Photodegradation of PAHs in passive water samplers

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ABSTRACT

Losses of deuterated polycyclic aromatic hydrocarbons (PAHs) used as performance reference compounds (PRCs) in semipermeable membrane devices deployed at fifteen coastal sampling sites near Harstad harbour in Northern Norway were used to investigate photodegradation of these photosensitive compounds. Unusual PRC dissipation profiles, especially for samplers exposed <5 m below the water surface are indicative of photodegradation. A strong correlation between loss rates for d_{12}-chrysene and d_{12}-benzo[e]pyrene with consistently higher losses of the latter was found. The observed photodegradation rates may be sufficiently high to impact PAH masses absorbed by a factor of two. This study demonstrates that photodegradation during exposure of passive water samplers needs to be taken into account, particularly with deployments close to the water surface, when using SPMD canisters, or when sampling in the Arctic.

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1. Introduction

Absorption-based passive sampling is increasingly being accepted as a representative monitoring technique for hydrophobic chemicals in water (Vrana et al., 2005). Much work has taken place over recent years to increase the robustness of this sampling technique. This, for example, has been achieved through laboratory-based calibration of the polymers used for passive sampling (Jonker et al., 2015; Lohmann, 2011; Smedes et al., 2009) and the development of appropriate models and techniques to estimate sampling rates from the dissipation of performance reference compounds (PRCs) during exposure (Booij et al., 1998; Booij and Smedes, 2010). Performance reference compounds are non-naturally occurring chemicals and often isotopically-labelled analogues of substances of interest that are added to passive samplers prior to exposure (Booij et al., 1998). Owing to isotropic exchange between the polymer and water, the dissipation of PRCs during exposure can be used to estimate the sampling rates of chemicals of interest.

With the increasing likeliness of passive sampling being used for the monitoring of contaminants in fresh and coastal waters according to the Water Framework Directive (Miège et al., 2015) or for the global monitoring of the world's ocean (Allan and Harman, 2011; Lohmann and Muir, 2010), the effect of environmental conditions during deployment on the robustness of passive sampling will also need to be considered. The impact of exposure of passive samplers to natural light and ultraviolet radiation during deployment in water has received relatively little attention. Komarova et al. (2009) demonstrated that photodegradation can have a substantial effect on passive sampling results when samplers are deployed in water with low turbidity. Polycyclic aromatic hydrocarbons (PAHs) and their deuterated analogues, often used as PRCs are UV-sensitive substances that have been shown to phototransform under natural sunlight and UV radiation (Brack et al., 2003; Forsberg et al., 2014; Komarova et al., 2009). The photodegradation of deuterated PAHs used as PRCs during exposure may affect the estimation of freely dissolved concentrations in water. These processes are very relevant for the deployment of passive samplers in Northern Norway (Arctic) where daylight hours are in excess of 20 h d^{-1} during spring/summer time.

In this study, we use data from semipermeable membrane devices (SPMDs) deployed at 15 marine monitoring sites in the vicinity of the town of Harstad (north of the Arctic Circle in Norway) to assess whether we can (i) identify photodegradation from profiles of PRC losses from SPMDs, (ii) evaluate the kinetics of PRC photodegradation and (iii) evaluate the impact of photodegradation on the accumulation of PAHs into SPMDs.

2. Material and methods

2.1. Chemicals and reagents

Standards for PAHs and their deuterated analogues were purchased from Chiron (Trondheim, Norway) and were of analytical purity. The purities were >99% for PAHs and >99.5% for deuterated PAHs. Solvents (hexane, dichloromethane) were from Rathburn (Walkerburn, Scotland) except for cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better. All glassware was rinsed with solvent and baked in a furnace (540 °C) prior to use. The ultrapure water used for rinsing the surface of SPMDs prior to solvent extraction of the passive samplers was from an Option 3 water purification system from Elga™.

2.2. Semipermeable membrane device deployment

Semipermeable membrane devices (SPMDs) with a nominal length of 92 cm between the inner low density polyethylene welds and width of 2.5 cm were obtained from ExposMeter AB (Tavelsjö, Sweden) and were all from the same production batch. The performance reference compounds added to the SPMDs during production and that we analysed were d_{10}-acenaphthene, d_{10}-fluorene, d_{10}-phenanthrene, d_{12}-chrysene and d_{12}-benzo[e]pyrene (individual PRC concentrations in the range 0.6–5 µg SPMD^{-1}).

SPMDs (one per sampling station) were deployed in seawater for 36 d from the 15th April 2010 to the 21st May 2010 at 15 locations near the town of Harstad (Fig. 1). The average cloud cover for Harstad (measured daily) was 4.9 oktas (~61%) for the period of exposure of SPMDs (data from the Norwegian Meteorological Institute, downloaded from www.eklima.met.no). We estimated Secchi depth to be ca. 5 m in April/May, however for sampling sites 1–8, Secchi depth may have been lower as a result of higher levels of suspended particulate matter in the water linked to snowmelt. The water temperatures were 5–7 °C and the salinity approximately 30 ppt. For the deployment, passive samplers were mounted onto spider holders and inserted into standard SPMD canisters. Moorings consisting of a surface buoy, a rope and anchor were used to suspend SPMD-containing canisters in the water. Deployment depths, depending on the location, ranged from 0.5 to 32 m. SPMDs, kept at −20 °C until deployment, were brought to the sampling sites on ice. A field control sampler was used to assess initial PRC concentrations and possible contamination during deployment and retrieval operations. Upon retrieval, samplers were placed back into clean metal tins and kept at −20 °C until analysis.

