Sampling approaches for time integrated monitoring of priority substances and their related effects in marine waters using passive and active samplers

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Introduction

International legislation demand the monitoring of both priority and new substances of concern released into the aquatic environment. Monitoring of these compounds in the open ocean by classical grab sampling is costly and difficult to realize, which often results in low resolution data sets. Additionally, pollutant concentrations in seawater are often too low to be detected in grab samples without time-consuming and labour-intensive enrichment techniques. As an alternative, passive sampling devices, which continuously concentrate waterborne pollutants in their tissues, can be used as natural active samplers. Furthermore, mussel deployed passive samplers are easy to handle, are low in costs and provide high quality data on concentration in near real-time. However, mussels can vary in size, growth and resistance against environmental influences like salinity and temperature, which may lead to variability of the pollutant enrichment processes. In contrast, artificial passive sampling devices made of e.g. silicone or low-density polyethylene mimic the active sampling through diffusion processes without the difficulties of natural variability. Both sampling strategies are cost effective and provide data of time-weighted average concentrations over the deployment period. In a joint research project of the Federal Maritime and Hydrographic Agency of Germany (BSH), the Helmholtz-Zentrum Geesthacht Zentrum für Material und Küstenforschung, Institute of Coastal Research (HZG) and the Center for Scientific Diving of the Alfred Wegener Institute for Polar and Marine Research (AWI) a variety of passive sampling devices as well as blue mussels (Mytilus edulis) are time-synchronously deployed at the COSYNA/MarGate underwater experimental field near Helgoland.

MarGate Underwater experimental site

A crucial point in monitoring programs are high-resolution measurements over long time periods, since most ship- or diver supported methods are only suited for short term campaigns and often provide a fragmented picture of processes and mechanisms. In the framework of COSYNA, the Alfred Wegener Institute for Polar and Marine Research (AWI) - Center for Scientific Diving, Institute of Coastal Research and forecast from this area and access to this infrastructure also for external research projects.

Fig. 1 Location and structure of the MarGate underwater experimental site near Helgoland

Fig. 2 Titanium sampling cage for deployment of multiple passive sampling types; cage shown before, during and after deployment

Passive sampling devices

- Low Density Polyethylene (LDPE) membranes (100µm; 3mm; 10µm thick; Polymersynthesewerke Rheinberg, Germany)
- Silicone Rubber Sheets (5.95cm, 500µm thick; Altec Products Limited, Bucks, GB)
- Chemcatcher® (University of Portsmouth) with an C12-(lipid-based) and C40-(silicone rubber sheets and Chemcatcher® respectively).

Workflow and targets

General processing of samplers after retrieval (in short): cleaning; application of internal standards; extraction with organic solvents; determination of the combined extracts for analysis by GC-MS and LC-MS/MS; centrifugation; further clean-up and volume reduction by aliquotation of the combined extracts for analysis by LC-MS/MS and MALDI-MS.

Challenges

- Incongruent deployment periods
- For the reason of weather conditions, especially in autumn/winter periods, marine sampling in temperate zones is unpredictable regarding length of sampling periods. The sampling capacity of the passive samplers has to be sufficient to buffer for a varying deployment time.
- Biomixing
- Due to the summer biomixing occurs on the samplers (fig. 4). The used open cage construction nonetheless guarantees a high flow rate. Freely shifting samplers are less overgrown than fixed ones so a movement allowing fixation of the samplers in the cage is desirable.

Workforce and targets

General processing of samplers after retrieval (in short): sampling; extraction of the different mussel tissues; preparation of different extracts for inorganic trace analysis (Micro wave assisted acid digestion) and protein extraction; extraction with organic solvents for PBDE analysis; analysis of the different sample aliquots by GC/MS, GC/MS, LC/MS/MS and NALDI-MS.

Fig. 3 Titanium sampling cage for deployment of preconditioned mussels; cage shown before, during and after deployment

Active sampling devices

- Blue Mussels (Mytilus edulis) (Cultured mussels of the same origin and from same field)
- 100 mussels were cleaned and placed inside the tannum cage
- DGT units (Diffusive Gradient in Thin Films) (DGT Research Ltd.)

Fig. 4 Biomixing affecting the different sampling cages (left, middle) as well as the different tested passive samplers (silicone rubber sheets and LDPE membranes)

Preliminary results and first conclusions

Data of TWACs from LDPE membranes deployed at MAR Gate and 100 tide grab samples from a sampling campaign done by ship offshore of helgoland show very good agreement regarding the concentration scale (fig. 5). Differences can be explained by grab samples undergoing liquid-liquid-extraction where suspended particles are co-extracted (total water concentration vs. dissolved fraction). Furthermore, the shown comparison is based on only one grab sampling campaign and position. Further investigations will include grab samples spread in time and space.

First physiological data sets include a slight improvement of the physiological status of the population deployed at Helgoland compared to those which has been deployed at a location near Cuxhaven. However more data sets are necessary to draw some more precise conclusions. Further parameters as mentioned in the target compound list are currently under investigation.

Fig. 5 Comparison of data obtained by passive sampling with LDPE membranes and data from grab sampling, “Catch me if you can – Emerging compounds (Nanoparticle, pharmaceuticals etc.) – Element species (TBT etc.) – Trace elements – Polybrominated Flame retardants – Biofouling affecting the different sampling cages (left, middle) as well as the different tested passive samplers (silicone rubber sheets and LDPE membranes)

Fig. 6 Development of the mussel condition index (CI) and the Gonado-somatic index (GSI) during the deployment period of two mussel populations of the same origin. The CI describes the fitness and the nutritional state. The GSI reflects the reproductive state of the population.