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Picogram per liter detections of pyrethroids and organophosphates in surface waters using passive sampling

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ABSTRACT

Pyrethroids and organophosphates are among the most toxic insecticides for aquatic organisms, leading to annual-average environmental quality standards (AA-EQS) in the picogram per liter range in surface waters. For monitoring purposes, it is therefore crucial to develop very sensitive analytical methods. Until now, it is very difficult to reach detection limits at or below given AA-EQSs. Here, we present a passive sampling method using silicone rubber (SR) sheets for the sampling of ten pyrethroids and two organophosphates in surface waters. An analytical method was developed, optimized and validated for the extraction of the insecticides from the SR sheets by accelerated solvent extraction followed by clean-up on C18 and silica gel and detection with GC–MS/MS in positive ionization mode. Good precision (<20%) and absolute recovery (>50%) was observed for all substances, accuracy was between 66% and 139%. Limits of detection between 6 and 200 pg/L were achieved for all substances in surface waters using average sampling rates for PCBs and PAHs. The lack of substance-specific sampling rates and missing performance reference compounds led to an uncertainty in the concentration estimation of factor three in both directions. In a large field study, comprising 40 environmental samples from nine Swiss rivers, eight out of 12 substances were detected (most frequently: chlorpyrifos, cypermethrin). Most of the estimated organophosphate concentrations were between 0.1 and 1 ng/L, most pyrethroid detections below 0.1 ng/L. Four substances (chlorpyrifos-methyl, cypermethrin, deltamethrin and lambda-cyhalothrin) showed exceedances of their respective AA-EQS in multiple samples, also when the uncertainties in the concentration estimation were considered. As pyrethroid and organophosphate detection by SR passive sampling is very practicable and allows sensitive analysis, it has the potential to become a new tool in the monitoring of non-polar pesticides.

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1. Introduction

Pesticides applied to agricultural fields or in urban areas can enter surface waters by different routes (e.g. runoff, spray drift, waste water treatment plants, storm water overflows) (Carter, 2000) and affect the aquatic ecosystem (Schäfer et al., 2007; Werner et al., 2004) Particularly insecticides have a high ecotoxicological potential (Schulz, 2004). The by far most toxic insecticides towards aquatic organisms are pyrethroids. Acute EC-50 values for to the amphipod *Hyalella azteca* for four of five frequently applied pyrethroids in the US are between 1.7 and 3.3 ng/L (Weston and Lydy, 2010). For cypermethrin, which is one of the new priority pollutants in the European Water Framework Directive (WFD) and which is the most frequently applied pyrethroid in Switzerland, an annual average environmental quality standard (AA-EQS) of 0.08 ng/L in surface waters was defined (EC Directive, 2013/39/EU, 2013). Hence, it is essential that appropriate analytical methods are developed for the detection of pyrethroids in the picogram per liter range in surface waters. Non-polar organophosphates are also toxic towards aquatic organisms; for chlorpyrifos, for example, the AA-EQS is 30 ng/L (EC Directive, 2013/39/EU, 2013).

Because most of these substances are highly non-polar ($\log K_{ow}$ 4–8), dissolved concentrations in the water are expected to be very low, as the compounds quickly sorb to sediments or suspended particles. Thus, pyrethroid monitoring studies have often focused on the measurement in the sediment and in the sediment pore water (Budd et al., 2007; Weston et al., 2004). Although only 0.4–1% of the pyrethroids in river water are expected to be present in the freely dissolved form (Liu et al., 2004), this fraction is bioavailable (Yang et al., 2006) and thus responsible for a large part of the toxicity. There are only studies in California and in Spain investigating dissolved pyrethroids (Feo et al., 2010c; Hladik and Kuivila, 2009; Weston and Lydy, 2010) with focus on peak concentrations in small creeks or drains from agricultural or residential sites (concentrations in the range of 5–50 ng/L). Predicted pyrethroid concentrations in small to medium sized rivers in Switzerland are between 0.001 and 0.01 ng/L, predicted organophosphate concentrations between 2 and 20 ng/L. These values were calculated using a runoff scenario with the model Exposit (Exposit 2.01, 2011) by taking into account site specific application rates, degradation in soil, polarity-dependent emission to surface waters and dilution in the stream.

