frozen ($-18\text{ }^{\circ}\text{C}$) until processing.

2.3. Sample preparation

The water samples (500 mL) including blanks ($n = 9$) were extracted by SPE following the procedure described by Gago-Ferrero et al. (2015) using four different SPE materials (200 mg Strata-X, 150 mg Isolute ENV+, 100 mg Strata-X-AW and 100 mg Strata-X-CV) simultaneously in one in-house mixed bed cartridge.

The sediment samples were air-dried in a fume hood and then extracted as duplicates using ultrasonication, as described previously (Golovko et al., 2016). In brief, 2 g (dry weight (dw)) of sediment sample was spiked with an IS mixture (20 ng absolute per sample aliquot) and extracted by a two-step ultrasonic bath extraction procedure with 4 mL acetonitrile and water mixture (1/1, v/v with 0.1% formic acid), followed by a 4 mL acetonitrile, 2-propanol, and water mixture (3/3/4, v/v/v with 0.1% formic acid). The extraction duration for each step was 15 min. Finally, the two supernatants were combined, mixed and filtered using a regenerated cellulose syringe filter (0.45 µm pores). For the analysis, 1 mL of extract was used.

2.4. Instrument analysis

The water and sediment extracts were analyzed using a DIONEX UltiMate 3000 ultra-high pressure liquid chromatography (UPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (MS/MS) (TSQ QUANTIVA, Thermo Scientific, Waltham, MA, USA). An Acquity UPLC BEH-C18 column (100 mm × 2.1 i.d., 1.7 µm particle size; Waters Corporation, Manchester, UK) was used as an analytical column. Heated electrospray ionization (H-ESI) was used to ionize the target compounds. The mobile phase consisted of Milli-Q with 5 mM ammonium acetate and acetonitrile. Xcalibur software (Thermo

Fisher Scientific, San Jose, CA, USA) was used for data acquisition. The data obtained were evaluated using TraceFinder™ 3.3. software (Thermo Fisher).

2.5. Quality assurance/quality control

Quality controls (QC) included analysis of blanks, limit of quantification (LOQ), matrix effect, and recovery. The calibration curves for substances in water (0.01–250 ng/L) and sediment (0.01–100 ng/L) generally had R-values >0.99 (data not reported). The method blanks were Milli-Q water ($n = 1$) and tap water ($n = 1$). The blanks were prepared and extracted in the same way as the samples and no target analytes were detected in method blanks. Matrix-matched standards were used to assess the matrix effect and were prepared from sample extract spiked with ISs and native OMPs at concentration levels equivalent to 50 ng/L and 100 ng/L, respectively, for water samples and 10 ng/g dw and 20 ng/g dw, respectively, for sediment samples.

For all studied OMPs LOQs were in the range of 0.07–4.0 ng/L for water samples and of 0.042–1.5 ng/g dw for sediment samples, respectively. The recoveries were in the satisfactory range from 62% to 135% for water samples and from 81% to 104% for sediment samples, respectively. Detailed information about QA/QC for water and sediment samples can be found elsewhere (Rehrl et al., 2020; Golovko et al., 2016).

The sediment/water partition coefficient (K_d) and organic carbon-water partitioning coefficient (K_{OC}) were used to evaluate the adsorption capacity of each chemical compound in water and sediment. K_d was calculated as:

$$K_d = c_s / c_w$$

where c_s (mg/kg) and c_w (mg/L) are the OMP concentration in sediment and water, respectively.

K_{OC} was then calculated as:

$$K_{OC} = K_d / f_{OC}$$

where f_{OC} is the fraction of organic carbon (OC) in sediment, 0–2 cm (Görvåln is 0.041 g/g, Ekoln is 0.0546 g/g and Skarven is 0.0288 g/g) (Sahlin et al., 2018).

The environmental risks were assessed based on the risk quotient (RQ) (European Commission, Tech, 2003), calculated as:

$$RQ = MEC / PNEC$$

where MEC is the measured environmental concentration and PNEC is the predicted no-effect concentration in water. RQ values are classified as no risk for $RQ < 0.01$, low risk for $RQ = 0.01–0.1$, medium risk for $RQ = 0.1–1$, and high risk for $RQ > 1$.

3. Results and discussion

3.1. Occurrence of OMPs in lake water

In total, 30 out of 111 OMPs were detected in at least one water sample from Lake Mälaren (Fig. 2, Table S1) in November. The dominant compounds were carbamazepine, lamotrigine, caffeine, and tolyltriazole, with average concentrations of 12, 50, 9.4, and 28 ng/L, respectively (Fig. 1). It should be noted that 11 of the 31 OMPs detected in water samples were not detected in sediment (sulisobenzon, diazepam, mirtazapine, pyrimethamine, propylparaben, DMDEE, diclofenac, furosemide, irbesartan, losartan, and clozapine) (Table SI 1).

