Environ Sci Pollut Res (2016) 23:18043–18054
DOI 10.1007/s11356-016-6778-y

RESEARCH ARTICLE

Suitability of passive sampling for the monitoring of pharmaceuticals in Finnish surface waters

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Received: 20 January 2016 / Accepted: 26 April 2016 / Published online: 3 June 2016

Abstract The occurrence of five pharmaceuticals, consisting of four anti-inflammatory and one antiepileptic drug, was studied by passive sampling and grab sampling in northern Lake Päijänne and River Vantaa. The passive sampling was performed by using Chemcatcher® sampler with a SDB-RPS Empore disk as a receiving phase. In Lake Päijänne, the sampling was conducted during summer 2013 at four locations near the discharge point of a wastewater treatment plant and in the years 2013 and 2015 at four locations along River Vantaa. The samples were analyzed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) in the multiple reaction monitoring mode. The concentrations of carbamazepine, diclofenac, ibuprofen, ketoprofen, and naproxen in Lake Päijänne determined by passive sampling ranged between 1.4–2.9 ng L^{-1}, 15–35 ng L^{-1}, 13–31 ng L^{-1}, 16–27 ng L^{-1}, and 3.3–32 ng L^{-1}, respectively. Similarly, the results in River Vantaa ranged between 1.2–40 ng L^{-1}, 15–65 ng L^{-1}, 13–33 ng L^{-1}, 16–31 ng L^{-1}, and 3.3–6.4 ng L^{-1}. The results suggest that the Chemcatcher passive samplers are suitable for detecting pharmaceuticals in lake and river waters.

Keywords Chemcatcher® · Lake water · Liquid chromatography · Mass spectrometry · Passive sampling · Pharmaceuticals · River water

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-016-6778-y) contains supplementary material, which is available to authorized users.

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Introduction

There is an increasing need for monitoring the aquatic environment, particularly the priority pollutants listed in EU Water Framework Directive and other persistent organic pollutants (POPs) but also pseudo-persistent compounds, such as pharmaceuticals which are constantly released into the aquatic environment (EC 2000; Vrana et al. 2006). The concentrations of pollutants dissolved in water are commonly very low, usually less than 1 ng L^{-1}. However, the low levels of contaminants in water can affect the reproduction of aquatic organisms even with very low concentration levels as they often bioconcentrate to relatively high levels in tissues (Meador and Rice 2001). For example, up to 1000 times higher levels of pharmaceuticals are found in the bile of fish compared to those in the water phase (Brozinski et al. 2013). Recently, more interest has been focused on polar organic chemicals, including pharmaceuticals and pesticides. Even though polar compounds do not have a high potential for bioaccumulation, they can pose a risk to aquatic organisms because they are often continuously present in the aquatic environment (Daughton 2002). Occurrence and distribution of chemicals in urban waters are linked to population density, consumption patterns,

and water use but also to physical and chemical properties of substances which determine their fate in the environment (Dickenson et al. 2011).

Sampling of the micro pollutants in aquatic environment is often a challenging task. Water bodies are not well mixed and therefore chemicals are not evenly distributed (Pawlowski et al. 2004). Especially, small rivers are often hydrologically very dynamic (Vermeirssen et al. 2006). In case of long-term monitoring studies which aim to link exposure of chemicals to effects in organisms, grab sampling can be applied successfully only when the concentrations of analytes are fairly stable. Conventional methods for monitoring of harmful substances in surface waters are based on frequent grab sampling at fixed time intervals. Traditionally, water is collected at specific sites while the sample clean-up and enrichment is performed in the laboratory (Alvarez et al. 2005). However, the volume of water can be insufficient to meet the detection limit requirement of common analytic methods. Grab sampling is expensive, labor intensive, and gives only instantaneous concentrations which may not describe the long-term average concentrations. Additionally, it can miss periodic and occasional fluctuations in the concentrations of pollutants caused by spills or storm water runoffs (Koester et al. 2003; Guo et al. 2004; Alvarez et al. 2005).

Passive sampling technique combines sampling and enrichment steps (Vrana et al. 2005). It is based on free flow of analytes from surrounding media to the receiving phase due to the difference between chemical potentials of the compounds in these two media (Gorecki and Namiesnik 2002). Chemicals diffuse and partition until the aqueous concentrations of substances reach the equilibrium between uptake and elimination into and from the sampling device over time (Vermeirssen et al. 2009). The mass transfer of compounds from water to the sampler includes diffusion and transport across barriers, such as aqueous boundary layer, biofilm layer, the diffusion-limiting membrane (if used), and the receiving phase (Huckins et al. 1999). Under constant aqueous concentration, the concentration in the sampler increases nearly linearly over time (Vermeirssen et al. 2008). After that, the increase flattens and the concentrations in the receiving phase and in the surrounding media reach equilibrium (Mayer et al. 2003).

Integrative passive sampling is commonly used to determine the time-weighted average (TWA) concentration of a substance when the uptake into the sampler is the dominating process (Vermeirssen et al. 2009). The amount of chemical in a sampler can be divided by the sampling rate (R_s) and the deployment time to calculate the TWA concentration. However, it is not straightforward to calculate TWA concentrations from passive sampling data because the diffusion and partitioning are influenced by temperature, turbulence around the sampler, salinity, and biofouling (Vrana et al. 2006; Booij et al. 2006; Togola and Budzinski 2007; Vermeirssen et al. 2008). In case of linear uptake, the amount of substance in the receiving phase can be calculated as expressed in Eq. 1 (Kingston et al. 2000; Shaw et al. 2009).

$$M_s(t) = C_w R_s t \quad (1)$$

where $M_s(t)$ is the amount of substance (ng) measured in the receiving phase after the deployment time t (days), C_w is the average concentration of substance (ng L^{-1}) in water and R_s the sampling rate, the extracted water volume per unit of time (L day^{-1}) (Vrana et al. 2006).

