



Extraction tools for identification of chemical contaminants in estuarine and coastal waters to determine toxic pressure on primary producers



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HIGHLIGHTS

- We investigated the use of spot water and passive sampling.
- SPE and passive sampling are complementary tools used in future EDA studies.
- The added value of SPE lies in its suitability for quantitative analysis.
- Calibration of passive samplers needs further investigation.
- The PAM assay can be used as a rapid screening tool for assessing toxic effects.

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ABSTRACT

The extent to which chemical stressors affect primary producers in estuarine and coastal waters is largely unknown. However, given the large number of legacy pollutants and chemicals of emerging concern present in the environment, this is an important and relevant issue that requires further study. The purpose of our study was to extract and identify compounds which are inhibitors of photosystem II activity in microalgae from estuarine and coastal waters. Field sampling was conducted in the Western Scheldt estuary (Hansweert, The Netherlands). We compared four different commonly used extraction methods: passive sampling with silicone rubber sheets, polar organic integrative samplers (POCIS) and spot water sampling using two different solid phase extraction (SPE) cartridges. Toxic effects of extracts prepared from spot water samples and passive samplers were determined in the Pulse Amplitude Modulation (PAM) fluorometry bioassay. With target chemical analysis using LC–MS and GC–MS, a set of PAHs, PCBs and pesticides was determined in field samples. These compound classes are listed as priority substances for the marine environment by the OSPAR convention. In addition, recovery experiments with both SPE cartridges were performed to evaluate the extraction suitability of these methods. Passive sampling using silicone rubber sheets and POCIS can be applied to determine compounds with different structures and polarities for further identification and determination of toxic pressure on primary producers. The added value of SPE lies in its suitability for quantitative analysis; calibration of passive samplers still needs further investigation for quantification of field concentrations of contaminants.

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1. Introduction

It has been proposed that chemical stressors in the estuarine and coastal environment can affect primary producers at the base of the pelagic food chain (Hylland and Vethaak, 2011). A large

variety of chemical contaminants has demonstrated to affect photosynthesis and other aspects of energy utilization and incorporation (Verity et al., 2002) and thus may have a direct impact on plankton communities. The most important compounds causing toxic effects on marine phytoplankton are biocides, especially those with a herbicidal mode of action (Hylland and Vethaak, 2011). For example, the antifouling booster agent irgarol 1051 (a triazine herbicide) is a strong inhibitor of the photosystem II (PSII) and reduces growth and productivity of sensitive phytoplankton

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species (Buma et al., 2009). Recently, findings of in situ experiments on board of a research vessel in the North-East Atlantic Ocean have indicated that the effect of complex mixtures of organic pollutants on oceanic phytoplankton communities can exceed the toxicity expected for a single pollutant by a factor of 1000 (Echveste et al., 2010). These findings indicate that toxic effects of a complex field sample can be underestimated, since laboratory experiments often focus on one specific compound or compound class.

Thousands of industrial chemical substances are entering the coastal and marine environment and are mainly the result of pressures from anthropogenic activities, such as urbanization, industry and agriculture (Laane et al., 2012). In Europe the chemical status of freshwaters, estuarine and coastal waters is predominantly assessed by means of chemical monitoring and compliance with environmental quality standards (EQSs) for individual compounds. However, the European Water Framework Directive (WFD) (European Commission, COM (2011) 876 final), currently identifies only 48 chemical substances of concern. In addition, the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic agreed to a list of 40 substances or group of substances for priority action in marine waters (OSPAR Commission, 2011). This list comprises a range of compounds including polychlorinated biphenyls (PCBs), pesticides, polyaromatic hydrocarbons (PAHs) and other chemicals like organohalogenes, metals, biocides, pharmaceuticals and phenols which can be present in estuarine and coastal waters. However, only a small selection of industrial substances is currently monitored, while many others may affect primary producers and other aquatic life.

The traditional approach to determine contaminants in water is spot sampling: collecting water samples at a specific time point, followed by an extraction, clean-up, a concentration step and instrumental analysis in the laboratory. An increasing number of scientific papers have reported on the value and usefulness of passive samplers as an alternative for spot sampling of surface waters (Alvarez et al., 2005; Escher et al., 2006). Unlike spot sampling, passive sampling enables determination of time weighted average concentrations of the contaminants of interest, permits sequestration of residues from episodic events, is not limited to constant water conditions, and allows the concentration of ultra traces and contaminant mixtures over extended periods of time.