The concentrations of most OMPs were highest at Ekoln and

lowest at Görvåln. The former can be explained by incoming receiving water from river Fyris carrying high concentrations of OMPs that originate mainly from a large-scale wastewater treatment plant in Uppsala (Söregård et al., 2019; Daneshvar et al., 2010). The highest concentrations in lake water were found for lamotrigine (89 ng/L), tolyltriazole (42 ng/L), carbamazepine (21 ng/L), and caffeine (12 ng/L) in Ekoln samples. These are compounds typically detected in wastewater effluent (Söregård et al., 2019; Gago-Ferrero et al., 2017; Daneshvar et al., 2010). Notably, fexofenadine was detected only in Ekoln. Carbamazepine, caffeine, and fexofenadine were also among the most frequently detected compounds in several previous studies of OMP occurrence in surface waters (Patel et al., 2019; Bai et al., 2018; Elliott and VanderMeulen, 2017). Dibutyl phosphate was found only in Görvåln, and may originate from industrial waste streams (Richard and Lewis, 2007). The concentrations of atenolol and metoprolol detected in water samples in this study were similar to levels reported previously for Swedish lakes (Daneshvar et al., 2010). The detected concentration of carbamazepine (23 ng/L) was similar to that reported for Lake Taihu, China (Hu et al., 2017). On the other hand, the concentrations of atenolol (1.4 ng/L), caffeine (5.9–12 ng/L), citalopram (0.16–1.1 ng/L), lidocaine (1.9–14 ng/L), DEET (0.81–3.2 ng/L), and metoprolol (1.1–9.5 ng/L) (ng/L) detected in this study were much lower than those reported for lakes in Rocky Mountain National Park, USA (Battaglin et al., 2018).

Water samples were collected at three different depths (0.5 m, 15 m, 30 m) in the Ekoln and Görvåln basins, while only surface water samples (0.5 m) were collected from Skarven (Skarven basin is well mixed all year round as the flow is high). No systematic differences were found between water samples from different depths (Fig. SI 2). This can be explained by the fact that the samples were collected in November, when the water in the Ekoln and Görvåln basins is generally well mixed (Rehrl et al., 2020). A recent study (Daneshvar et al., 2010) reported similar results for carbamazepine, metoprolol, and atenolol, and a similar distribution of these compounds at different depths. Clozapine was detected only in Ekoln (depth 15 m), and at a very low concentration (0.045 ng/L), which was close to LOQ.

3.2. Occurrence of OMPs in sediment

In total, 24 out of 111 OMPs were detected in at least one sediment sample from Lake Mälaren in November (Fig. 2 and Table SI 1). Metoprolol, citalopram, and cetirizine were the dominant compounds in sediment (Fig. 2). Most OMPs (metoprolol, tramadol, citalopram, TBEP, cetirizine, propranolol, bisoprolol, venlafaxine, desvenlafaxine, sertraline, and amitriptyline) were present in higher concentrations in Ekoln sediment than in sediment from the other locations, as also found for the water samples. Atenolol, methylparaben, and dibutyl phosphate were found only at Skarven. The tolyltriazole concentration was highest at Görvåln (3 ng/g dw) and similar at Ekoln and Skarven (1.7 and 1.9 ng/g, respectively). Venlafaxine and sertraline were only found at Ekoln (7.8 ng/g dw and 2.8 ng/g dw, respectively), but the venlafaxine metabolite desvenlafaxine was found at all sampling locations, with the highest concentration at Ekoln (3.7 ng/g dw). This indicates that desvenlafaxine has stronger persistency than its parent compound. The higher concentration of OMPs in Ekoln sediment may be because this basin is close to a large urban center, and domestic sewage could be the main source of OMPs in the aquatic system (Söregård et al., 2019; Paíga and Delerue-Matos, 2017; Kramer et al., 2018). Among the pharmaceuticals detected in sediment samples, metoprolol, citalopram, cetirizine, and venlafaxine showed the highest concentrations (13, 28, 9.7, and 7.8 ng/g dw, respectively). Taking into account the log Kow values of citalopram

