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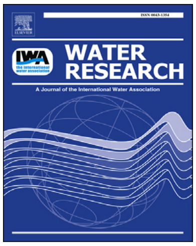

Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers

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ABSTRACT

In a large field study, the in-situ calibration of the Chemcatcher® passive sampler – styrenedivinylbenzene (SDB) covered by a polyether sulfone (PES) membrane – was evaluated for 322 polar organic micropollutants. Five rivers with different agricultural and urban influences were monitored from March to July 2012 with two methods i) two-week time-proportional composite water samples and ii) two-week passive sampler deployment. All substances – from different substance classes with $\log K_{ow}$ −3 to 5, and neutral, anionic, cationic, and zwitterionic species – were analyzed by liquid-chromatography high-resolution tandem mass spectrometry. This study showed that SDB passive samplers are well-suited for the qualitative screening of polar micropollutants because the number of detected substances was similar (204 for SDB samples vs. 207 for composite water samples), limits of quantification were comparable (median: 1.3 ng/L vs. 1.6 ng/L), and the handling in the field and laboratory is fast and easy. The determination of in-situ calibrated sampling rates (field R_s) was possible for 88 compounds where the R^2 from the regression (water concentration vs. sampled mass on SDB disk) was >0.75. Substances with moderately fluctuating river concentrations such as pharmaceuticals showed much better correlations than substances with highly fluctuating concentrations such as pesticides ($R^2 > 0.75$ for 93% and 60% of the investigated substances, respectively). Flow velocity (0.05–0.8 m/s) and temperature (5–20 °C) did not have an evident effect on the field R_s. It was observed that ionic species had significantly lower field R_s than neutral species. Due to the complexity of the different transport processes, a correlation between determined field R_s and $\log D_{ow}$ could only predict R_s with large uncertainties. We conclude that only substances with relatively constant river concentrations can be quantified accurately in the field by passive sampling if substance-specific R_s are determined. For that purpose, the proposed in-situ calibration is a very robust method and the substance specific R_s can be used in future monitoring studies in rivers with similar environmental conditions (i.e., flow velocity, temperature, pH).

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1. Introduction

Passive sampling in the field has been shown to be an alternative to ambient water samples for monitoring polar organic micropollutants such as pesticides, pharmaceuticals, and industrial chemicals (e.g., Allan et al., 2006; Harman et al., 2012; Mills et al., 2014). Two general designs of passive samplers have been used to date for the detection of polar substances in water – the polar organic compound integrative sampler (POCIS) and the polar version of Chemcatcher®. Most published work is about POCIS, with less information available about Chemcatcher (Mills et al., 2014), although the Chemcatcher is easier to handle. Both types consist of a receiving material which is usually Oasis HLB powder for POCIS and a styrenedivinylbenzene (SDB) disk for Chemcatcher. In the case of POCIS, the receiving material is sandwiched between two membranes. These are usually made of polyether sulfone (PES). In the case of Chemcatcher, a PES membrane is optional, but is often used to extend the linear uptake phase.

Due to the relatively easy handling during deployment and extraction, passive samplers can serve as a cost-effective and robust monitoring tool. Over 300 compounds have been shown to accumulate in POCIS (e.g., >100 pesticides, >90 pharmaceuticals, >30 industrial chemicals, Harman et al., 2012). Uptake studies using 22 substances showed that sampling rates of POCIS and Chemcatcher are correlated and that Chemcatchers have slightly higher sampling rates when correcting sampling rates for differences in sampler surface areas (Vermeirssen et al., 2012). Therefore, it can be hypothesized that a similar number of substances can accumulate in SDB disks as in POCIS.

For a proper quantification, robust sampling rates (R_s) are critical for all sampler types (Harman et al., 2012). R_s are substance specific and there is an intense discussion underway about whether or not R_s can be predicted from physico-chemical properties. Different studies have investigated the relationship between R_s and $\log K_{ow}$ or $\log D_{ow}$, but have obtained very different results (e.g., Morin et al., 2013; Shaw et al., 2009; Vermeirssen et al., 2013).

Without a direct link to physico-chemical properties, many studies have focused on calibrating the passive samplers for single substances. Different methods exist in laboratory-scale (e.g., static renewal, static depletion, flow-through systems), but all methods yield different R_s and there is no standard calibration method yet (Mills et al., 2014; Morin et al., 2013). Because R_s are also dependent on water matrix properties such as temperature, pH, ionic strength, and dissolved organic matter (Harman et al., 2012), R_s calculated at laboratory conditions, usually done with nanopure or tap water, do not simulate field conditions very well (i.e., river water, wastewater).

To account for the influence of the water matrix, the use of flow channels which run with river water is a very good alternative (e.g., Vermeirssen et al., 2008). With this approach, different flow velocities can also be tested under controlled conditions, as flow velocities can have a large effect on R_s, too (Vermeirssen et al., 2009). However, determining R_s for a large number of substances under varying environmental conditions is time- and resource-consuming.

Methods exist that correct for varying environmental conditions such as flow velocity and biofouling in-situ, such as the use of performance reference compounds (PRCs), but their reliability for calibrating passive samplers for polar compounds has not yet been fully demonstrated (Harman et al., 2012; Mills et al., 2014). Due to the fact that the POCIS and Chemcatcher normally have two phases (receiving phase and diffusive limiting membrane), an isotropic exchange cannot be expected, per se. Shaw et al. (2009) for example found that uptake and release is not isotropic when using SDB disks covered with a PES membrane. SDB disks alone have a two-phasic release, as shown in a previous study of our research group (Vermeirssen et al., 2013).

As an alternative to laboratory experiments or flow channel experiment that run under controlled conditions, R_s can also be calibrated in-situ by analyzing ambient water samples and passive samples taken at the same location during the same time. Harman et al. (2012) stated that when no PRC approach is possible, the calibration of R_s in-situ "*will provide the best possible approximation of time weighted average concentrations*", because it accounts for differences in water matrix and flow conditions. However, up to now, in-situ calibration has only occasionally been performed for POCIS and Chemcatchers (Harman et al., 2011; Vermeirssen et al., 2009; Zhang et al., 2008). In all cases, they were able to successfully calibrate the sampler for one investigated site. It is therefore hypothesized that if different rivers with varying water matrix and flow conditions are used for the calibration, all field differences will even out, so that the generated field R_s can be adapted to other rivers with similar environmental parameters.

The presented paper therefore approaches the different research gaps by a large field study that investigated a broad number of substances using styrenedivinylbenzene disks modified with sulfonic acid groups (SDB-RPS) covered by a PES membrane (further referred as SDB passive sampler). The goals of the study were i) to check how many and which substances accumulate on the SDB passive sampler, ii) to compare the obtained limits of quantification (LOQ) by the SDB passive sampler with those in ambient water samples, iii) to determine field R_s for a large number of substances by in-situ calibration, iv) to assess the influence of environmental parameters on the quantity and robustness of the field R_s, and v) to test with a large data set (88 field R_s), whether $\log K_{ow}$ and $\log D_{ow}$ can predict R_s.

Using an extensive screening with liquid chromatography – high-resolution tandem mass spectrometry (LC-HR-MS/MS), 322 substances from different compound classes were investigated in five rivers over five months. Large temporal and spatial differences in flow velocities, temperatures, and micropollutant concentrations were present in the rivers, covering a broad range of environmental conditions.

2. Materials and methods

2.1. *Field study*

A large field study investigating five medium-sized Swiss rivers (Furtbach, Limpach, Mentue, Salmsacher Aach, Surb;