Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

COSYNA

Catch me if you can - Sampling approaches for time integrated monitoring of priority substances and their related effects in marine water bodies using passive and active samplers

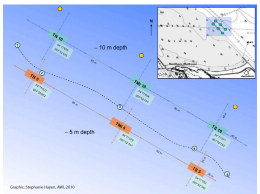
BUNDESAMT FÜR SEESCHIFFFAHRT UND HYDROGRAPHIE

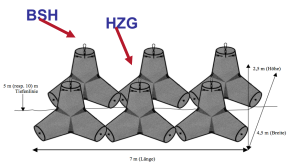
Uta R. Kraus[1], Daniel Pröfrock[2], Burkhard Erbslöh[2], Stephan Lassen[2], Heike Helmholz[2], Christiane Ruhnau[2], Andreas Prange[2], Christoph Walcher[3], Philipp Fischer[3], Norbert Theobald[1]

[1] Department of Marine Sciences, Federal Maritime and Hydrographic Agency of Germany, Hamburg (BSH); email: uta.kraus@bsh.de
[2] Department for Marine Bioanalytical Chemistry, Institute for Coastal Research/Biogeochemistry in coastal seas, Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research (HZG)
[3]Center for Scientic Diving, Alfred Wegener Institute for Polar and Marine Research (AWI)

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 realise, 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 mussels, which continuously concentrate waterborne pollutants in their tissues, can be used as natural active samplers. Furthermore, mussels provide information on bio-molecular effects. 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 sampler 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 together with the Helmholtz-Zentrum Geesthacht, Institute of Coastal Research is in the process of construction of "MarGate", a new underwater experimental and monitoring area near Helgoland in about 10 m water depth. There, active and passive sampling devices as well as electronic equipment can be easily exposed and maintained year round by specially trained scientific divers. Furthermore, underwater electric power (max. 48V) and underwater Gbit data connection for standard UW sensors (like CTD, ADCP etc. etc.) as well as generic probes will be available from summer 2012 on. As standard service, COSYNA will provide validated online data for operational hydrograph, modelling 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

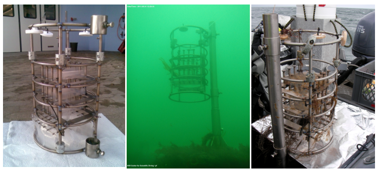


Fig. 2 Titanium sampling cage for deployment of multiple passive sampling types; cage shown before, during and after deployment

Devices for active and passive sampling

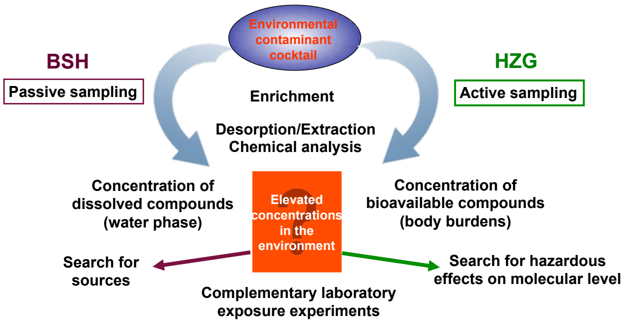


Fig. 3 Titanium sampling cage for deployment of preconditioned mussel cultures; cage shown before, during and after deployment

Passive sampling devices

- Low Density Polyethylene (LDPE) membranes (100x2.5cm; 100µm thick; Polymersynthesewerke Rheinberg, Germany)
- Silicone Rubber Sheets (5.5x9cm, 500µm thick, Altec Products Limited, Bude, GB)
- Chemcatcher® (University of Portsmouth) with an C_{18} Empore^{TM} disk
- All devises were mounted in duplicate or triplicate respectively

Workflow and targets

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

Target compounds:

- 14 polycyclic aromatic hydrocarbons (PAH)
- 15 halogenated pesticides
- 4 polychlorinated biphenyls (PCB)
- 26 polar pesticides
- 9 perfluorinated compounds
- 5 phosphorous and brominated fire retardants
- 6 pharmaceuticals

- calculation of time-weighted average concentrations (TWAC) for the determination of the average analyte concentration during the sampling period according to [1, 2, 3] for LDPE membranes, silicone rubber sheets and Chemcatcher®, respectively.