R_s is an important parameter in order to reach a proper quantification (Harman et al. 2012). R_s is established for each device and compound by performing lab or field experiments (MacLeod et al. 2007). R_s needs to be determined for each substance which can be time and resource-consuming in case of a large number of substances. It has been discussed if R_s can be predicted based on physicochemical properties of substances (Shaw and Mueller 2009; Morin et al. 2013; Vermeirssen et al. 2013). So far, passive samplers have been calibrated in a laboratory scale by, e.g., static renewal, static depletion, and flow-through systems (Alvarez et al. 2004; Vrana et al. 2006; MacLeod et al. 2007; Harman et al. 2009; Morin et al. 2012). However, all methods give different R_s and no standard method is yet available (Morin et al. 2013; Mills et al. 2014). Water matrix properties, such as temperature, pH, dissolved organic matter, and ionic strength, strongly affect the R_s value, and R_s calculations at laboratory conditions with nanopure or tab water do not simulate field conditions (i.e., lake or river water) very well (Harman et al. 2012). Therefore, TWA concentrations calculated with R_s values based on lab experiments goes with uncertainties (Hyne and Aistrope 2008).

There are various passive sampler designs available but only two have been used to detect polar substances in water: polar organic chemical-integrated sampler (POCIS) and the polar version of Chemcatcher (Alvarez et al. 2004; MacLeod et al. 2007; Ahkola et al. 2014). Most of the published research is about POCIS and less information is available about Chemcatcher (Schäfer et al. 2008; Mills et al. 2014). For example, over 300 compounds have been shown to accumulate in POCIS, including pesticides (>100), pharmaceuticals (>90), and industrial chemicals (>30) (Harman et al. 2012). Chemcatcher passive samplers have been used for, e.g., DDT and its metabolites (de la Cal et al. 2008), polar herbicides (Stephens et al. 2005; Tran et al. 2007), and pesticides (Gunold et al. 2008) but rarely to determine the concentrations of pharmaceuticals in the aquatic environment (Vermeirssen et al. 2009). Both samplers use adsorbent material, commonly styrenedivinylbenzene-reversed phase sulfonate (SDB-RPS) for Chemcatcher and Oasis HLB powder for POCIS, and undergo reversed phase interactions with polar substances

(Kingston et al. 2000; Alvarez et al. 2004). The SDB-RPS Empore disks contain a hydrophilic copolymer modified with sulfonic acids and show a high retention of polar organic compounds (Hennion et al. 1998). Among Chemcatcher phases, SDB-RPS sorbent is the most efficient for polar compounds due to the higher ratio of sorbent mass per surface area (Stephens et al. 2005).

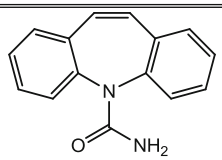
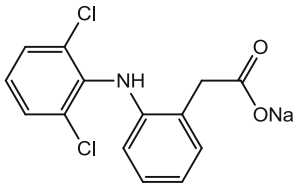
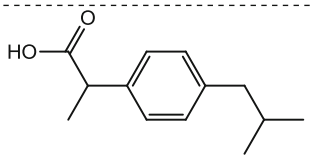
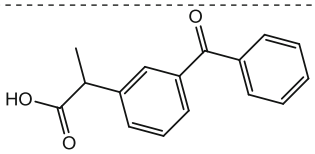
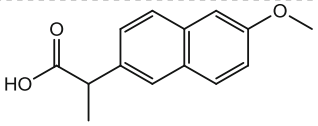
Recently, a variety of analysis methods of pharmaceuticals was reviewed and the occurrence of selected anti-inflammatory and antiepileptic drugs was studied in lake water of northern Lake Päijänne by grab sampling from different sampling sites and depths in the summer and winter time (Lindholm et al. 2014; Lindholm-Lehto et al. 2015; Lindholm-Lehto et al. 2016). In this study, Chemcatcher passive sampling results of selected anti-inflammatory and antiepileptic drugs in Lake Päijänne and River Vantaa were analyzed as well as the results of grab sampling. Lake Päijänne is the source of raw water for the production of drinking water for the capital area of Finland, comprising about one million people and River Vantaa the backup raw water source in case water from Lake Päijänne is not available.

Experimental

Materials and chemicals

Analytical standards carbamazepine, diclofenac, ibuprofen, ketoprofen, and naproxen (purity 98 %) were purchased from Alfa Aesar (Karlsruhe, Germany). Their chemical structures, applications, and annual consumptions are listed in Table 1. HPLC grade methanol and acetonitrile were obtained from J.T Baker. The water used in the analyses was ultra high-quality (UHQ) water (Millipore, Bedford, MA, USA). The standard solutions (100 μg mL^{-1}) were prepared by dissolving an accurate amount of pure standard in HPLC grade methanol and filtered with membrane filter 0.2-μm pore size, ME 24. Standard solutions were stored in the dark at 4 °C. The

Table 1 Chemical structures, applications and consumptions of selected pharmaceuticals

Pharmaceutical	CAS-number	Chemical structure	DDD values[a]	Application, consumption[b]
Carbamazepine CBZ	298-46-4		1 g	antiepileptic, 3200 kg a^{-1}
Diclofenac DIC	15307-86-5		0.1 g	anti-inflammatory 900 kg a^{-1}
Ibuprofen IBU	15687-27-1		1.2 g	anti-inflammatory, 108000 kg a^{-1}
Ketoprofen KET	22071-15-4		0.15 g	anti-inflammatory, 370 kg a^{-1}
Naproxen NPX	22204-53-1		0.5 g	anti-inflammatory, 5500 kg a^{-1}

[a] Defined Daily Dose, statistical measure of drug consumption, defined by WHO

[b] Finnish Medicines Agency Fimea, 2013, kg per year

Chemcatcher sampler housing made of polycarbonate was purchased from MP-Plast Inc. (Muurame, Finland). Empore SDB-RPS disks (47 mm) were purchased from Agilent Technologies (Waghaeusel-Wiesenthal, Germany).

Passive samplers

A SDB-RPS Empore disk (diameter 47 mm, surface area 15.9 cm^2) was used as a receiving phase and conditioned before use by immersing in methanol followed by immersing in UHQ water (Kingston et al. 2000). The conditioned disk was fitted in a polycarbonate Chemcatcher sampler housing which was kept in methanol overnight and rinsed with UHQ water, closed and stored in zip-lock bags at 4 °C until exposure. After the deployment time, the SDB-RPS disk was carefully removed from the sampler into Kimax tube and stored at -18 °C prior to analysis.