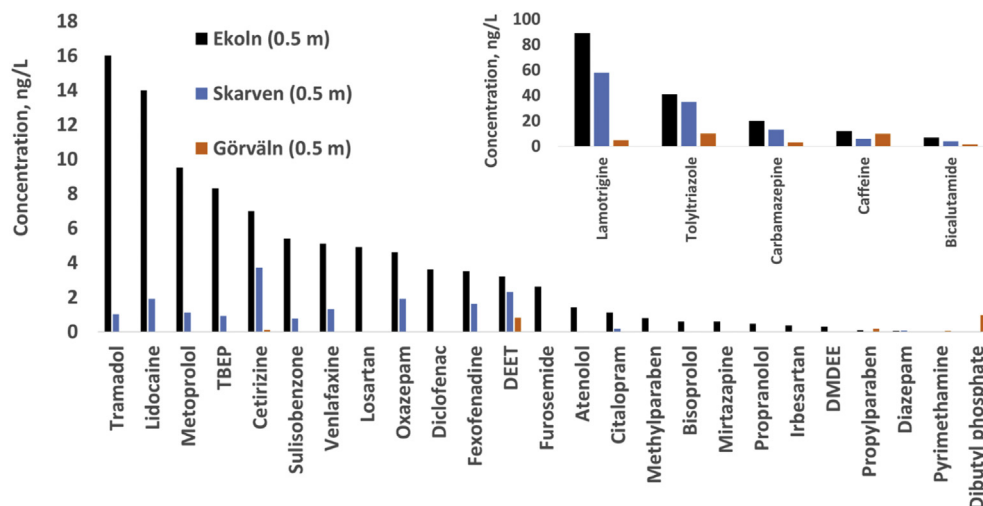


Fig. 1. Concentrations (ng/L) of organic micropollutants (OMPs) in surface water (0.5 m) from the basins Ekoln, Skarven, and Görvåln in Lake Mälaren.

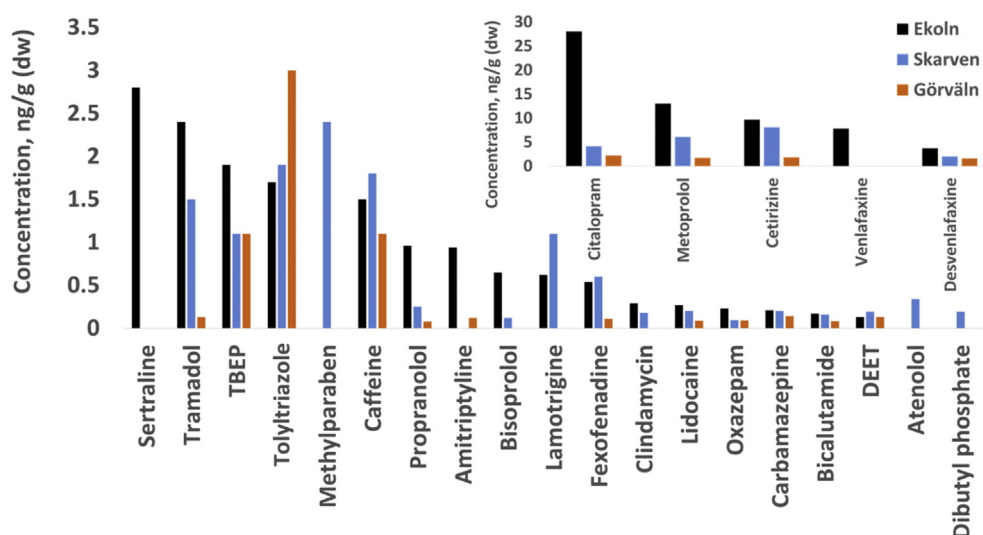


Fig. 2. Concentrations (ng/g dw) of organic micropollutants (OMPs) in upper surface (0–2 cm) sediment samples from the basins Ekoln, Skarven, and Görvåln in Lake Mälaren.

and venlafaxine (3.74 and 3.28 ng/g dw, respectively; Table 1) in the water/sediment distribution these OMPs can be expected to partition to sediment. Citalopram and venlafaxine are among the most frequently detected compounds in aquatic environments worldwide (Patel et al., 2019).

Using K_d and K_{OC} values, the fate of OMPs in the aquatic environment can be predicted. In total, 17 out of 111 OMPs were detected in both water and sediment samples, including carbamazepine, DEET, tolyltriazole, bicalutamide, caffeine, lamotrigine, and cetirizine (Table SI 1). Log K_d values varied between 0.84 for lamotrigine and 4.4 for citalopram, while log K_{OC} values varied between 2.1 for lamotrigine and 5.9 for citalopram (Table 1). The OMPs with the highest log K_d values, and thus the strongest sorption to sediment, were citalopram (4.4) and cetirizine (4.1). These results indicate that sorption to sediment is a way to remove these OMPs from the water column. The K_d values obtained in this study are similar to those reported in the scientific literature for carbamazepine, metoprolol, fexofenadine, citalopram, tramadol, and venlafaxine (Koba et al., 2018).