We compared different extraction methods to identify and quantify contaminants that cause an effect on microalgae in the Pulse Amplitude Modulation (PAM) fluorometry assay. The PAM assay is a sensitive and rapid high-throughput screening assay used for direct inhibition measurement of photosynthesis of algal species (Juneau et al., 2002). It has been applied using a range of test species including sea grass, corals, but mainly microalgae (Ralph et al., 2007). The change of PAM fluorescence signal is related to the physiological state of the species and can therefore be used as reliable indicator of different environmental stressors.

Spot water samples extracted with hydrophilic-lipophilic-balanced (HLB) and mixed-mode cation exchange (MCX) SPE cartridges were compared to extracts from two passive samplers types (silicone rubber sheets and polar organic chemical integrative samplers, POCIS) exposed in estuarine water at Hansweert (The Netherlands) during different seasons. These methods have different mechanisms of adsorption of molecules and can be used to extract compounds with different polarities and chemical structures. The objective of the present study was to evaluate the differences between the extraction methods, and assess the advantages and disadvantages of the sampling strategies and their suitability to determine inhibitors of PSII activity in estuarine and coastal waters.

2. Materials and methods

2.1. Chemicals and materials

Chemicals used in this study are described in [Supplementary information](#). Silicone rubber sheets (AlteSil™ translucent material) with 0.5 mm thickness and a size of 5.5 × 9.5 cm were purchased from Deltares (Utrecht, The Netherlands) and stored at −20 °C until deployment. For POCIS, stainless steel rings with a specific surface area of 45 cm² were filled with 2 polyethersulfone (PES) membranes (Pall GmbH, Dreieich, Germany) containing 300 mg Septra ZT (pyrrolidone modified styrenedivinylbenzene polymer, 30 μm, 85 Å, Phenomenex) between them. POCIS were wrapped in aluminum foil and stored at −20 °C until deployment.

2.2. Recovery experiments using solid phase extraction

The recovery obtained with the HLB and MCX SPE cartridges was determined by quantitative chemical analysis of compounds spiked to artificial marine water. This water was prepared in two clear glass bottles containing 5 L of Milli-Q water to which sea salt (33‰) was added. One bottle was spiked with 5 mL of a standard solution containing 18 PAHs, 9 PCBs, and 30 pesticides in acetone at individual concentrations in the range of 10–25 ng L^{−1}; the other bottle was enriched with 5 mL of an acetone solution only. The concentrations represented field concentrations observed in the Dutch coastal zone (Ministry of Infrastructure and the Environment, Waterbase database). After stirring for 4 d, the water was filtered through a glass fiber filter (GF/F, pore size 0.7 μm, Whatman, England) to remove suspended particles and divided into five 1 L portions of spiked water and five 1 L portions of unspiked water before extraction using SPE. The SPE method was adapted from Kolpin et al. (2002), for details see [Supplementary information](#). In short, after preconditioning, sample volumes of 1 L marine water were passed through the HLB and MCX cartridges. Elution of HLB cartridges was performed with methanol followed by methanol acidified with trichloroacetic acid (0.1% v/v). MCX cartridges were eluted with methanol followed by 5% ammonium hydroxide in methanol.

Filters used in the recovery experiment were extracted to determine losses of compounds due to filtration (for details see [Supplementary information](#)).

2.3. Field sampling location

Spot water samples (5 L) were taken and passive samplers were exposed at Hansweert in the Western Scheldt estuary in the Netherlands in 2010. The Western Scheldt estuary is a heterotrophic ecosystem with a pronounced total productivity (Baeyens et al., 1998). From monitoring studies, the estuary and the location Hansweert are known to be polluted with a wide variety of contaminants from shipping, water run-off from agriculture and industry along the river Scheldt. Water samples were taken with a zinc bucket, stored at 4 °C in brown glass bottles and extracted within 2 d after sampling. Water samples were taken in spring, summer and autumn 2010 at the installation and collection of the passive samplers. Three POCIS containing 300 mg sorbent each and 6 silicone rubber sheets were exposed for 56–68 d in spring, summer and autumn 2010. POCIS were placed in a stainless steel cage for protection, with holes for free water flow, while silicone rubber sheets were placed on a rack and exposed at a depth of 1–2 m. After deployment, POCIS were wrapped in aluminum foil and sheets were stored in brown glass bottles, transported in a cool box and frozen at −20 °C until extraction.

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