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Ethylene vinyl acetate polymer as a tool for passive sampling monitoring of hydrophobic chemicals in the salmon farm industry

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ABSTRACT

Current monitoring programs are focused on hydrophobic chemicals detection in aquatic systems, which require the collection of high volumes of water samples at a given time. The present study documents the preliminary use of the polymer ethylene vinyl acetate (EVA) as a passive sampler for the detection of a hydrophobic chemical used by salmon industries such as cypermethrin. Initially, an experimental calibration in laboratory was performed to determine the cypermethrin equilibrium between sampler and aquatic medium, which was reached after seven days of exposure. A logarithm of partitioning coefficient EVA–water ($\log K_{EVA-W}$) of 5.6 was reported. Field deployment of EVA samplers demonstrated average concentrations of cypermethrin in water to be 2.07 ± 0.7 ng L^{-1} close to salmon cages, while near-shore was 4.39 ± 0.8 ng L^{-1}. This was a first approach for assessing EVA samplers design as a tool of monitoring in water for areas with salmon farming activity.

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1. Introduction

During the last decade, the salmon industry has shown an important growth in aquaculture. However, the susceptibility of farmed salmon to diseases outbreaks has lead to decline in production and has led to economic losses by the industry (Johnson et al., 2004). The occurrence of parasitic diseases in salmon farming in southern Chile has intervened in the growth of the salmon industry (González and Carvajal, 2003; Hamilton-West et al., 2012; FAO, 2012), being the parasitic copepod *Caligus rogercresseyi* the main parasite in the marine culture in Chile (Boxshall and Bravo, 2000). Therefore, for effective mitigation, management and control of the parasitic diseases, the salmon industry requires the use of chemotherapeutic treatment such as antiparasitic pesticides (Roth, 2000).

Synthetic pyrethroid has been used for parasite control in salmon farm, with high efficiency at low concentrations (Hill, 1989). These veterinary products are applied through bath treatments at a concentration of 3–5 μg L^{-1} during 60 min, after which they are released into the marine environment. The pyrethroid application frequency will depend of parasite occurrence in salmons. Cypermethrin is a pesticide pyrethroid with low solubility in water and volatility. However, its hydrophobic properties ($\log K_{OW} > 5$) allows for it to be absorbed onto the organic fraction available in the water column, and being transported over long distances with potential to affect non-target aquatic organisms (Ernst et al., 2001). Its mechanism of action is to interfere with the central nervous system function of invertebrates, by action on the sodium channels of the nerve cells (Soderlund et al., 2002). The toxicity by cypermethrin is dependent upon the isomerization of the chemical, *cis* or *trans*, the *cis* isomer shows a toxic potential 10 times higher (Ray, 2004). Several studies have shown a potent acute and chronic effects on marine invertebrates such as copepods (Barata et al., 2002a,b; Medina et al., 2002, 2004; Willis and Ling, 2004; Willis et al., 2005), benthonic crustaceans (Gowland et al., 2002a) and mussels (Gowland et al., 2002b; Köprücü et al., 2010; Ait Ayad et al., 2011).

In Chile, vigilance and/or monitoring programs are based in the collection of high volumes of water samples at a specific time; however, sampling may be affected during pollution events. Lately, passive monitoring methods have been developed with the aim to estimate the dissolved or bioavailable fraction of organic contaminants in water (Vrana et al., 2005). Some examples of devices used as passive samplers in water are semi-permeable membranes (SPMDs) (Huckins et al., 1990), polar organic chemical integrative sampler (POCIS) (Alvarez et al., 2004), polyethylene (PE) (Choi et al., 2013), low-density polyethylene (LDPE) (Lohmann, 2012), silica rubber (Rusina et al., 2010), ethylene vinyl acetate (EVA) (St George et al., 2011), among others. These have been proven to be efficient tools for measuring dissolved chemical concentrations

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for a large range of hydrophobic organic pollutants, such as polychlorinated biphenyl (PCBs), polycyclic aromatic hydrocarbons (PAH), new generation pesticides, pharmaceuticals and personal care products.

A passive sampler is defined as a sampling technique based on the free flow of the analyte or chemical from a sampled environment to the sampler, as a result of the difference in the chemical potentials of the two environments. The total flow of the chemical between different mediums continues until equilibrium is achieved. The kinetics of exchange between a passive sampler and the polluted aquatic medium can be expressed through the first-order Eq. (1),

$$C_S\ (t) = C_W k_1/k_2\ (1 - e^{-k}2^t) \quad (1)$$

where C_S is the chemical concentration in the sampler as a function of time (t), C_W is the concentration in the aquatic environment, whereas k_1 and k_2 are the constant rates of uptake and release, respectively (Mayer et al., 2003; Vrana et al., 2005). At the equilibrium phase, the partition coefficient between the passive sampler and the water phase must be known. When equilibrium is reached, the concentration in water can be determined by the following Eq. (2),

$$C_W = C_S/K_{SW} \quad (2)$$

where K_{SW} is the partition coefficient between the sampler and the environment sampled (Mayer et al., 2003).

