



# A passive sampling method for detecting analgesics, psycholeptics, antidepressants and illicit drugs in aquatic environments in the Czech Republic



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## HIGHLIGHTS

- Field calibration of POCIS was carried out at a wastewater treatment plant.
- Bioavailable concentrations of psychoactive drugs were monitored in surface waters.
- Total concentrations of compounds ranged from 463 to 6447 ng POCIS<sup>-1</sup>.
- Different pattern was found for water and POCIS concentration.

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## ABSTRACT

The goal of this study was to assess the bioavailable concentrations of analgesics, psycholeptics, antidepressants and illicit drugs in the surface waters of the Czech Republic. All of the sampling sites are located within the most important water quality monitoring profiles at the Czech Hydrometeorological Institute. The total concentrations of the compounds ranged from 463 to 6447 ng POCIS<sup>-1</sup> (Polar Organic Chemical Integrative Sampler). Carbamazepine (196–2690 ng POCIS<sup>-1</sup>) and tramadol (160–2250 ng POCIS<sup>-1</sup>) were the most abundant compounds at every site. The most polluted sites were those that received communal wastewater effluent and had a low dilution factor (ratio of wastewater effluent and river flow). The aqueous concentrations of the target compounds were estimated using sampling rate values obtained during a field calibration experiment. Patterns in the aqueous concentrations of the compounds (after back calculation from POCIS extracts) and the POCIS concentrations are different, possibly leading to discrepancies between the toxicity assessments conducted using POCIS extracts and those conducted using grab samples of water from the same location.

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## 1. Introduction

Studies from around the world have reported the occurrence of drugs in waste- and surface water (Berset et al., 2010; Castiglioni et al., 2008; Gheorghe et al., 2008; Irvine et al., 2011). The primary sources of illicit drugs, as well as pharmaceuticals, in the aquatic environment are wastewater treatment plants (WWTPs). Compounds usually enter waterways via urban wastewater after being excreted (Buchberger, 2007). Analysing drug residues in influent wastewater can provide reliable information on drug usage patterns at the local (Zuccato et al., 2008), and international levels (Thomas et al., 2012); recent environmental drug studies have focused on wastewater analysis (Bijlsma et al., 2012; Karolak et al., 2010).

The presence of drugs in aquatic ecosystems is garnering increasing amounts of attention because the compounds might adversely affect aquatic life. It has been shown that anxiolytic drugs in surface waters alter animal behaviour and thus can have ecological and evolutionary consequences. Juvenile European perch were exposed to oxazepam at environmentally relevant concentrations, and the effects on their behaviour and feeding rates were observed (Brodin et al., 2013). Additionally, the bioaccumulation of oxazepam in fish muscle tissue was reported. Feito and co-authors determined evidence of acute lethal and chronic sub-lethal toxicity in vascular plants exposed to environmentally relevant concentrations of the antidepressant venlafaxine (Feito et al., 2013). Therefore, drug monitoring in aquatic environments is important because it forms a basis for risk assessment for aquatic organisms.

The goal of this study was to assess the bioavailable concentrations of analgesics, psycholeptics, antidepressants, and illicit drugs in surface waters from rivers in the Czech Republic. Water quality is regularly

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monitored by the Czech Hydrometeorological Institute (CHMI) using a passive sampling (PS) approach. Thirty-seven compounds were analysed: three analgesics (buprenorphine, codeine, tramadol), one anaesthetic (ketamine), six antidepressants (amitriptyline, citalopram, mianserin, paroxetine, sertraline, venlafaxine), two anti-epileptics (carbamazepine, clonazepam), six drug metabolites (2-oxy-3-hydroxy-lysergic acid diethylamide (2-oxy-3-hydroxy-LSD), THC-COOH (Tetrahydrocannabinol) 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), benzoylecgonine, norbuprenorphine glucuronide, norketamine), 10 illicit drugs (amphetamine, cathinone, cocaine, lysergic acid diethylamide (LSD), N-methyl-1,3-benzodioxolylbutanamine (MBDB), 3,4-methylenedioxyamphetamine (MDA), 3,4-methylenedioxy-N-ethylamphetamine (MDEA), 3,4-methylenedioxy-N-methylamphetamine (MDMA), mephedrone, methamphetamine), seven psycholeptics (alprazolam, haloperidol, methylphenidate, midazolam, oxazepam, risperidone, zolpidem), and two synthetic opioids (methadone, oxycodone). The list of selected drugs includes commonly consumed drugs (or their metabolites), such as methamphetamine, MDMA, cocaine, and THC-COOH (Thomas et al., 2012), as well as medicinal compounds for which nonmedical use is prohibited, such as ketamine and tramadol. Certain compounds, such as oxazepam, are known to have adverse effects on non-target species, which underscores the importance of including them in environmental risk assessments (Brodin et al., 2013).

Polar Organic Chemical Integrative Samplers (POCISs) were deployed for 21 days in the spring of 2012. Passive sampling can overcome the limitations of conventional sampling and provide time-integrated data (Bueno et al., 2009). A further advantage of passive sampling is the ability to mimic biological uptake precluding the use aquatic organisms for biomonitoring (Alvarez et al., 2005; Kot et al., 2000). Unfortunately, the limitation of this approach is a lack of calibration data. The available sampling rate values are limited to a small number of compounds (Bartelt-Hunt et al., 2011; Harman et al., 2011). Therefore, the data obtained from POCIS monitoring were used for comparative purposes.

