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Extended evaluation of polymeric and lipophilic sorbents for passive sampling of marine toxins

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ABSTRACT

Marine biotoxins are algal metabolites that can accumulate in fish or shellfish and render these foodstuffs unfit for human consumption. These toxins, released into seawater during algal occurrences, can be monitored through passive sampling.

Acetone, methanol and isopropanol were evaluated for their efficiency in extracting toxins from algal biomass. Isopropanol was chosen for further experiments thanks to a slightly higher recovery and no artifact formation. Comparison of Oasis HLB, Strata-X, BondElut C18 and HP-20 sorbent materials in SPE-mode led to the choice of Oasis HLB, HP-20 and Strata-X. These three sorbents were separately exposed as passive samplers for 24 h to seawater spiked with algal extracts containing known amounts of okadaic acid (OA), azaspiracids (AZAs), pinnatoxin-G (PnTX-G), 13-desmethyl spirolide-C (SPX1) and palytoxins (PlTXs). Low density polyethylene (LDPE) and silicone rubber (PDMS) strips were tested in parallel on similar mixtures of spiked natural seawater for 24 h. These strips gave significantly lower recoveries than the polymeric sorbents. Irrespective of the toxin group, the adsorption rate of toxins on HP-20 was slower than on Oasis HLB and Strata-X. However, HP-20 and Strata-X gave somewhat higher recoveries after 24 h exposure. Irrespective of the sorbent tested, recoveries were generally highest for cyclic imines and OA group toxins, slightly lower for AZAs, and the lowest for palytoxins.

Trials in re-circulated closed tanks with mussels exposed to *Vulcanodinium rugosum* or *Prorocentrum lima* allowed for further evaluation of passive samplers. In these experiments with different sorbent materials competing for toxins in the same container, Strata-X accumulated toxins faster than Oasis HLB, and HP-20, and to higher levels. The deployment of these three sorbents at Ingril French Mediterranean lagoon to detect PnTX-G in the water column showed accumulation of higher levels on HP-20 and Oasis HLB compared to Strata-X.

This study has significantly extended the range of sorbents for passive sampling of marine toxins. In particular, sorbents were included that had previously been evaluated for polyhalogenated contaminants, pharmaceuticals, phytochemicals or veterinary residues. Moreover, this study has for the first time demonstrated the usefulness of the polymeric Oasis HLB and Strata-X sorbents in laboratory and field studies for various microalgal toxins.

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1. Introduction

Marine toxins are an important international issue for public health and the fish and shellfish industry. Indeed, toxins produced by a number of naturally occurring planktonic and benthic/epiphytic microalgae can accumulate in seafood and render them improper for human consumption. To protect consumers from intoxication, many countries, essentially those with important shellfish industries, have set up monitoring programs. Traditional monitoring through phytoplankton monitoring and shellfish testing has proven to be an effective warning method. However, phytoplankton samples can only describe a 'snapshot' of the microalgal community at a single point in space and time (Lane et al., 2010), and some microalgal species are too small (<20 μm) or benthic/epiphytic. Such algae are hard to identify or detect as identification is difficult for organisms below 20 μm in size and benthic/epiphytic algae require specific, additional sampling protocols (MacKenzie, 2010). For these reasons, Solid Phase Adsorption Toxin Tracking (SPATT) has been introduced as a passive sampling technique to detect and accumulate toxins released into the water during algal blooms (MacKenzie et al., 2004). Another advantage of the SPATT technique is the fact that the targeted toxins do not undergo biotransformation unlike in shellfish (Jauffrais et al., 2013). Thus, the identification of microalgae through toxin profiles in passive samplers is simplified.

Many different sorbents have been used for passive sampling all over the world, from HP-20 to SEPABEADS type resins (Fux et al., 2008; Li et al., 2011; Pizarro et al., 2013; Zhao et al., 2013), for the accumulation of microalgal or cyanobacterial toxins of different polarities (Kudela, 2011; Lacaze, 2012; Zhao et al., 2013). In the environment, passive sampling has proven to be useful to detect toxins released into seawater by benthic or very small pelagic microalgae like Pinnatoxins (PnTXs) (MacKenzie et al., 2011) or Azaspiracids (AZAs) (Fux et al., 2009), using HP-20 sorbent. This sorbent was also efficient in accumulating ciguatoxin and maitotoxin in *Gambierdiscus pacificus* cultures (Caillaud et al., 2011).

