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Passive sampling of wastewater as a tool for the long-term monitoring of community exposure: Illicit and prescription drug trends as a proof of concept

J.A. Baz-Lomba [a, b, *], Christopher Harman [a], Malcolm Reid [a], Kevin V. Thomas [a, 1]

[a] Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, NO-0349 Oslo, Norway
[b] Faculty of Medicine, University of Oslo, PO box 1078 Blindern, 0316 Oslo, Norway

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ABSTRACT

A passive sampling device, the Polar Organic Chemical Integrative Sampler (POCIS), was calibrated in-situ over a 4-week period in Oslo (Norway) for 10 illicit drugs and pharmaceuticals with the goal of developing an approach for monitoring long-term wastewater drug loads. The calibrations were performed in triplicate using three different overlapping calibration sets under changing environmental conditions that allowed the uncertainty of the sampling rates to be evaluated. All 10 compounds exhibited linear uptake kinetics and provided sampling rates of between 0.023 and 0.192 L d^{-1}. POCIS were deployed for consecutive 2-week periods during 2012 and 2013 and the calculated time-weighted average (TWA) concentrations used to define different drug use trends. The relative uncertainty related to the POCIS data was approximately 40% and, except for citalopram, 85% of all the long-term measurements of pharmaceuticals were within the confidence interval levels calculated to evaluate the effects of changing environmental conditions on the TWA estimations. POCIS was demonstrated to be sufficiently robust to provide reliable annual drug use estimates with a smaller number of samplers (n = 24) than recommended for active sampling (n = 56) within an acceptable level of sample size related uncertainty < 10%. POCIS is demonstrated to be a valuable and reliable tool for the long-term monitoring of certain drugs and pharmaceuticals within a defined population.

1. Introduction

Monitoring drug use has traditionally been performed by questionnaire-based surveys and police statistics. Estimating population drug use through the analysis of wastewater samples has been established as an approach for monitoring patterns of community drug use (Castiglioni et al., 2014). Wastewater-based epidemiology (WBE) studies for drugs have provided valuable information, showing spatial and temporal differences across different countries (Ort et al., 2014b; Thomas et al., 2012). More recently, WBE results have been also compared with other sources of information confirming its potential as a complementary approach for obtaining a more accurate picture of the drug use situation (Baz-Lomba et al., 2016b; Been et al., ; Zuccato et al.,). Furthermore, WBE has recently been applied to assess the community level exposure of humans to a range of environmental stressors (Gracia-Lor et al., 2016; Rousis et al., 2016, 2017) as well as their combined response to such stressors (Ryu et al., 2016). The generation of community level exposure data that can be compared with other complementary sources of data has a clear potential within environmental epidemiology.

Despite good agreement with the other sources of data, it is possible that wastewater data may be typified by low temporal representativeness and high spatial variability due to the use of different substances and spatial and temporal trends in availability. WBE results therefore need to be carefully interpreted (Baz-Lomba et al., 2016b). Thus far, the temporal coverage of most of the WBE studies performed has been typically limited to a one-week sampling program (Ort et al., 2014b). In order to more accurately estimate the representative mean annual substance use by WBE a recent study recommended the use of stratified random sampling

* Corresponding author. Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, NO-0349 Oslo, Norway.
E-mail address: Joseantonio.baz@niva.no (J.A. Baz-Lomba).
[1] Current address: Queensland Alliance for Environmental Health Science (QAEHS), University of Queensland, 39 Kessels Road, Coopers Plains QLD 4108, Australia.

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schemes (typically 56 samples per year) (Ort et al., 2014a). Furthermore, different sampling strategies based on the sampling frequency or composite sampling mode have been evaluated in order to decrease the sampling uncertainty (Ort et al., 2010). However, increasing the sampling frequency implies an additional costs together with the power and space requirements of an automated sampling device and such a frequency may still prove inadequate in certain circumstances such as the short-term changes in use patterns or variations in concentrations associated with other external factors such as precipitation (Ort et al., 2014a).

Passive sampling devices (PSD) are an alternative sampling tool to overcome some of the above-mentioned issues. PSD have been demonstrated as a good alternative for the monitoring of drugs and other micropollutants in wastewater providing time-integrated estimates that compensate for fluctuating concentrations (Harman et al., 2011b; Kaserzon et al., 2014). PSD may also decrease the limits of quantification compared with traditional sampling and be used as a screening tool for the detection of emerging compounds present at very low concentrations (Alvarez et al., 2014). Furthermore, the use of PSD over a specified period can be performed without human intervention, without any power requirements and at low cost. For example, the annual monitoring of drugs in wastewater can be performed with as few as 26 PSD (Harman et al., 2011b).