Many factors influence the fate and transport of OMPs in aquatic

environments (Pal et al., 2010; Yamamoto et al., 2009). For example, it has been suggested that chemicals with low log K_d or K_{OC} values (<2) are highly mobile in the solid phase and can be expected to occur primarily in the water phase and, those with high log K_d or K_{OC} values are strongly adsorbed onto sediment or organic matter. Differences in the occurrence of some OMPs between sampling sites could be due to varying sources (e.g., wastewater effluent) or differences in their persistence in water. For example, carbamazepine has a moderate sorption affinity to sediment (log $K_d = 1.0$ –1.7), but due to high persistence in aquatic environments (Löffler et al., 2005), it is commonly detected in water and sediment (Patel et al., 2019; Koba et al., 2018), as also found in this study. Despite the low log K_d (<2) of oxazepam and lidocaine, they were found in sediment at all three sampling locations, Table SI 1. Lamotrigine showed low sorption affinity to sediment (log $K_d < 2$) and was detected in sediment at low concentrations (0.62–1.1 ng/g dw). The concentrations of OMPs in sediment may provide information about the history of pollution in lakes and the risk to the benthic ecosystem (Petrie et al., 2015), and thus monitoring of the water phase is not sufficient to estimate the environmental impact

Table 1

Water/sediment sorption coefficient ($\log K_d$), octanol-water partitioning coefficient (K_{ow}), and organic carbon-water partition coefficient (K_{oc}) of the 17 OMPs detected in both water and sediment samples from Lake Mälaren.

Compound	Category	Type	$\log K_d$			K_{ow}^a	$\log K_{oc}$		
			Görväln	Ekoln	Skarven		Görväln	Ekoln	Skarven
Carbamazepine	Pharmaceutical	Antiepileptic	1.7	1.0	1.2	2.45	3.1	2.3	2.7
DEET	Pesticide	Insect repellent	2.3	1.6	1.9	2.18	3.6	2.9	3.5
Tolyltriazole	Industrial chemical	Corrosion inhibitor	2.4	1.6	1.7	1.71	3.8	2.9	3.3
Bicalutamide	Pharmaceutical	Antineoplastic agent	1.8	1.4	1.6	2.3	3.1	2.6	3.1
Caffeine	Stimulant		2.1	2.2	2.5	-0.07	3.4	3.4	4.0
Lamotrigine	Pharmaceutical	Antiepileptic	N.C.	0.84	1.3	0.99	N.C.	2.1	2.8
Metoprolol	Pharmaceutical	Beta blocker	N.C.	3.1	3.7	1.88	N.C.	4.4	5.3
Fexofenadine	Pharmaceutical	Antihistamine	N.C.	2.2	2.6	2.81 ^a	N.C.	3.4	4.1
Tramadol	Pharmaceutical	Analgesics (painkiller)	N.C.	2.2	3.2	2.51	N.C.	3.4	4.7
Citalopram	Pharmaceutical	Antidepressant	N.C.	4.4	4.4	3.74	N.C.	5.6	5.9
Oxazepam	Pharmaceutical	Sedative	N.C.	1.7	1.7	3.34	N.C.	3.0	3.2
Lidocaine	Pharmaceutical	Anesthetic	N.C.	1.3	2.0	2.44	N.C.	2.5	3.6
TBEP	Flame retardant		N.C.	2.3	3.1	3.75 ^b	N.C.	3.6	4.6
Cetirizine	Pharmaceutical	Antihistamine	4.1	3.1	3.3	-0.61	5.5	4.4	4.9
Propranolol	Pharmaceutical	Beta blocker	N.C.	3.4	N.C.	2.6	N.C.	4.6	N.C.
Bisoprolol	Pharmaceutical	Antihypertensive	N.C.	3.1	N.C.	1.84	N.C.	4.3	N.C.
Venlafaxine	Pharmaceutical	Antidepressant	N.C.	3.2	N.C.	3.28	N.C.	4.4	N.C.

N.C. not calculated - compound was not detected in the water or sediment sample.

^a Chemical Risk Information Platform (CHRIP). Biodegradation and Bioconcentration. Tokyo, Japan: Natl Inst Tech Eval. Available from, as of Nov 7, 2014: <http://www.safe.nite.go.jp/english/db.html>.

^b (Dürig et al., 2019).

of OMPs on the lake ecosystem.