Challenges

Inconsist 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.

Biofouling

Especially in summer biofouling 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.

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

Active sampling devices

- Blue Mussel (*Mytilus edulis*) (Cultured mussels of the same origin and size from Sylt)
- 100 mussels were cleaned and placed inside the titanium cages
- DGT units (Diffusive Gradients in Thin Films) (DGT Research Ltd.)

Workflow and targets

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

Target compounds:

- Trace elements
- Element species (TBT etc.)
- Polybrominated Flame retardants
- Biomarkers (Stressmarker, detoxification proteins, etc.)
- Emerging compounds (Nanoparticle, pharmaceuticals etc.)
- Pathogens (AWI cooperation G.Gerdts)
- Physiological parameters (Condition Index, Cellular energy allocation, etc.)

Preliminary results and first conclusions

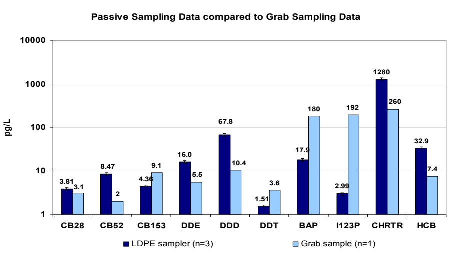
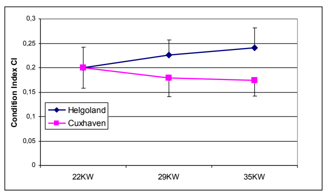


Fig. 5 Comparison of data obtained by passive sampling with LDPE membranes and data from grab sampling. CB28 = Polychlorinated Biphenyl 28; CB52= Polychlorinated Biphenyl 52, CB153=Polychlorinated Biphenyl 153; DDE=p,p'-Dichlorodiphenyldichloroethylene; DDD=p,p'-Dichlorodiphenyldichloroethane; p,p'-Dichlorodiphenyltrichloroethane (DDTPP); BAP=Benzo-a-pyrene; I123P=Indeno(1,2,3-cd)pyrene;CHRTR=Chrysene; HCB=Hexachlorobenzene

Data of TWACs from LDPE samplers deployed at MARGATE and 100 litre 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 indicate a slight improvement of the physiological status of the population deployed at Helgoland compared to those which has been deployed at a station 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.



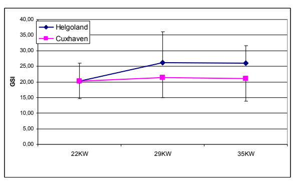


Fig. 6/7 Development of the mussel condition index (CI) and the Gonadosomatic index (GSI) during the deployment period of two mussel populations of the same origin. The CI describes the fitness and the nutritional state. The GSI reflects the reproductive state of the population.

- ➢ A modular, diver operated underwater sampling infrastructure has been realised, which allows the continuous deployment of either active and passive sampling devices. The open design of the deployment cages helps to minimise both mechanical stress and biofouling and permits high flow rates throughout the deployment period.
- ➢ Sensoric infrastructure, which is about to be installed within MarGate, provides high resolution oceanographic data sets, opening new possibilities for the interpretation of the results obtained by active and passive sampling.
- ➢ The combination of active and passive sampling strategies may allow a better assessment of environmental contamination levels and will provide insight into possible contaminant related effects on the molecular level.

[1] I. J. Allan, K. Booij, A. Paschke, B. Vrana, G. A. Mills, R. Greenwood *Environ. Sci. Technol.* 43, (2009), 5383-5390; [2] F. Smedes, R. W. Geertsma, T. van der Zande, K. Booij, *Environ. Sci. Technol.* 43, (2009), 7047-7054; [3] B. Vrana, G. A. Mills, E. Dominiak, R. Greenwood, *Environmental Pollution* 142(2), (2006), 333-343

This study was partly funded by the The Federal Environment Agency.