Calibration experiment

A calibration experiment was performed in laboratory conditions in order to determine the R_s of each studied pharmaceutical. Ten passive samplers were exposed in a constant concentration system under controlled conditions of temperature, water turbulence, and analyte concentration. The experiment was performed in a dark room at 18 °C. The system consisted of a 31-L cylindrical glass tank filled with 19 L of UHQ water spiked with a 100 μL of selected pharmaceutical standards in methanol. Nominal concentration of 500 ng L^{-1} of each analyte was maintained throughout the experiment. The spiked UHQ water was renewed throughout the experiment every 3 or 4 days. Grab samples of 500 mL were collected from the exposure tank and the concentrations of pharmaceuticals were measured before and after each renewal.

Ten samplers were tied to an overhead stirrer with cable ties two at a time. The holder was interconnected to an overhead stirrer and it was rotated at a constant stirring speed of 90 rpm (33 cm s^{-1}). The exposure took place for 14 days expecting a linear uptake. Duplicate samplers were removed after 3, 6, 8, 10, and 14 days and the concentrations of accumulated chemicals were determined. The R_s were calculated according to Eq. 1.

Field experiment

Lake Päijänne

Selected pharmaceuticals (carbamazepine, diclofenac, ibuprofen, ketoprofen, and naproxen) were analyzed from water of

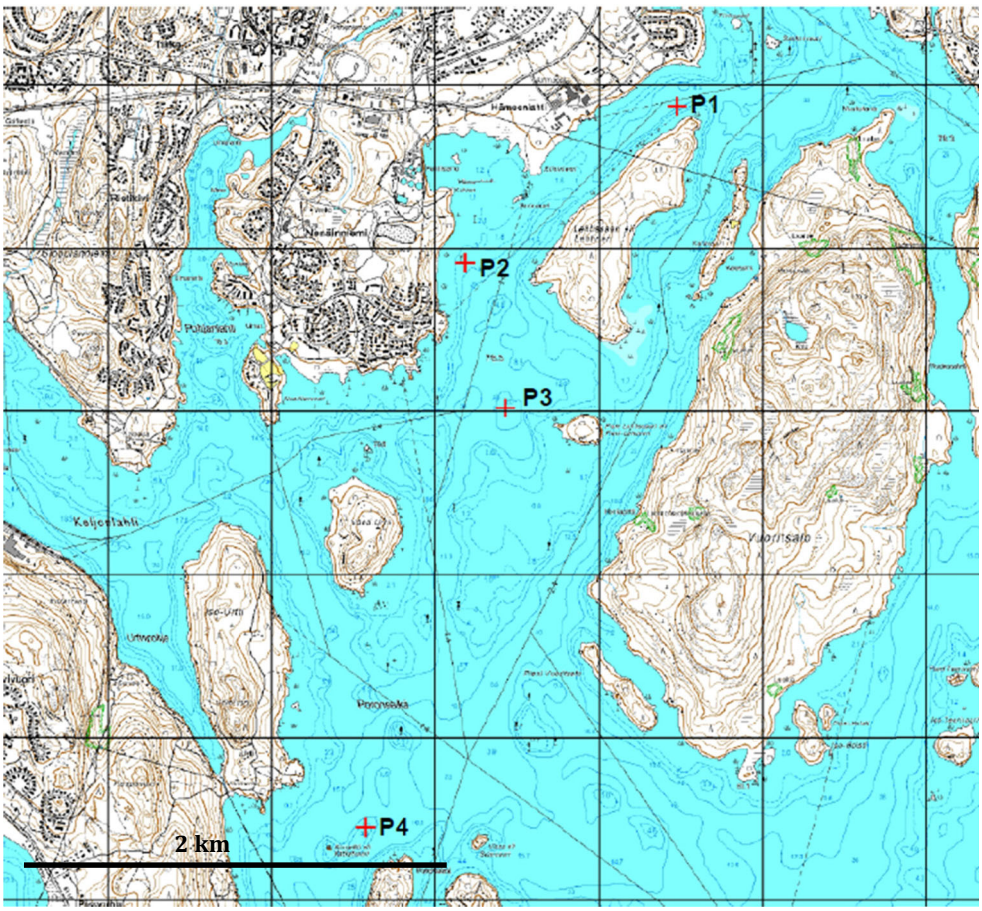


Fig. 1 Locations P1–P4 indicate the sampling sites of grab and passive sampling in northern Lake Päijänne. The main direction of the water current is to south, towards sampling site P4

Lake Päijänne by passive sampling and grab sampling during summer 2013. Lake Päijänne (1080 km^2, average depth 16.2 m), the source of raw water for production of drinking water for the capital area of Finland, is located in central Finland (Fig. 1). The flow rate of water via Lake Päijänne is on average 240 $m^3\ s^{-1}$ (S1). The lake receives effluent from the municipal wastewater treatment plant (WWTP) (influent 35,000 $m^3\ day^{-1}$, at sampling site P2) of the city of Jyväskylä (population 150,000). The wastewater treatment process comprises primary clarification, removal of phosphorous with ferrosulphate and an activated sludge process.

The passive samplers were deployed at four sampling sites (P1–P4) in a depth of 1 m for 2 weeks at a time in Lake Päijänne (Fig. 1). Duplicate samplers were exposed at the sites for seven times during summer 2013. Grab water samples (500 mL) were collected with Ruttner water sampler from four locations (sites P1-P4) from the depth of 1 m. Water samples, in total eight from each location, were taken in glass bottles before and after each deployment time period of the passive samplers. Originally, the samples were taken for the method development and studies of occurrence reported by Lindholm-Lehto et al. (2015). The water samples were stored in HDPE bottles at -18 °C prior to analysis.

River Vantaa

The five selected pharmaceuticals were studied from water of River Vantaa by passive sampling and grab sampling in 2013 and 2015. River Vantaa is a 101-km-long river located in southern Finland and flows into the Gulf of Finland (river basin 1685 m^2, flow rate 1.4–317 $m^3\ s^{-1}$). Flow velocities along River Vantaa increase towards the sea shore mostly due to flows from river branches (Fig. 2, S2). River Vantaa is used as a backup fresh water source for the capital city area in case of limited fresh water supply from Lake Päijänne. More than half of the river basin area comprises of forest, a third is in agricultural use, the rest being population centers or in industrial use. Altogether, 1.1 million people live along River Vantaa. The water in River Vantaa is naturally brown and turbid due to clayey soil, especially during rainy seasons.