3.3. Environmental risk assessment

The environmental risks of OMPs were assessed based on the risk quotient (RQ). According to the Technical Guidance Document of the European Commission (European Commission, Tech, 2003), PNEC is calculated by dividing the median lethal dose (LC50) or half-maximal effective concentration (EC50) by an appropriate assessment factor. The worst-case scenario for environmental risk assessment was conducted using the maximum MEC (Table 2). The RQ for most of the target OMPs (21 out of 29) was below 0.01, probably reflecting low or no environmental risk to the lake. Tolyltriazole, bicalutamide, fexofenadine, oxazepam, cetirizine, and diclofenac were identified as low risk, irbesartan showed medium risk (RQ = 0.19), and lamotrigine showed high risk (RQ = 3.18) (Table 2).

A low risk (RQ = 0.01) was found for the corrosion inhibitor tolyltriazole, which has been detected previously in river and lake water (Söregård et al., 2019) and in drinking water at concentrations up to 70 ng/L (Janna et al., 2011). In addition, tolyltriazole has been shown to bioaccumulate in mollusks in the Bohai Sea, China (Jia et al., 2019). We suggest to include tolyltriazole in monitoring in order to protect aquatic organisms, and to reduce its input to the environment by improving wastewater treatment. Oxazepam (RQ = 0.01) has previously been shown to affect wild fish behaviors, raising potential concerns for aquatic ecosystems (Brodin et al., 2013). The other compound with low risk potential (RQ = 0.01) found in this study was the anti-cancer drug bicalutamide. Bicalutamide has been detected in wastewater treatment facilities, with low removal efficiency during treatment (Söregård et al., 2019). To the best of our knowledge, this is the first study to show occurrence of bicalutamide in lake water. With increasing incidence of cancers, anti-cancer compounds such as bicalutamide are increasingly being used (Brezovšek et al., 2014; Franquet-Griell et al., 2017), so further research is needed to determine the potential ecotoxic and genotoxic effects of bicalutamide on non-target organisms (Toolaram et al., 2014).

Two antihistamine drugs, cetirizine and fexofenadine, which are used for the treatment of allergic reactions, showed low RQ values

for algae (0.02 and 0.07, respectively). These compounds have been detected previously in municipal wastewater effluent and surface water (Söregård et al., 2019; Kosonen and Kronberg, 2009). It has been shown that aquatic insects may change behavior after being exposed to low concentrations of fexofenadine found in aquatic systems receiving wastewater effluent (Johnson et al., 2007).

Diclofenac, which is found worldwide in surface water, groundwater, and drinking water (Yang et al., 2017), showed RQ values of 0.01 and 0.03 for fish and algae, respectively. Although diclofenac is removed by natural processes (biodegradation, photodegradation), residues remain in the environment (Lonappan et al., 2016). Previous studies have found that diclofenac may cause renal lesions and gill alterations in rainbow trout (Triebkorn et al., 2004), or elevate vitellogenin-like proteins in the gonads of female Mediterranean mussels (*Mytilus galloprovincialis*) after one week of exposure at environmentally relevant concentrations (Gonzalez-Rey and Bebianno, 2014).

Antiepileptic drugs such as carbamazepine and lamotrigine are reported to be poorly removed in wastewater treatment plants (Söregård et al., 2019; Yang et al., 2017), and carbamazepine has been found to be toxic to bacteria and algae (Heye et al., 2019). Carbamazepine showed RQ values below 0.01 in this study, but may still have adverse ecological effects in aquatic environments (Heye et al., 2019). Lamotrigine showed the highest RQ values in this study for *Daphnia* (RQ = 3.18) and for fish (RQ = 0.02), confirming results in a recent study (Söregård et al., 2019). The neuroactive properties of lamotrigine make it a potential aquatic life hazard, similarly to other psychoactive pharmaceuticals which demonstrated to have an effect on predator-prey relationships among aquatic organisms (Foster et al., 2010). The high environmental risk determined for lamotrigine necessitates its inclusion in routine monitoring programs and improvement of wastewater treatment and management in the region.

4. Conclusions

Analysis of the occurrence and distribution of OMPs in water and sediment from Lake Mälaren in November 2017 revealed that carbamazepine, lamotrigine, caffeine, and tolyltriazole were the dominant compounds in both water and sediment. The results

Table 2
Risk quotient (RQ) values based on the maximum detected organic micropollutant (OMP) concentrations in Lake Mälaren (in bold if a value is equal or above 0.01). Median lethal dose (LC50) or half-maximal effective concentration (EC50) (in mg/L) was used to calculate predicted no-effect concentration (PNEC) (by dividing LC50 or EC50 by an assessment factor of 1000) for fish, *Daphnia* (*Daphnia magna*), and algae^a.