## 2. Materials and methods

### 2.1. Chemicals and solvents

A standardised pesticide configuration of POCIS (Pest-POCIS) was purchased from Exposmeter AB (Tavelsjö, Sweden). The sequestration medium of Pest-POCIS consists of a triphasic admixture of a hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous adsorbent (Ambersorb 1500) dispersed on a styrene divinylbenzene copolymer (S-X3 Bio Beads).

Details regarding the preparation of analytical standards have been described previously (Fedorova et al., 2013b; Grabic et al., 2012). Mixtures of the standard solutions for all analytes and surrogate standards were prepared in methanol at  $1 \mu\text{g mL}^{-1}$  and stored at  $4^\circ\text{C}$ .

Methanol (LiChrosolv Hypergrade), acetonitrile (LiChrosolv Hypergrade), toluene (Suprasolv) and dichloromethane (Suprasolv) were purchased from Merck (Darmstadt, Germany). Formic acid (FA) was used to acidify the mobile phases (Labcicom, Olomouc, Czech Republic). Ultrapure water was obtained from an aqua-MAX-Ultra system (Younglin, Kyounggi-do, Korea).

### 2.2. Sampling sites and field deployment of POCIS

A POCIS field calibration experiment was carried out at the WWTP in České Budějovice, Czech Republic from January 27 to February 16, 2011. The major source of input is domestic wastewater, as well as wastewater from two breweries and a dairy that account for less than 5%. Triplicates of POCIS were placed in protective cages and deployed in the effluent water for 1, 2, and 3 weeks. The mean water velocity at

the outlet was  $530 \text{ L s}^{-1}$ , and the average integrated flow was  $45 620 \text{ m}^3 \text{ day}^{-1}$ .

Wastewater samples for the POCIS calibration experiment were collected using an automated sampler (time proportional sampling, ASP-STATION 2000 sampler, Endress + Hauser). The samples were collected at 15-min intervals and were mixed after 24 h to obtain the daily mean. Each pooled sample was divided into three subsamples and frozen. The water temperature in the effluent channel was continuously monitored during the experiment and was stable throughout the calibration period. The concentrations of the target compounds ranged from low  $\text{ng L}^{-1}$  to several  $\mu\text{g L}^{-1}$ . The details of the POCIS calibration experiment can be found in a report by Fedorova et al. (2013a).

Passive sampling of river water was carried out at 21 sites located within the riverine profiles in the Czech Republic that are regularly monitored by the CHMI (Fig. 1). The locations of the sampling sites are listed with a short description in Table 1. All sampling sites are located within the most important water quality monitoring profiles in the CHMI. Most sites were situated at river outlets. The POCISs were placed in protective cages and deployed in the river water for 21 days during the spring of 2012. The water temperature was continuously monitored during the sampling period. After the exposure period, the samplers were cleaned with ultrapure water and transported on ice to the laboratory to be stored at  $-18^\circ\text{C}$ .

### 2.3. Extraction of target analytes

The chemical residues of interest were extracted from the passive samplers according to standardised procedures (Alvarez et al., 2005). The POCISs were carefully disassembled, and the sorbent was transferred into glass gravity-flow chromatography columns (1 cm i.d.) plugged with glass wool. A dichloromethane/methanol/toluene (8:1:1, v:v:v) mixture (50 mL) was used for elution during the recovery of sequestered analytes from the sorbent. Internal standards were added (20 ng per sample). The extracts were concentrated to approximately 1 mL by rotary evaporation. The residual water and traces of nonpolar solvents could cause the extract to separate into two phases. Because the presence of an eluent that is stronger than methanol is undesirable, we added methanol (10 mL) to the concentrated samples. Repeated evaporation removed any traces of toluene and DCM as an azeotropic mixture with methanol. Afterward, the samples were transferred to autosampler vials, and evaporated to 0.5 mL under a gentle stream of nitrogen.

The blank samples were processed the same way as the POCIS extracts to ensure that the target analytes were not introduced from laboratory procedures or sample handling.

### 2.4. In-line SPE/LC/MS/MS and LC/MS/MS analysis

A Q-Exactive mass spectrometer and a triple stage quadrupole MS/MS TSQ Quantum Ultra Mass Spectrometer (both from Thermo Fisher Scientific, San Jose, CA, USA) were each coupled with an Accela 1250 LC pump and Accela 600 LC pump (Thermo Fisher Scientific), and a HTS XT-CTC autosamplers (CTC Analytics AG, Zwingen, Switzerland) and used to analyse the water and POCIS samples, respectively. A Cogent Bidentate column (50 mm  $\times$  2.1 mm ID  $\times$  4  $\mu\text{m}$  particles; Microsolv Technology Corporation, Eatontown, NJ, USA) was used to separate the target analytes. The POCIS extracts were diluted twice with ultrapure water and analysed using conventional LC injection (5  $\mu\text{L}$  of sample per injection).

The filtered and spiked water samples were analysed using an in-line-SPE-LC fitted with a C18 column (Hypersil Gold, 20 mm  $\times$  2.1 mm i.d., 12  $\mu\text{m}$  particles; Thermo Fisher Scientific) (Fedorova et al., 2013b). The in-line SPE enabled the pre-concentration and analysis of samples in a single run, making large volumes and time-consuming SPE extraction unnecessary. The extraction and analytical process required only 15 min and used only 1 mL of sample.

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