There are several municipal wastewater treatment plants along River Vantaa which treat together 31 500 $m^3\ day^{-1}$ of wastewater (250–12,000 $m^3\ day^{-1}$) (S3). One of them, Riihimäki WWTP, treats municipal wastewater of 28,000 residents (12,600 $m^3\ day^{-1}$) and industrial wastewater from a dairy product producer. It was rebuilt during 2013–2014 to enhance the pretreatment, nitrogen, and phosphorous removal and to increase its capacity (Riihimäki waterworks 2014). Its nitrogen removal is based on a biological denitrification-nitrification process and the phosphorous is precipitated mainly by ferrosulphate. In addition, a tertiary treatment stage has been built to ensure the phosphorous removal also in special cases.

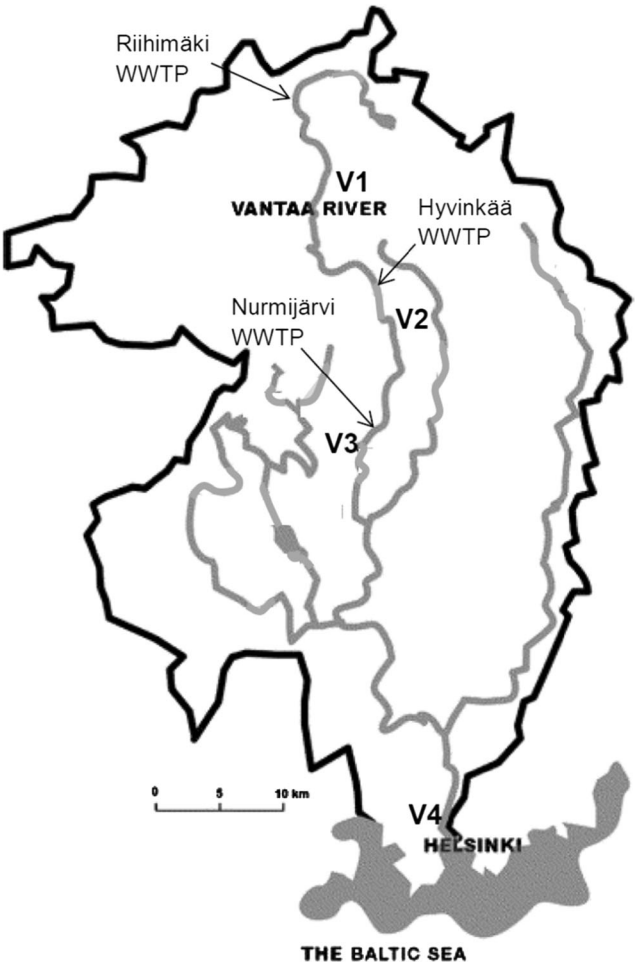


Fig. 2 Locations V1–V4 indicate the sampling sites along River Vantaa (August 2013 and May 2015)

Hyvinkää WWTP serves 32,900 residents and treats 10, 300 $m^3\ day^{-1}$ of municipal wastewater (Kalteva WWTP 2011). The treatment process is based on chemical and biological nitrification–denitrification with chemical precipitation of phosphorous by ferrosulphate. The Hyvinkää WWTP reaches excellent removal efficiency (BOD_7 99 %, COD_{Cr} 96 %, P_{tot} 97 %, and N_{tot} 81 %).

Nurmijärvi WWTP treats municipal wastewater (2700 $m^3\ day^{-1}$) of 5800 residents (Nurmijärvi WWTP 2011). The treatment process includes biological nitrogen removal combined with chemical precipitation. Ferrosulphate is used for the precipitation of phosphorous. The Nurmijärvi WWTP reaches good removal efficiency (BOD_7 97 %, P_{tot} 93 %, and N_{tot} 51 %).

Data on pharmaceuticals were collected by passive samplers and grab samples from four locations (sites V1–V4; Fig. 2), first in August 2013 and later in May 2015. The selected sampling sites belong to the regular monitoring of harmful substances in River Vantaa (Vahtera et al. 2013). The grab samples, six from each location, were taken before and after 2 weeks of deployment time of passive samplers.

Table 2 The sampling rates, R_s (L day^{-1}) with standard deviations (SD) determined by the calibration experiment

Pharmaceutical	R_s SD
Carbamazepine	0.158 ± 0.047
Diclofenac	0.048 ± 0.022
Ibuprofen	0.091 ± 0.030
Ketoprofen	0.099 ± 0.033
Naproxen	0.094 ± 0.033

Sample preparation

Grab samples

Water samples were treated according to Lindholm-Lehto et al. (2015). In brief, the samples were concentrated with solid-phase extraction (SPE) cartridges (Varian bond Elut C18, 500 mg) which were first conditioned with 3 mL methanol followed by 3 mL UHQ water before loading the samples. The analytes were eluted with 3 mL of acetone, evaporated to dryness under a stream of nitrogen. Subsequently, they were redissolved in 300 μL of methanol and water (1:1, *v*/*v*), filtered through syringe cartridges (Cronus 0.45 μm PTFE) and analyzed immediately with liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS).

Passive samplers

The Empore disks were eluted first with 10 mL of acetone in an ultrasonic bath for 10 min and the solvent was collected. The procedure was repeated by using 10 mL of methanol. The solvents were combined and evaporated to a small volume by a rotary evaporator. The samples were then filtrated through (Cronus 0.45 μm PVDF) syringe cartridges and evaporated to dryness under a stream of nitrogen. Finally, they were redissolved in 300 μL of methanol and water (1:1, *v*/*v*) and analyzed with LC-MS/MS.