Compound	MEC ng/L	Fish	Daphnia	Algae	Fish	Daphnia	Algae
		LC50 mg/L	LC50 mg/L	EC50 mg/L	RQ		
Carbamazepine	20	22	27	27	0.00	0.00	0.00
DEET	3.2	47	55	20	0.00	0.00	0.00
Tolyltriazole	41	91	36	6.0	0.00	0.00	0.01
Bicalutamide	7.0	37	69	0.52	0.00	0.00	0.01
Caffeine	12	231	194	14	0.00	0.00	0.00
Lamotrigine	89	4.5	96	0.03	0.02	0.00	3.18
Metoprolol	9.5	254	72	8.0	0.00	0.00	0.00
Fexofenadine	3.5	129	58	0.05	0.00	0.00	0.07
Tramadol	16	70	28	8.7	0.00	0.00	0.00
Citalopram	1.1	4.5 ^b	0.65 ^b	0.36 ^b	0.00	0.00	0.00
Oxazepam	4.6	0.37	110	0.57	0.01	0.00	0.01
Lidocaine	14	390 ^b	215 ^b	140 ^b	0.00	0.00	0.00
TBEP	8.3	42 ^b	26 ^b	28 ^b	0.00	0.00	0.00
Cetirizine	7.0	153	398	0.41	0.00	0.00	0.02
Propranolol	0.46	3.5	9.8	1.2	0.00	0.00	0.00
Atenolol	1.4	14438 ^b	6799 ^b	2337 ^b	0.00	0.00	0.00
Methylparaben	0.8	163	95	29	0.00	0.00	0.00
Bisoprolol	0.59	76	40	3.2	0.00	0.00	0.00
Venlafaxine	5.1	16 ^b	10 ^b	13 ^b	0.00	0.00	0.00
Sulisobenzone	5.4	3.5	42	13	0.00	0.00	0.00
Diazepam	0.05	2.8	11	0.58	0.00	0.00	0.00
Mirtazapine	0.59	18	100	0.41	0.00	0.00	0.00
Pyrimethamine	0.03	35	7.3	0.05	0.00	0.00	0.00
Propylparaben	0.09	63	62	8.2	0.00	0.00	0.00
DMDEE	0.29	189000 ^b	79187 ^b	16657 ^b	0.00	0.00	0.00
Diclofenac	3.6	0.63	43	0.14	0.01	0.00	0.03
Furosemide	2.6	5.3	14	0.71	0.00	0.00	0.00
Irbesartan	0.37	1.2	1.2	0.002	0.00	0.00	0.19
Losartan	4.9	5.4 ^b	3.7 ^b	5.9 ^b	0.00	0.00	0.00

^a Experimental OMP toxicity data (LC50 or EC50) for fish, *Daphnia*, and algae were obtained from Aalizadeh et al. (2017).

^b (Thesoftwa) Experimental LC50 or EC50 values for fish, *Daphnia*, and algae were obtained from ECOSAR. The ECOSAR software is freely available at <https://www.epa.gov/tsc-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>.

indicate that sorption is a minor natural attenuation pathway for studied OMPs in surface water, except for citalopram cetirizine, which showed high sorption potential. The environmental risks of OMPs were assessed based on the RQ values. For most of the target OMPs, including tolyltriazole, bicalutamide, fexofenadine, oxazepam, cetirizine, and diclofenac, the RQ values were below 0.01, indicating low or no risk to lake ecosystems. However, the environmental risk was estimated to be medium for irbesartan (RQ = 0.19) and high for lamotrigine (RQ = 3.18), indicating that more research is needed about recirculation of OMPs in lake systems and their effects on aquatic ecosystems. The results obtained in this study provide valuable decision support for programs aiming to reduce OMP emissions to aquatic environments by e.g., emission controls and improving wastewater treatment technologies to protect aquatic organisms. However, new OMPs are continually being introduced on the market and these need to be investigated in ongoing monitoring work. It is also important to consider that aquatic organisms are not exposed to individual compounds, but to a mixture of compounds, and that the toxicity of mixtures may be higher than that of individual components due to additive, antagonistic or synergistic actions.

Declaration of competing interest

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Oksana Golovko: Formal analysis, Conceptualization, Methodology, Writing - original draft. **Anna-Lena Rehrl:** Methodology,

Resources, Writing - review & editing. **Stephan Köhler:** Conceptualization, Writing - review & editing. **Lutz Ahrens:** Project administration, Conceptualization, Methodology, Resources, Writing - review & editing.

Acknowledgements

The analytical part of study was financially supported by Norrvatten a communal drinking water producer of the greater Stockholm region and by the DRICKS network, a Centre for drinking water research hosted by Chalmers with researchers in Chalmers, LTH in Lund and SLU in Uppsala. We also kindly acknowledge the funding from LakePOPs Fordslmas project (2016-01173).