Besides SPATT designed for toxin monitoring, various passive samplers were developed for the monitoring of polar or hydrophobic organic contaminants (HOCs), such as Polar Organic Chemical Sampler (POCIS), or Low Density PolyEthylene (LDPE) and Polydimethylsiloxane (PDMS) strips. There are two different POCIS configurations: the pharmaceutical POCIS and the pesticide POCIS. In the first one the membrane encloses Oasis HLB sorbent, while in the second the sorbent is a triphasic mixture of Isolute ENV$^+$ polystyrene divinylbenzene and Ambersorb1500 carbon dispersed on S-X3 Biobeads (Alvarez et al., 2004; Harman et al., 2012). POCIS devices are often used in aquatic environments to monitor polar organic chemicals (Alvarez et al., 2004; Harman et al., 2012; Kaserzon et al., 2012). For hydrophobic compounds, the first passive sampling device developed was the Semipermeable membrane device (SPMD) which is made of a layflat low density polyethylene (LDPE) membrane tube that contains a liquid film of triolein (Huckins et al., 1990). However, the use of SMPD can lead to various difficulties related to possible tearing of the membrane (loss of triolein) or the separation of triolein from HOCs. Moreover, a disadvantage of triolein is that it is too specific to be generically used for the monitoring of compounds of different polarities (Lacaze, 2012). Next to SMPD, single-phase polymeric sheets and films like LDPE (Allan et al., 2013; Bao et al., 2012) or silicone rubber (PDMS) (Rusina et al., 2007; Shea et al., 2006) have also been used for the accumulation of lipophilic compounds.

This study aims to evaluate the ability of Oasis® HLB, Strata-X™, BondElut™ C18, LDPE and PDMS as passive samplers to accumulate marine toxins. Although passive sampling has been successfully used several times to monitor microalgal toxins using different bulk polymeric sorbents, Oasis HLB has, to our knowledge, never been evaluated as a passive sampling sorbent for phycotoxins, and Strata-X has been evaluated only once as a passive sampler for the accumulation of cyanotoxins (Wood et al., 2011). In this study we also evaluated the use of LDPE and silicone membrane strips for the accumulation of lipophilic toxins other than brevetoxins (BTXs) (Shea et al., 2006). This is also the first attempt to test samplers containing a low amount of sorbent (300 mg, ten times less than the amount typically used). Furthermore, in addition to lipophilic azaspiracids (AZAs), 13-desmethyl spirolide-C (SPX1), okadaic acid (OA), dinophysistoxin-1 (DTX1) and PnTX-G (Fig. 1), we have also tested our passive samplers for their ability to accumulate the amphiphilic palytoxins (PlTXs).

Different types of sorbents were investigated through various protocols: i) screening and optimisation of sorbents in SPE-mode, and choice of the sorbents appropriate for passive sampling; ii) passive samplers immersed in spiked seawater; iii) passive samplers in experimental tanks and iv) passive samplers in the field. Throughout the different protocols, sorbents and samplers were compared according to the amount of toxins they had accumulated.

2. Materials and methods

2.1. Chemicals and sorbent material

Certified standard solutions of OA, 13-DesMe-C (SPX1), AZA-1, 2 and 3, and PnTX-G were obtained from the National Research Council in Halifax, Canada. Purified Palytoxin (PlTX) standard was from Wako (Japan). Methanol, acetonitrile, butanol, isopropanol, hexane, ethyl acetate and acetone were obtained as HPLC grade solvents from AtlanticLabo (Bordeaux, France) and Sigma Aldrich (Steinheim, Germany). Acetic acid eluent for LC-MS and ammonium hydroxide (28–30%) were also acquired from Sigma–Aldrich. Milli-Q water was produced in-house to 18 MΩ/cm quality, using a Milli-Q integral 3 system (Millipore). For analyses with the high resolution mass spectrometry instrument, acetonitrile and water of very high purity grade were obtained from Fischer Scientific (Illkirch, France).

Diaon® HP-20 polymeric resin was purchased as bulk resin from Sigma–Aldrich. Strata-X™ (200 mg, 500 mg cartridges and bulk) and Oasis® HLB (30 mg, 200 mg and bulk) were supplied by Phenomenex (Le Pecq, France) and Waters (Saint Quentin Yvelines, France), respectively. Reverse phase BondElut™ C18 cartridges (500 mg) and