Instrumental analysis

The concentrations of target analytes in the extracts were quantified using LC-MS/MS as described by Lindholm-Lehto et al. (2015). The analysis was performed with 1290 Infinity series liquid chromatograph equipment coupled to a 6460 Triple Quad triple-quadrupole mass analyzer (MS/MS) with an electrospray ionization source (Agilent Technologies). The analysis method was validated by performing experiments with spiked water samples (recoveries for carbamazepine 89.6 %, naproxen 89.3 %, ketoprofen 86.3 %, ibuprofen 90.6 %, and diclofenac 87.6 %). The LOQ of water samples (ng L^{-1}) are CBZ 0.1, DIC 25, IBU 12, KET 5.1, and NPX 9.2, and the LOQ of passive samplers (ng L^{-1}) are CBZ 0.1, DIC 130, IBU 32, KET 22, and NPX 23.

Results and discussion

Calibration experiment

The R_s determined by the laboratory calibration are presented in Table 2. The highest R_s was measured for carbamazepine and the lowest for diclofenac. The R_s of ibuprofen, ketoprofen, and naproxen were at the same level.

The R_s values were in the similar range than those reported in the literature. For example, DiCarro et al. (2014) and Tanwar et al. (2015) studied pharmaceuticals by POCIS passive samplers and reported somewhat higher R_s values of ibuprofen and ketoprofen than those of diclofenac (IBU 0.075, KET 0.066, DIC 0.058). Additionally, MacLeod et al. (2007) and Li et al. (2010) reported higher R_s values of carbamazepine than ibuprofen, ketoprofen, and naproxen (CBZ 0.348–0.397, IBU 0.254, KET 0.135, NPX 0.116–0.298).

Lake Päijänne

The concentrations of selected pharmaceuticals collected both by grab and passive sampling at sites P1–P4 are shown in Table 3. The concentrations based on passive sampling were calculated by using Eq. 1 and R_s determined in the laboratory calibration (Table 2).

The highest concentrations of pharmaceuticals are detected mainly at the sampling site P2 which is located at the point of effluent discharge from the WWTP (Table 3; Figs. 1 and 3). This applies to both passive and grab sampling. Generally, the concentrations were decreasing with increasing distance from

Table 3 The mean concentrations and standard deviations (SD), nanogram per liter of the studied pharmaceuticals in Lake Päijänne by grab (n = 8) and passive sampling (n = 14) in June–September 2013

Pharmaceutical	Grab P1	Passive P1	Grab P2	Passive P2	Grab P3	Passive P3	Grab P4	Passive P4
Carbamazepine	1.0 (±0.6)	0.4 (±0.1)	1.7 (±1.0)	1.5 (±0.6)	2.1 (±2.1)	0.8 (±0.2)	1.1 (±0.6)	0.8 (±0.1)
Diclofenac	52 (±53)	2.8 (±0.9)	41 (±48)	17 (±11.3)	40 (±42)	4.8 (±2.1)	29 (±32)	6.1 (±1.9)
Ibuprofen	227 (±186)	8.6 (±0)	164 (±191)	17 (±14)	149 (±112)	7.7 (±4.4)	61 (±214)	6.9 (±2.8)
Ketoprofen	97 (±70)	14 (±4.7)	92 (±39)	17 (±7.0)	59 (±33)	12 (±4.1)	76 (±28)	12 (±3.7)
Naproxen	12 (±6.1)	5.1 (±4.2)	34 (±15)	17 (±9.7)	27 (±7.3)	6.8 (±2.8)	58 (±67)	8.0 (±4.5)

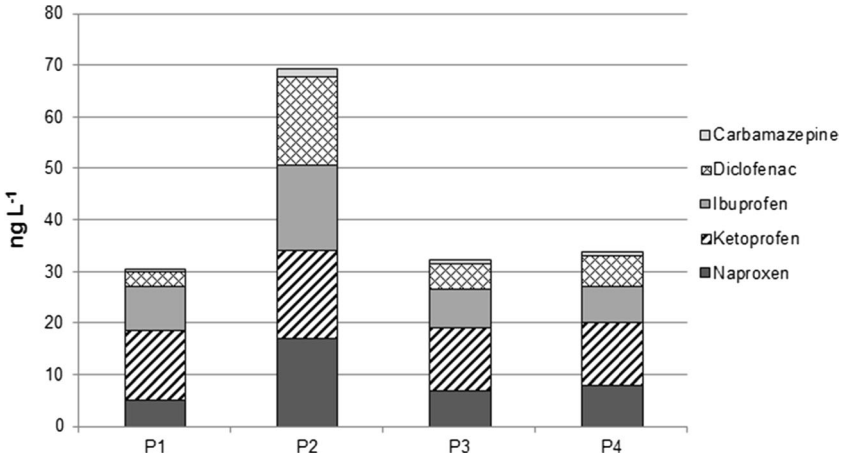


Fig. 3 Mean concentrations of selected pharmaceuticals in Lake Päijänne at sampling sites P1–P4 by passive sampling, June–September 2013

the WWTP. However, all selected pharmaceuticals were also detected at site P1 even though it is located upstream from the WWTP. According to Krogerus et al. (2013), the sampling site P1 is counter current to WWTP suggesting another source of contaminants. This is supported by the different profile of pharmaceuticals in the samples from this site compared to other sites, even though differences do also occur between other sites. In grab samples, ibuprofen dominated at all sites, with the highest mean concentration at site P1 but at site P2 in passive samples (Fig. 3). At site P2, the mean concentrations of diclofenac, ibuprofen, ketoprofen, and naproxen were at a similar level in water determined with passive sampling, while at other sites ketoprofen showed the highest concentrations (Table 3; Fig. 3).

Generally, the concentrations of selected pharmaceuticals are in the similar range, tens of nanograms per liter, like the previous results of grab and passive sampling of lake and river waters (Lindqvist et al. 2005; Vieno 2007; Moschet et al. 2015). Especially, in the case of carbamazepine, the concentrations are similar both by passive sampling and grab sampling (Table 3). However, in the case of ibuprofen and diclofenac, the concentrations of grab sampling are up to ten times higher than those of passive sampling (Table 3). Additionally, others have reported higher concentrations by grab sampling compared to passive sampling. For example, Moschet et al. (2015) reported concentrations of naproxen and diclofenac ten times higher by grab sampling compared to passive sampling.