Most pyrethroid analytics are carried out by gas chromatography (GC) coupled to electron-caption detection (ECD) or mass spectrometry (MS). Newer technologies include GC coupled to tandem MS (MS/MS) or two-dimensional GC coupled to high-resolution (HR)MS (Feo et al., 2010a). Extraction of the water samples is normally done by liquid–liquid extraction (LLE) or solid phase extraction (SPE) (Feo et al., 2010a). A recent review by Loos (2012) stated that it is *"extremely difficult, if not impossible with current methods"* to reach detection limits of cypermethrin in the low picogramm per liter range in ambient water samples. For example, Vorkamp et al. (2014) showed that, despite extraction of 12 L of water combined with very sensitive HRMS, the AA-EQS value for cypermethrin could not be reached. There are only two studies which reached detection limits in the sub-ng/L range for some pyrethroids using SPE followed by detection on GC-electron ionization (EI)-MS (Hladik and Kuivila, 2009) and ultrasound-assisted emulsification-extraction (UAEE) followed by GC-negative chemical ionization (NCI)-MS/MS, respectively (Feo et al., 2011).

Recently, we found with a comprehensive pesticide screening performed by liquid chromatography-HR-MS/MS, that pyrethroids and non-polar organophosphates were the only substance classes which cannot be adequately measured (Moschet et al., 2014). This can lead to a considerable underestimation of the insecticidal toxicity of environmental samples.

One way to overcome this problem is the use of passive sampling (Huckins et al., 2006; Namieśnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005), a sampling tool that is under discussion for regulatory compliance monitoring (Allan et al., 2006). Passive sampling for non-polar substances has been established with semipermeable membrane devices (SPMD) (e.g., Stuer-Lauridsen (2005)), low density polyethylene (LDPE, e.g. Rusina et al. (2007)) and more recently with silicone rubber sheets (SR), also known as polydimethylsiloxane (PDMS) (e.g., Smedes and Booij (2012)). For non-polar PCBs and PAHs, the use of SR has been investigated intensively during the last years (Rusina et al., 2007, 2010b; Smedes and Booij, 2012; Smedes et al., 2009). The main advantage of passive sampling is that non-polar substances have very high sampling rates, in the range of liters per day, which drastically reduces the detection limits (Smedes and Booij, 2012). Another advantage is that sorption to sampling equipment such as collection tubes and storage containers is avoided. Compared to water samples, where pyrethroids sorbed to dissolved organic carbon are also measured (Liu et al., 2004), only truly dissolved substances sorb to passive samplers. It is currently under discussion if passive sampling can be used in regulatory monitoring within the WFD, because EQS are defined for the whole water concentration and thus passive sampling is not in compliance with the WFD approach (Mills et al., 2014). Challenges in the quantification of water concentrations remain because the PMDS sampling rate is dependent on a number of parameters such as flow rate, temperature, salinity, and biofouling (Smedes and Booij (2012)). Because hardly any sensitive ambient water sampling methods exist for pyrethroids, passive sampling is a promising strategy nevertheless (Loos, 2012; Mills et al., 2014).

The goals of this study were (i) to develop a practicable, selective and sensitive SR based passive sampling method for the detection of highly toxic pyrethroids and organophosphates in surface waters with LODs at or below their respective AA-EQS values (often picogramm per liter range), and (ii) to apply the method in surface water monitoring of nine streams in Switzerland.

2. Materials and methods

2.1. Analytes and solvents

Following solvents were used for the development and application of the analytical method: ethyl acetate (purity

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