The polar organic chemical integrative sampler (POCIS) has thus far been applied for the analysis of over 300 polar organic substances in water (Harman et al., 2012; Morin et al., 2012). This includes a number of pharmaceuticals and illicit drugs, as well as other polar contaminants such as pesticides (Gonzalez-Rey et al., 2015; Jones-Lepp et al., 2004; Metcalfe et al., 2011). The physicochemical properties of the compounds will determine whether they accumulate in the sampler based on the different solute-solvent-sorbent interactions (i.e. the version of POCIS presented in this study has a good selectivity for compounds with log K_{ow} approximately between 2 and 4) (Harman et al., 2011b). The theory and modelling of chemical uptake by POCIS have been explained in detail elsewhere (Alvarez et al., 2004; Huckins et al., 1993; Vermeirssen et al., 2012). There are however few studies that consider modelling uptake rates for real in situ environmental exposures. Depending on sampler design, PSD can be used in either equilibrium or time-weighted average (TWA) modes to give concentrations of the desired analyte. In contrast to PSDs for hydrophobic compounds, where sampling rates (R_S) can be modelled by physicochemical properties such as molecular weight, R_S for POCIS must first be calibrated experimentally. Laboratory generated R_S can vary significantly between different studies depending on the different calibration methods and conditions used and standardization of the different calibration methods has been recommended in order to reduce these discrepancies (Harman et al., 2012; Morin et al., 2012). Furthermore, R_S generated in the laboratory under controlled exposure conditions may not be representative of the actual values under different and variable environmental conditions that can lead to biased data when calculating TWA concentrations (Miller et al., 2016).

One of the primary uncertainties associated with the calculation of POCIS R_S, which in turn fundamentally affects the reliability of POCIS derived TWA concentrations, is the influence of environmental factors, such as the rate of water flow (Kaserzon et al., 2013; Li et al., 2010b), temperature (Li et al., 2010a), pH (Li et al., 2011) and biofouling (Harman et al., 2009). Different approaches have been proposed, such as the use of external R_S corrections (Alvarez et al., 2007), the performance reference compounds (PRC) approach used for hydrophobic PSD (Huckins et al., 2002) and more recently the development of the diffusive gradient in thin-film sampler for organics (Challis et al., 2016). All of these approaches have challenges, but a comprehensive method for relating the uptake in POCIS to environmental factors remains elusive (Harman et al., 2012). In-situ calibration of POCIS has been proposed as an alternative strategy to generate more reliable and constant R_S for a specific site, however only a few papers have published in-situ R_S values (Harman et al., 2011b; Jacquet et al., 2012; Mazzella et al., 2010; Zhang et al., 2008). However, in-situ calibration is also not without its challenges; largely due to the extra costs and the need for more extensive water sampling, compared with laboratory methods. An overall lack of understanding of the sorption phenomena for different compounds means that it is prudent to consider POCIS derived water concentration data as semi-quantitative (Harman et al., 2011a; Miège et al., 2015). Dalton and colleagues (Dalton et al., 2014) have described the variability of in-situ R_s associated with environmental factors (Morin et al., 2012) and more recently, Poulier and colleagues (Poulier et al., 2014) estimated that the uncertainty related to their POCIS data for several pesticides might be as high as 138%.

The aim of the current study was to evaluate whether POCIS are a suitable and cost-effective alternative to grab sampling for the long-term monitoring of substance use and potentially exposure at community level through WBE. The in-situ R_S was determined for a number of pharmaceuticals (atenolol, citalopram, carbamazepine, oxazepam, metoprolol, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP) and morphine) and illicit drugs (cocaine, benzoylecgonine and methamphetamine) in POCIS to estimate substance use trends over 2012 and 2013. The reproducibility of R_S was estimated by overlapping three in-situ calibrations to mitigate the potential confounding effects and impact of different environmental conditions. The accuracy of the POCIS R_S was evaluated by assessing two different uncertainty levels, taking into account the coefficient of variation of the three R_S calculated during the three different calibration periods and the repeatability for each of the triplicates deployed during subsequent long-term (2-yr) monitoring.

2. Materials and methods

2.1. Chemicals, materials and POCIS samplers

Information on chemicals, materials and POCIS samplers is provided in the Supporting Information.

2.2. Wastewater and POCIS extraction and analysis

Information on wastewater and POCIS extraction and analysis is provided in the Supporting Information.

2.3. Quality assurance

Information on quality assurance is provided in the Supporting Information.

2.4. In situ calibration study design

All samples were collected at the VEAS wastewater treatment plant (WWTP) in Oslo (Norway). VEAS treats sewage for approximately 600,000 people of which the city contributes about 70.5% and the adjoining areas representing the other 29.5% (8% from Asker and 21.5% from Bærum, see Fig. S1). The total length of the sewer line is 42.3 km and the mean residence time in the sewer system is 5 h (see www.veas.nu for further details).

The in situ calibration took place during February 2014. The calibration experiment was performed over a 4-week period using triplicate POCIS deployed for varying periods of time and in three