Ibuprofen is the most commonly used non-prescription drug in Finland (Table 1). Most likely, this explains the high detected concentrations, especially at site P2 near the WWTP. In the beginning of August, exceptionally high concentrations were detected both by passive and grab sampling (Fig. 4). At that time, the Neste Oil Rally took place in the Jyväskylä area. As previously reported, an organized event with thousands of visitors increases the consumption of anti-inflammatory drugs, especially ibuprofen (Daneshvar et al. 2012; Lindholm-Lehto et al. 2015).

The large range of concentrations detected by grab sampling suggests variability in concentrations over time (Table 3, Figs. 4, 5, and 6). For example, high variation in concentrations of diclofenac was detected (Fig. 5). The samples close to the WWTP (P2) showed the highest concentrations while the others decreased with distance. It is widely reported that diclofenac undergoes photochemical degradation reactions under sun light in surface waters (e.g., Packer et al. 2003; Bartels

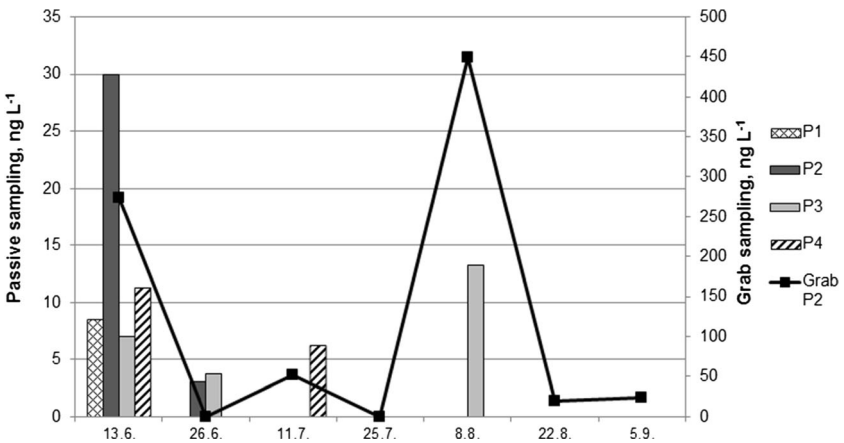


Fig. 4 Mean concentrations of ibuprofen in Lake Päijänne at sampling sites P1–P4 by passive sampling and at site P2 by grab sampling (June–September 2013)

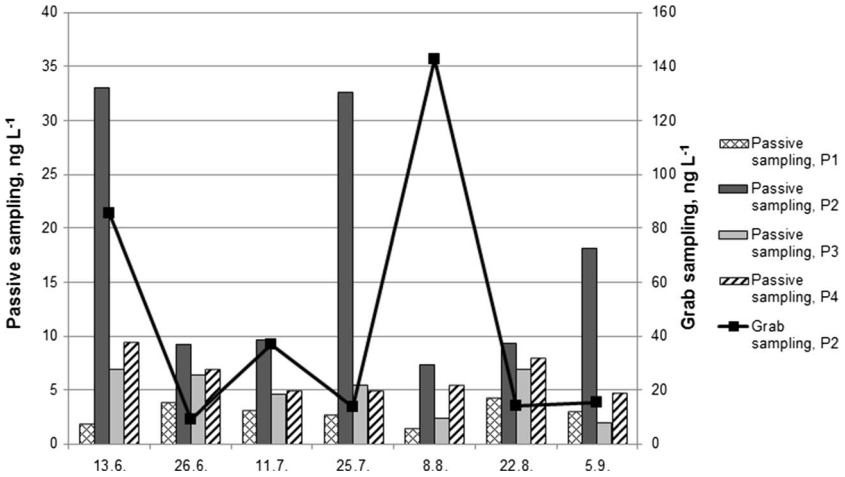


Fig. 5 Mean concentrations of diclofenac in Lake Päijänne at sampling sites P1–P4 by passive sampling and at site P2 by grab sampling (June–September 2013)

and von Tümpling Jr. 2007). Therefore, the concentrations can decrease over long distances in surface waters. It has been reported that the concentrations of diclofenac increase rapidly in deeper water layers in Lake Päijänne (Lindholm-Lehto et al. 2015). Additionally, mixing of water can lead to wide variety of concentrations by grab sampling even in the surface water.

Generally, the concentrations of carbamazepine detected by passive sampling follow the concentrations of grab sampling (Fig. 6). The values are fairly constant over the sampling period but in case of samples collected by passive sampling, they increase slightly towards fall. The solar radiation is the most intense in central Finland during summer months, especially in June and July (June 5.4 kWh m^{-2}, July 5.4 kWh m^{-2}, August 3.6 kWh m^{-2}, S1). The grab samples and the passive samples were taken from the depth of 1 m which is clearly included in the photic layer of the lake enabling the UV light-induced reactions (Secchi depth 1.6–2.0 m, S1). This can explain the slight increase in concentrations in late summer (Fig. 6).

Also in this case, the highest concentrations detected by passive sampling are found at sampling site P2 at the point of effluent discharge from the WWTP decreasing with distance (Fig. 6). However, the concentrations at site P1 are also found, throughout the sampling period. The site P1 is located upstream from the WWTP indicating a release of contaminants from sediment or another unknown source (Krogerus et al. 2013). This remains as a subject for further research.

River Vantaa

The concentrations of the studied pharmaceuticals ranged from few nanograms per liter of passive samples to hundreds of nanograms per liter of grab samples (Tables 4 and 5, Figs. 7 and 8). Despite the variation, they are in the similar range as in other studies where Chemcatcher was deployed in river waters (e.g., Vieno 2007). For example, similar levels of carbamazepine and diclofenac were reported by Äystö et al. (2014) in River Vantaa.