Ethylene vinyl acetate polymer (EVA) has been used as a sampler for several environmental compartments, such as air (Harner et al., 2003; Farrar et al., 2005; Wu et al., 2008), sediments (Golding et al., 2007; Meloche et al., 2009) and seawater (St George et al., 2011). EVA is a flexible polymer which can be easily processed and adapted to different substrates. In addition, it is resistant to high pressures, temperatures, UV radiation and it is also water proof, making it an effective polymer for the purpose of capturing hydrophobic chemicals in the aquatic environment (Adams et al., 2007; St George et al., 2011).

This is a preliminary study that aims (1) to establish the equilibrium time and partition coefficient between the cypermethrin pesticide and the EVA polymer through the laboratory calibration test and (2) to detect cypermethrin concentrations during a treatment period in salmon cages using the EVA polymer as a passive sampler design. This approach would allow sampling for the concentrations of pesticides in the water column which would provide valuable information related to the potential effects of cypermethrin on non-target crustaceans.

2. Materials and methods

2.1. EVA sampler preparations

Ethylene vinyl acetate pellets (EVA, Elvax 40W, DuPont Canada) were cleaned with organic solvent methanol and stored in glass jar at room temperature until use. An EVA coating solution was prepared by dissolving 2 g of EVA pellets in 100 mL of dichloromethane (DCM). The solution was magnetically stirred for approximately 2 h until there were no visible signs of EVA pellets. Whatman™ glass fiber filters (GF/F, GE Healthcare, Little Chalfont UK), of 70 mm diameter, were used as adhesion substrate of the polymer. The filters were baked at 420 °C for 6 h, cooled, weighed and stored prior to use. Each weighted GF/F was coated with EVA solution through an immersion time of five seconds. The filters were then dried in a dessicator and bell until complete evaporation of DCM solvent. Further, the dessicator allowed avoiding contamination and moisture absorption. Each coated filter was weighed again to calculate EVA mass (see SI in Table S1).

The average weight of EVA added to each filter and the EVA density (ρ = 0.93 g cm^{-3}) was used to calculate the volume of EVA for each sampler. The average volume was estimated in ~0.058 cm^3 for each sampler. With the estimated volume (cm^3) and the total exposed area of the EVA sampler (76.9 cm^2) the average thickness was calculated to be ~7 μm (calculation in SI).

2.2. Calibration design

Three solutions were prepared in glass jars with 1.5 L of milli-Q water. Each jar had a known concentration of 3.5 mg L^{-1} cypermethrin (CAS number 52315-07-8; 94.3% purity, mixture of isomers, Pestanal) purchased at Sigma-Aldrich (St. Louis USA). One jar without cypermethrin was used as the calibration blank. During the experimental calibration, the solutions were kept under constant stirring for fifteen days at room temperature between 13 °C and 15 °C. The jars with solutions and blanks were covered in aluminum foil to avoid photolytic degradation. For each solution, one filter coated with EVA was placed within. Water samples were collected every day (for 15 days) to detect changes of cypermethrin concentration over time. The concentration in the EVA sampler was estimated indirectly according to the water concentration measured. However, after fifteen days the samplers were analyzed to confirm the cypermethrin final concentration.

2.3. Deployment of EVA sampler

The EVA samplers were deployed into Manao Bay located in the north of Chiloé Island, Chile (Fig. 1). This study area is characterized by the presence of mussel and salmon farms, predominant currents with southwest-northeast direction and strong tidal influences (see SI). According to the hydrodynamic in the area, devices with EVA samplers were deployed in the marine water into cylindrical stainless steel baskets at a depth between 2 and 5 m (SI in Figs. S1 and S2). During a treatment in salmon cages with cypermethrin formulation (BETAMAX®), the devices were deployed in the seawater. The samplers were positioned near treated salmon cage and close to shore for a total period of seven consecutive days. After the sampling period was over, each sampler was removed and rinsed with milli-Q water for the debris removal. Samples were finally stored at −4 °C in aluminum foil envelopes until analysis in the laboratory.

2.4. Extraction

Extraction of cypermethrin from water samples were carried out by liquid-liquid chromatography method. A volume of 30 mL of water was extracted with 10 mL of organic solvent n-hexane. The solutions were agitated for 1 min with a vortex and cleaned through sodium sulfate and glass fiber wool columns. This extraction procedure was repeated three times. On the other hand, filter coated with EVA were rinsed and placed in 100 mL of methanol for 48 h. The solutions were cleaned through sodium sulfate and glass fiber wool columns.

Later, the extracts were reduced by rotary evaporation until reaching a volume ~2 mL. The final volume was transferred into a GC vial and evaporated under flow of nitrogen. The solvent was exchanged into toluene to a final volume of 1.5 mL for analysis.

2.5. Analysis

Cypermethrin concentrations were determined using a gas chromatography equipped with an electron capture detector (GC-ECD), which provides more selectivity to halogenated compounds. Injector and detector temperatures were kept at 240 °C and 370 °C, respectively. A 30 m PTE-5 column with film thickness of 0.25 μm

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