We would like to thank Fredrik Pilström, Joel Segersten, Johannes Kikuchi, and Frank Menger for technical support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.127293>.

References

- Aalizadeh, R., von der Ohe, P.C., Thomaidis, N.S., 2017. Prediction of acute toxicity of emerging contaminants on the water flea *Daphnia magna* by Ant Colony Optimization–Support Vector Machine QSTR models. *Environ. Sci.: Process. Impacts* 19 (3), 438–448.
- Bai, X., et al., 2018. Occurrence, distribution, and seasonality of emerging contaminants in urban watersheds. *Chemosphere* 200, 133–142.
- Battaglin, W.A., et al., 2018. Pharmaceuticals, hormones, pesticides, and other bioactive contaminants in water, sediment, and tissue from Rocky Mountain National Park, 2012–2013. *Sci. Total Environ.* 643, 651–673.

- Brezovšek, P., Eleršek, T., Filipič, M., 2014. Toxicities of four anti-neoplastic drugs and their binary mixtures tested on the green alga *Pseudokirchneriella subcapitata* and the cyanobacterium *Synechococcus leopoliensis*. *Water Res.* 52, 168–177.
- Brodin, T., et al., 2013. Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations. *Science* 339 (6121), 814–815.
- Brooks, B.W., Riley, T.M., Taylor, R.D., 2006. Water quality of effluent-dominated ecosystems: ecotoxicological, hydrological, and management considerations. *Hydrobiologia* 556 (1), 365–379.
- Daneshvar, A., et al., 2010. Seasonal variations in the occurrence and fate of basic and neutral pharmaceuticals in a Swedish river–lake system. *Chemosphere* 80 (3), 301–309.
- Dürig, W., et al., 2019. Development of a suspect screening prioritization tool for organic compounds in water and biota. *Chemosphere* 222, 904–912.
- Elliott, S.M., VanderMeulen, D.D., 2017. A regional assessment of chemicals of concern in surface waters of four Midwestern United States national parks. *Sci. Total Environ.* 579, 1726–1735.
- European Commission, 2003. Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances and Commission Directive (EC) 98/8 on Biocides, second ed. European Commission, Luxembourg, Part II.
- Falás, P., et al., 2012. Occurrence and reduction of pharmaceuticals in the water phase at Swedish wastewater treatment plants. *Water Sci. Technol.* 66 (4), 783–791.
- Fedorova, G., et al., 2014. Storage effect on the analysis of pharmaceuticals and personal care products in wastewater. *Chemosphere* 111, 55–60.
- Foster, H.R., et al., 2010. Chronic exposure to fluoxetine (Prozac) causes developmental delays in *Rana pipiens* larvae. *Environ. Toxicol. Chem.* 29 (12), 2845–2850.
- Franquet-Griell, H., et al., 2017. Anticancer drugs: consumption trends in Spain, prediction of environmental concentrations and potential risks. *Environ. Pollut.* 229, 505–515.
- Gago-Ferrero, P., et al., 2015. Extended suspect and non-target strategies to characterize emerging polar organic contaminants in raw wastewater with LC-HRMS/MS. *Environ. Sci. Technol.* 49 (20), 12333–12341.
- Gago-Ferrero, P., et al., 2017. Impact of on-site, small and large scale wastewater treatment facilities on levels and fate of pharmaceuticals, personal care products, artificial sweeteners, pesticides, and perfluoroalkyl substances in recipient waters. *Sci. Total Environ.* 601–602 (Suppl. C), 1289–1297.
- Golovko, O., et al., 2016. Development of fast and robust multiresidual LC-MS/MS method for determination of pharmaceuticals in soils. *Environ. Sci. Pollut. Control Ser.* 23 (14), 14068–14077.
- Gong, J., et al., 2012. Association of endocrine-disrupting chemicals with total organic carbon in riverine water and suspended particulate matter from the Pearl River, China. *Environ. Toxicol. Chem.* 31 (11), 2456–2464.
- Gonzalez-Rey, M., Bebianno, M.J., 2014. Effects of non-steroidal anti-inflammatory drug (NSAID) diclofenac exposure in mussel *Mytilus galloprovincialis*. *Aquat. Toxicol.* 148, 221–230.
- Heye, K., et al., 2019. Ecotoxicological characterization of the antiepileptic drug carbamazepine using eight aquatic species: baseline study for future higher tier tests. *J. Environ. Sci. Health A* 54 (5), 441–451.
- Hu, X.-L., et al., 2017. Occurrence of 25 pharmaceuticals in Taihu Lake and their removal from two urban drinking water treatment plants and a constructed wetland. *Environ. Sci. Pollut. Control Ser.* 24 (17), 14889–14902.