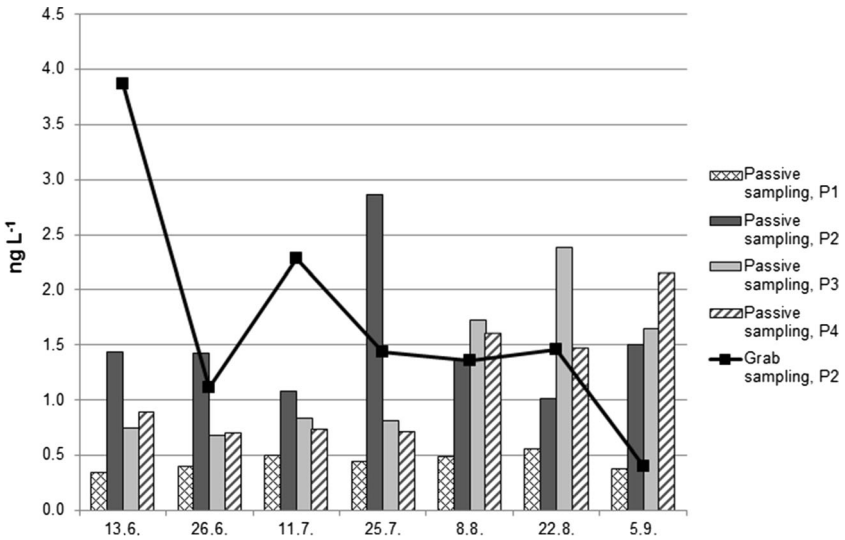


Fig. 6 Mean concentrations of carbamazepine in Lake Päijänne, sampling sites P1–P4 by passive sampling and at site P2 by grab sampling (June–September 2013)

Table 4 Mean concentrations and standard deviations (SD), nanogram per liter of the studied pharmaceuticals in River Vantaa by passive ($n = 8$) and grab sampling ($n = 12$) at sites V1–V4 in August 2013

Pharmaceutical	Grab V1	Passive V1	Grab V2	Passive V2	Grab V3	Passive V3	Grab V4	Passive V4
Carbamazepine	57 (±43)	22 (±8.0)	50 (±28)	25 (±7.9)	65 (±28)	31 (±13)	15 (±7.8)	0.8 (±0.5)
Diclofenac	187 (±180)	26 (±27)	96 (±57	5.1 (±3.8)	99 (±49)	8.7 (±10)	11 (±2.7)	11 (±8.5)
Ibuprofen	89 (±28)	20 (±18)	67 (±19)	nd	50 (±0.0)	nd	9.7 (±0.0)	nd
Ketoprofen	230 (±250)	8.2 (±2.5)	100 (±50)	10 (±9.3)	140 (±210)	17 (±10)	120 (±140)	18 (±18)
Naproxen	12 (±0.0)	5.3 (±1.6)	20 (±9.3)	2.2 (±0.0)	40 (±38)	3.5 (±0.0)	nd	nd

nd not detected

Moschet et al. (2015) detected 6–110 ng L^{-1} of carbamazepine, 1.4–320 ng L^{-1} diclofenac, and 26–87 ng L^{-1} naproxen in Swiss rivers by using Chemcatcher passive samplers.

Overall, the concentrations were ten times higher in August 2013 than in May 2015 (Tables 4 and 5; Figs. 7 and 8), excluding diclofenac. Most likely, the lower levels in 2015 are caused by the higher water flow in the spring time and dilution of the trace substances in the river water (April 2015, 7.8–28 m^3 s^{-1}; May 2015, 6.8–19.6 m^3 s^{-1}, S2, S3). Year 2013 was unusually dry and warm (79 % of average rainfall and 1.2–1.8 °C warmer (OIVA 2015)). The water flow has an effect on the accumulation factor of selected pharmaceuticals which can affect the results of passive sampling (Ahkola et al. 2014). Furthermore, the WWTP of Riihimäki was rebuilt in 2014 which might have improved the removal efficiency of pharmaceuticals. In addition, higher concentrations detected by grab sampling in August 2013 might only be due to occasional variations while passive samplers represent the more long-term situation.

All in all, the lowest levels of pharmaceuticals were measured at site V4 near the sea shore in 2013, excluding ketoprofen (Table 4; Figs. 7 and 8). The average flow of River Vantaa increases towards the sea shore suggesting increased dilution of trace substances (1.3–4.8 m^3 s^{-1}, S2). However, the similar levels of pharmaceuticals between sites V2 and V3 suggest several point sources of pharmaceuticals. There are several other municipal WWTPs along River Vantaa releasing their effluents to the river. The point of discharge from a local WWTP is located near all the selected sampling sites. In addition to the Riihimäki WWTP close to the site V1, there is the point of effluent discharge from the Hyvinkää WWTP (10,300 m^3 day^{-1}) near the site V2 and near the site V3 the point of effluent discharge from the Nurmijärvi WWTP (2700 m^3 day^{-1}).

Ketoprofen showed the highest concentrations of grab sampling (Table 4; Fig. 8), while Äystö et al. (2014) detected no ketoprofen in fall 2013 in River Vantaa. Carbamazepine showed the highest concentrations collected by passive samplers in 2013, while diclofenac dominated in passive samplers in 2015 (Table 4), excluding site V4.

Other factors than point sources can also contribute to the greater amount of ketoprofen towards the sea shore (Fig. 8), especially when studied by passive samplers. Ketoprofen has the ability to accumulate in the environment during winter, but in the summer, it has more labile properties (Daneshvar et al. 2010; Vystavna et al. 2013). In addition to human consumption released via WWTPs, ketoprofen is also used as a veterinary drug which might end up in the fields after consumption by farm animals and later back to the river (Vystavna et al. 2013). Along River Vantaa, there are several animal farms with horses, lambs, and cattle which may have a contribution to the load of ketoprofen. Therefore, it is possible that the concentration of ketoprofen builds up in the river water towards the sea shore (Fig. 8).

Generally, the concentrations of carbamazepine and diclofenac decreased towards the sea shore (Tables 4 and 5).