2.3. Passive sampler extraction and analyses

The surface of field control and exposed SPMDs was cleaned by rinsing with ultrapure water and wiped with a clean tissue. SPMDs were then placed in a glass jar and soaked in 150 mL of hexane. The procedure was repeated after 24 h with fresh hexane. Recovery standards (d_8-naphthalene, d_{10}-biphenyl, d_8-acenaphthene, d_{10}-pyrene, d_{12}-benz[a]anthracene, and d_{12}-perylene) were added to the glass jar during the first hexane extraction step. Hexane extracts were combined and reduced through a gentle stream of nitrogen to 1 mL. The solvent was changed to dichloromethane prior to clean-up by gel permeation chromatography (GPC). The solvent of the resulting samples was changed to cyclohexane and reduced to 200 µL prior to analysis. For additional details on methods, we refer to previous work (Allan et al., 2010; Allan et al., 2011).

SPMD extracts were analysed on a HP-6890 Plus gas chromatograph with a HP 5973 mass selective detector. The detector was operated in single ion monitoring mode with electron impact ionisation at 70 eV. PAHs and deuterated PAHs were separated using a 30 m DB-5 column with an internal diameter of 0.25 mm and a film thickness of 0.25 µm (from Agilent JW Scientific, Santa Clara, USA) and with a helium flow of 1 mL min^{-1}. The splitless injection volume was 1 µL. The GC oven temperature programme was as follows: held for 2 min at 60 °C before increasing to 250 °C at a rate of 7 °C min^{-1}. The final stage was an
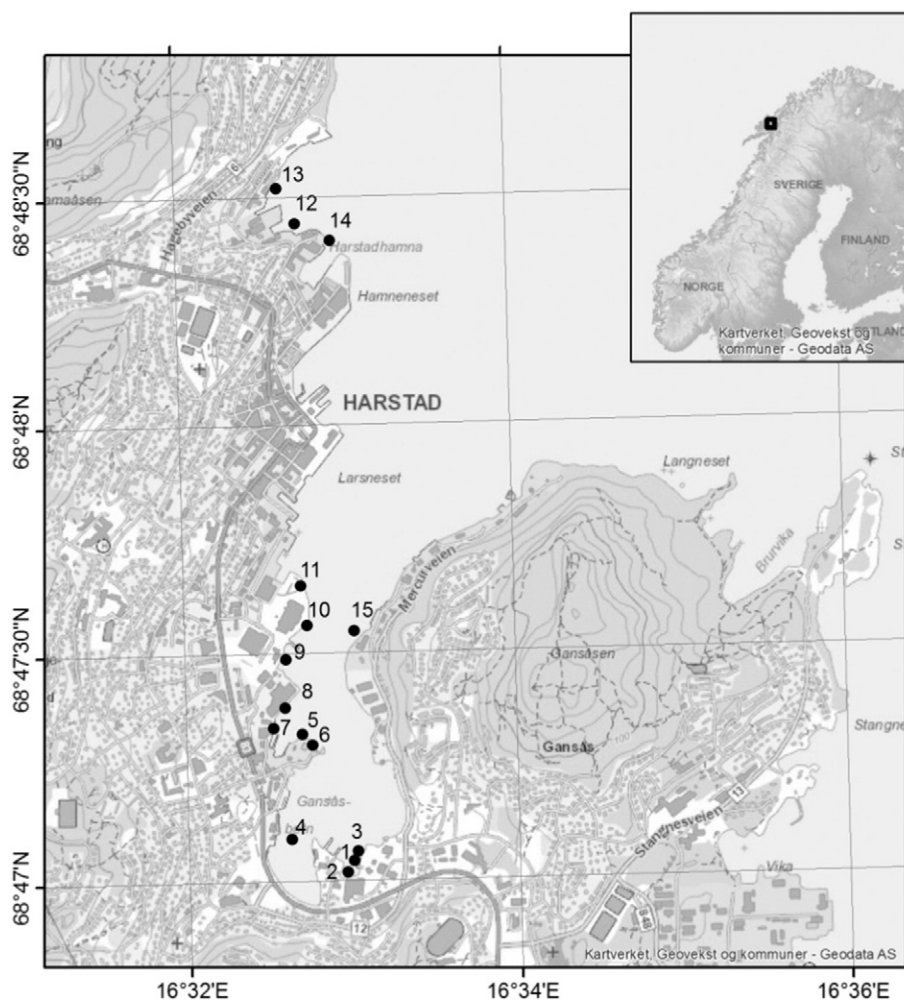
Fig. 1. Passive sampler deployment locations around the town of Harstad (North of Norway).