- Janna, H., et al., 2011. From dishwasher to tap? Xenobiotic substances benzotriazole and tolyltriazole in the environment. *Environ. Sci. Technol.* 45 (9), 3858–3864.
- Jia, J., et al., 2019. Occurrence of and human exposure to benzothiazoles and benzotriazoles in mollusks in the Bohai Sea, China. *Environ. Int.* 130, 104925.
- Johnson, D.J., et al., 2007. Toxicity and hazard of selective serotonin reuptake inhibitor antidepressants fluoxetine, fluvoxamine, and sertraline to algae. *Ecotoxicol. Environ. Saf.* 67 (1), 128–139.
- Koba, O., et al., 2018. Transport of pharmaceuticals and their metabolites between water and sediments as a further potential exposure for aquatic organisms. *J. Hazard Mater.* 342, 401–407.
- Kosonen, J., Kronberg, L., 2009. The occurrence of antihistamines in sewage waters and in recipient rivers. *Environ. Sci. Pollut. Control Ser.* 16 (5), 555–564.
- Kramer, R.D., et al., 2018. The influence of solid-liquid coefficient in the fate of pharmaceuticals and personal care products in aerobic wastewater treatment. *Environ. Sci. Pollut. Control Ser.* 25 (25), 25515–25525.
- Liu, J.-L., Wong, M.-H., 2013. Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China. *Environ. Int.* 59, 208–224.
- Löffler, D., et al., 2005. Environmental fate of pharmaceuticals in water/sediment systems. *Environ. Sci. Technol.* 39 (14), 5209–5218.
- Lonappan, L., et al., 2016. Diclofenac and its transformation products: environmental occurrence and toxicity - a review. *Environ. Int.* 96, 127–138.
- Paíga, P., Delerue-Matos, C., 2017. Anthropogenic contamination of Portuguese coastal waters during the bathing season: assessment using caffeine as a chemical marker. *Mar. Pollut. Bull.* 120 (1), 355–363.
- Pal, A., et al., 2010. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. *Sci. Total Environ.* 408 (24), 6062–6069.
- Patel, M., et al., 2019. Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods. *Chem. Rev.* 119 (6), 3510–3673.
- Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. *Water Res.* 72, 3–27.
- Rehrl, A.-L., et al., 2020. Spatial and seasonal trends of organic micropollutants in Sweden's most important drinking water reservoir. *Chemosphere* 249, 126168.
- Richard, J., Lewis, Sr (Eds.), 2007. *Hawley's Condensed Chemical Dictionary, fifteenth ed.* John Wiley & Sons, Inc., Hoboken, NJ. x + 1380 pp. \$150.00. ISBN 978-0-471-76865-4. *Journal of the American Chemical Society*, 2007. 129(16): pp. 5296–5296.
- Rostvall, A., et al., 2018. Removal of pharmaceuticals, perfluoroalkyl substances and other micropollutants from wastewater using lignite, Xylit, sand, granular activated carbon (GAC) and GAC+Polonite® in column tests – role of physicochemical properties. *Water Res.* 137, 97–106.
- Sahlin, J., Tjensvoll, I., Forsberg, J., 2018. *Metaller och Organiska Föreningar I Sediment Från Mälaren* Sedimentprovtagning Mälaren. Lst Västmanland.
- Söregård, M., et al., 2019. Mass loads, source apportionment, and risk estimation of organic micropollutants from hospital and municipal wastewater in recipient catchments. *Chemosphere* 234, 931–941.
- ECOSAR, The ECOSAR software is freely available at: <https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>.
- Toolaram, A.P., Kümmerer, K., Schneider, M., 2014. Environmental risk assessment of anti-cancer drugs and their transformation products: a focus on their genotoxicity characterization-state of knowledge and short comings. *Mutat. Res. Rev. Mutat. Res.* 760, 18–35.
- Triebtskorn, R., et al., 2004. Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part II. Cytological effects in liver, kidney, gills and intestine of rainbow trout (*Oncorhynchus mykiss*). *Aquat. Toxicol.* 68 (2), 151–166.
- Yamamoto, H., et al., 2009. Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: laboratory photolysis, biodegradation, and sorption experiments. *Water Res.* 43 (2), 351–362.
- Yang, Y., et al., 2017. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: a review. *Sci. Total Environ.* 596–597, 303–320.
- Zoppini, A., et al., 2014. Organic priority substances and microbial processes in river sediments subject to contrasting hydrological conditions. *Sci. Total Environ.* 484, 74–83.