Table 5 Mean concentrations and standard deviations (SD), nanogram per liter of the studied pharmaceuticals in River Vantaa by passive ($n = 6$) and grab sampling ($n = 12$) at sites V1–V4 in April–May 2015

Pharmaceutical	Grab V1	Passive V1	Grab V2	Passive V2	Grab V3	Passive V3	Grab V4
Carbamazepine	14 (±6.7)	4.6 (±0.2)	8.3 (±3.6)	3.4 (±0.1)	7.6 (±3.2)	3.9 (±1.0)	4.7 (±0.5)
Diclofenac	34 (±18)	46 (±28)	23 (±29)	20 (±5.4)	15 (±12)	19 (±21)	19 (±11)
Ibuprofen	8.6 (±4.1)	11 (±6.4)	9.7 (±1.8)	8.2 (±8.9)	5.2 (±1.2)	9.9 (±11)	10 (±0.0)
Ketoprofen	19 (±8.4)	3.9 (±0.0)	25 (±10)	5.6 (±0.0)	35 (±20)	7.4 (±5.7)	29 (±7.2)
Naproxen	5.6 (±1.7)	3.1 (±0.0)	nd	nd	nd	nd	nd

In the year 2015, passive samples from site V4 were not collected due to technical reasons

nd not detected

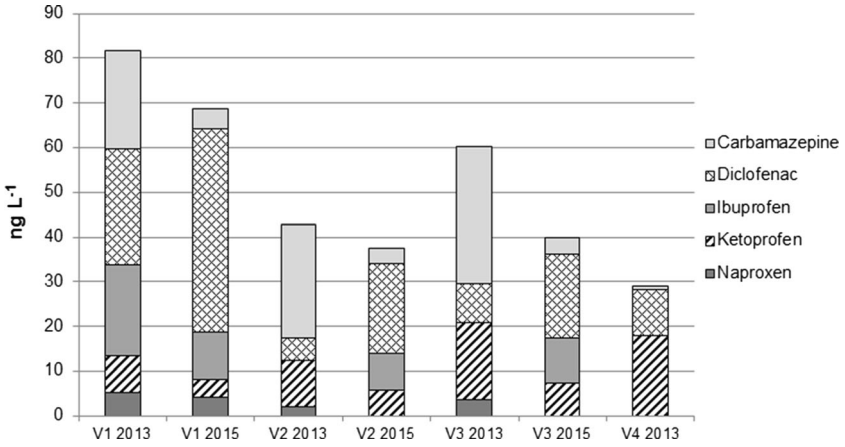


Fig. 7 Mean concentrations of selected pharmaceuticals in River Vantaa by passive sampling, at sampling sites V1–V4 in August 2013 and V1–V3 in April–May 2015

The concentrations are tens of nanograms per liter when detected by passive samplers and are similar to those reported by Äystö et al. (2014). Additionally, Äystö et al. (2014) reported decreased levels of carbamazepine in the sea shore. Carbamazepine in river water most likely originated from the multiple municipal WWTPs along River Vantaa. Carbamazepine is known to undergo transformation and dissociation reactions under sun light (Andreozzi et al. 2003). However, the reactions of carbamazepine proceed relatively slowly with half-life times of hundreds of days and it is constantly released by the effluents. In addition, the water of River Vantaa is turbid and contains humic substances which are known to decrease or even reverse the UV light-induced transformation reactions (Andreozzi et al. 2003). The highest amounts of humic substances are met in the upstream of River Vantaa due to forests and their soil properties (OIVA 2015).

Concluding remarks

Results show that all selected pharmaceuticals are present both in northern Lake Päijänne and in River Vantaa. Generally, the concentrations detected by passive samplers follow those of grab samples. Therefore, the results can be considered reliable and the Chemcatcher passive samplers suitable for the monitoring of pharmaceuticals in lake and river water. Passive sampling gives results of a long-term situation while grab sampling shows occasional fluctuations of concentrations.

The highest concentrations were detected by passive sampling in Lake Päijänne at sampling site P2 at the point of effluent discharge from the WWTP. Decreasing concentrations with greater distance from the WWTP confirm that the WWTP is the main local source of pharmaceuticals. The occurrence of pharmaceuticals at the site P1 upstream from the WWTP at a similar level but with different profile suggests another source calling for further research. Although high concentrations of selected pharmaceuticals are only occasionally detected, the cocktail of different substances requires further studies, especially related to long-term toxicity to aquatic organisms.

Pharmaceuticals, such as carbamazepine and diclofenac occurred at greater concentrations in River Vantaa than in Lake Päijänne. The difference in the dominating pharmaceuticals between River Vantaa and Lake Päijänne is most likely explained by the different sources of pharmaceuticals. There are

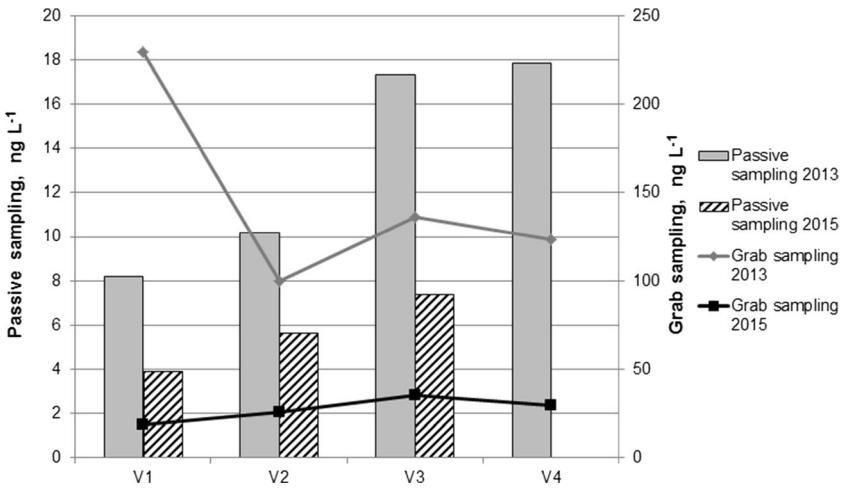


Fig. 8 Mean concentrations of ketoprofen in River Vantaa, collected by grab and passive sampling, August 2013 and April–May 2015

more and different types of point sources along River Vantaa than in Lake Päijänne. Additionally, the environmental conditions and the dilution of the pharmaceuticals vary due to different loads and different types of water bodies. Sampling time and environmental factors most likely explain the differences in River Vantaa water between samplings in 2013 and 2015.

In conclusion, Chemcatcher passive sampler with SDB-RPS disk is suitable for detecting pharmaceuticals in river and lake waters. It can be expected that there will be the need for more extensive monitoring of pharmaceuticals in the near future due to restricting environmental legislation. Passive sampling gives a good alternative for long-term monitoring of environmental pollutants compared to traditional grab sampling and gives an inexpensive and less labor-intensive option also for screening of pollutants in obligatory environmental monitoring.

Acknowledgements Financial support from Maa- ja vesitekniikan tuki ry. is gratefully acknowledged.

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